ETH Library

# 20th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies. ModVal 2024

## Book of Abstracts

**Conference Proceedings**

**Publication date:**
2024

**Permanent link:**
https://doi.org/10.3929/ethz-b-000662523

**Rights / license:**
In Copyright - Non-Commercial Use Permitted

This page was generated automatically upon download from the ETH Zurich Research Collection.
For more information, please consult the Terms of use.

PAUL SCHERRER INSTITUT

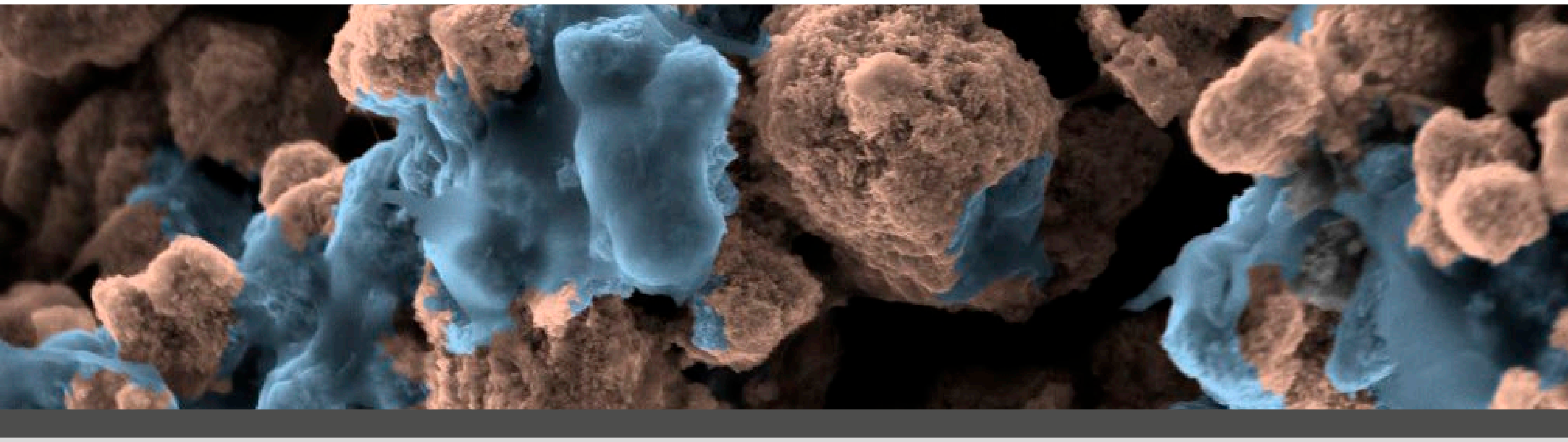
Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

**Swiss Federal Office of Energy SFOE**

# 20th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies

## ModVal 2024



# Book of Abstracts

March 13–14, 2024
Baden, Switzerland

www.modval2024.ch

COVER PHOTO:

SEM image of an anode catalyst layer for a polymer electrolyte water electrolyzer cell (catalyst brown and ionomer blue).
Related article: EES Catalysis 2 (2024) 585-602
(DOI: 10.1039/D3EY00279A)

# Book of Abstracts

## 20th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies (ModVal 2024)

This document is available from Research Collection, ETH Zurich’s Institutional Repository
https://www.research-collection.ethz.ch
DOI: 10.3929/ethz-b-000662523

**Publisher**
Electrochemistry Laboratory Paul
Scherrer Institut
5232 Villigen PSI

**Editorial Team**
Pierre Boillat
Felix N. Büchi
Mario El Kazzi
Jens Eller
Cordelia Gloor
Lorenz Gubler
Juan Herranz
Sigita Trabesinger

**Printing**
Paul Scherrer Institut
ModVal 2024 Book of Abstracts

**Version**
Repository (31-March-2024)

© Paul Scherrer Institut

# Table of Contents

**Page**

# Welcome to ModVal 2024

The ModVal symposia were initiated in 2004 by the Swiss Federal Office of Energy and have since then taken place annually in locations alternating between Switzerland and Germany, initially focusing on pertinent topics in the development of fuel cells, in particular the polymer electrolyte fuel cell (PEFC) and the solid oxide fuel cell (SOFC). Over the years, the scope of the symposium has expanded to rechargeable batteries and now also includes water and $CO_2$ electrolyzers as well as flow batteries. All of these are clustered under the general term ‘electrochemical energy technologies, highlighting their intended use as energy storage and conversion devices for a range of applications, ranging from electromobility, decentralized power generation, to stationary energy storage and use in industrial processes.

ModVal aims at disseminating new results in research, fostering the exchange of ideas, notably between experimentally oriented and simulation centered research, promoting personal contacts, and stimulating new collaborations. It is targeted at colleagues from academic and governmental institutions as well as industry.

We wish to thank all the plenary and invited speakers, oral and poster presenters for contributing to ModVal 2024 and all the participants for making this a stimulating and memorable event. Furthermore, we gratefully acknowledge the sponsors for financial support, and thank the colleagues of the Electrochemistry Laboratory of PSI for assistance in organizational matters.

The ModVal 2024 Organizing Committee

February 2024

How to cite contributions:
{Author list}, “{Title}”, 20th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies (ModVal 2024), Book of Abstracts, P. Boillat, M. El Kazzi, J. Eller, C. Gloor, L. Gubler, J. Herranz, S. Trabesinger (Eds.), Baden, Switzerland, March 13-14, 2024, {pages} (DOI: 10.3929/ethz-b-000662523)

# Sponsors

**Swiss Federal Office of Energy (SFOE)**

**www.bfe.admin.ch**

**Comsol**

**www.comsol.com**

**Equilabrium**

**www.equilabrium.com**

**Johnson Matthey**

**www.matthey.com**

**Math2Market**

**www.math2market.de**

**Metrohm**

**www.metrohm.ch**

**RHD Instruments**

**www.rhd-instruments.de**

**Thermo Fisher Scientific**

**www.thermofisher.com**

**Toyota**

**www.toyota.eu**

# Program

## *Tuesday March 12th, Evening*

| | |
|---|---|
| 18:30 | Registration desk opens |
| 19:00 | Welcome Get-Together with Apéro Riche<br>(Trafo Halle 37) |
| 21:30 | Closing |

## *Wednesday March 13th, Morning 1*

| | | |
|---|---|---|
| 8:00 | Registration desk opens | |
| 8:45 | Welcome, Room 36-2 | |
| 9:00 | Plenary 1, Chair: L. Gubler, Room 36-2<br>**U. Krewer**<br>Electrosynthesis: Modeling Processes at Electrodes | |
| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
| 9:50 | Short Break | |
| 10:00 | Session A1: *Durability*<br>Chair: C. Fink | Session B1: *Electrolyte*<br>Chair: E. Knobbe |
| 10:00 | **J. Heitz**<br>Unraveling the Influence of Ionomer on Catalyst Layer Degradation in Proton Exchange Membrane Fuel Cells: A Hierarchical Modeling Approach | **C. Schwetlik**<br>A model for Solvation in Battery Electrolytes and analysis of Electrochemical Double Layer differential capacitance |
| 10:20 | **L. Klass**<br>Bootcamp for Neural Networks: Boost Neural Network Training using Physical Simulation Models and Transfer Learning for Fuel Cell Operation Monitoring | **T. Ayadi**<br>Ab initio study of the thermodynamic properties of the $Li_6PS_5Cl$ solid electrolyte |
| 10:40 | **A. Abd El Kader**<br>Investigating the Impact of Air Pollutants on Fuel Cell Performance and Durability: Experimental and Modelling Approaches | **B. Ruhstaller**<br>Extracting Ion Density and Mobility - Transient Current Method Revisited |
| 11:00 | Coffee Break | |

## *Wednesday March 13th, Morning 2*

| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
|---|---|---|
| 11:30 | Session A2: *Solid Oxide Fuel Cell (SOFC)*<br>Chair: F. Büchi | Session B2: *Processing*<br>Chair: W. Bessler |
| 11:30 | **R.K. Jeela**<br>Multiphase-field Simulation studies on Coarsening in FIB-SEM reconstructed Ni/CGO SOFC Anodes | **B. Kellers**<br>Systematic Workflow for Efficient Identification of Local Representative Elementary Volumes |
| 11:50 | **S. Golani**<br>Impedance model for SOFC stacks | **M. Prasad**<br>Influence of Passive Material Distribution and its Structural Properties on Cathode Performance |
| 12:10 | **N. Sawant**<br>Towards SOFC modeling with the Lattice Boltzmann method | **G. Lenne**<br>Modeling Li-ion battery electrodes accounting for microstructure properties: The Newman's model revisited |
| 12:30 | Lunch & Poster Session (Halle 37) | |

## *Wednesday March 13th, Afternoon 1*

| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
|---|---|---|
| 14:00 | Session A3: *PEFC Water Management*<br>Chair: M. Hanauer | Session B3: *Cathode*<br>Chair: A. Latz |
| 14:00 | Invited A3<br>**J. Pauchet**<br>Liquid water formation and transport in Membrane Electrode Assembly of PEMFC: liquid injection, vapor condensation and mixed scenario | Invited B3<br>**I. Castelli**<br>Computational Workflows for an Accelerated Design of Novel Materials and Interfaces |
| 14:30 | **Y. Sun**<br>Effect of liquid saturation transients on electrochemical impedance of PEM fuel cell | **O. Furat**<br>Quantifying the impact of operating conditions on particle cracking in Li-ion battery cathodes, using super-resolution of SEM images and stereology |
| 14:50 | **P. Oppek**<br>Empirical PEMFC model for local performance and resistance prediction | **S. Daubner**<br>Investigation of nano-porous cathode particles for battery cell simulations |
| 15:10 | **L. König**<br>Predicting the performance of real fuel cells with a fast MATLAB model | **J. Naumann**<br>Understanding the effect of hierarchically structured cathode morphology on the performance of intercalation battery cells |
| 15:30 | Coffee Break & Poster Session (Halle 37) | |

## *Wednesday March 13th, Afternoon 2*

| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
|---|---|---|
| 16:00 | Session A4: *Two-Phase Flow* Chair: J. Pauchet | Session B4: *Methods & Analytics*<br>Chair: E. Ayerbe |
| 16:00 | **I. Dorner**<br>Model-assisted Analysis of Carbon-free Silver Gas Diffusion Electrode Designs for Performance Enhancement in Electrochemical $CO_2$ Reduction | **E. Hagopian**<br>Improving the Relationship between State of Charge, Charge History and Voltage Hysteresis Evolution in First Order Differential Equation Voltage Hysteresis Models |
| 16:20 | **T.C. Ma**<br>Modeling the Interface between Transport and Catalyst Layer and its Influence on Water Electrolysis Performance | **X. Raynaud**<br>Optimization and Parameterization of Electrochemical Systems in BattMo, the Battery Modeling Toolbox |
| 16:40 | **L. Feierabend**<br>Numerical and Experimental Analysis of Two-phase Flow in Porous Transport Layers in Water-Electrolysis Processes | **J. Valenzuela**<br>Parametrization of a Thermochemical-Kinetic Model for Gas Analysis of Lithium-ion Batteries |
| 17:00 | (talk canceled) | **N. Hallemans**<br>Characterising diffusion in lithium-ion batteries from operando impedance measurements during relaxation |
| 17:30<br>19:00 | Poster Session with Snacks & Drinks (Halle 37) | |

| | |
|---|---|
| 19:30 | Conference Dinner (Trafohalle) |
| 22:30 | Closing |

## *Thursday March 14th, Morning 1*

| | | |
|---|---|---|
| 9:00 | Plenary 2, Chair: S. Trabesinger, Room 36-2<br>**A. Latz**<br>Battery Design by Modeling and Simulation: From Particle over Electrode Structure to Cell Performance | |
| 9:50 | Short Break | |
| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
| 10:00 | Session A5: *Redox Flow Battery (RFB)*<br>Chair: J. Schumacher | Session B5: *Lithium Plating*<br>Chair: I. Castelli |
| 10:00 | **M. Barzegari**<br>Topology optimization of porous electrodes for redox flow batteries using the finite element method | **S. Sahu**<br>A continuum model for lithium plating and dendrite formation in lithium-ion batteries: formulation and validation against experiment |
| 10:20 | **R.P. Schärer**<br>An Open-source Model for High-throughput Flow Battery Cell Performance Predictions | **M. Lagnoni**<br>Interplay between charging and plating in graphite electrodes via phase-field modelling and operando optical microscopy |
| 10:40 | **M. Jałowiecka**<br>Tracking $CO_2$ bubble flow in a direct formic acid fuel cell, numerical and experimental investigation | **N. Bless**<br>A complementary model-based approach with electrochemical and operando microscopy experiments to unravel Li plating in Lithium-ion batteries |
| 11:00 | Coffee Break & Poster Session (Halle 37) | |

## *Thursday March 14th, Morning 2*

| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
|---|---|---|
| 11:30 | Session A6: *Stacks & Systems*<br>Chair: J. Eller | Session B6: *State of Charge*<br>Chair: F. Röder |
| 11:30 | **S. Mull**<br>Experimental and simulative analysis of the dependence between liquid water amount and mass transfer in a planar membrane humidifier | **T. Hofmann**<br>The ΔQ-Method: State of Health and Degradation Mode Estimation for Lithium-Ion Batteries Using a Mechanistic Model with Relaxed Voltage Points |
| 11:50 | **S. Nicolay**<br>Model-based design of a strategy for switching stacks in a multi-stack PEM fuel cell system | **X. Gao**<br>Predicting failure behaviors in lithium-ion batteries subjected to thermal abuse following long-term degradation |
| 12:10 | **E. Revello**<br>Thermal Management Design and Optimization for Hydrogen-Powered Fuel Cell Systems in Aviation | **S. O'Kane**<br>Lithium-Ion Battery Degradation: the Missing Piece in Model Validation |
| 12:30 | **Y. Fischer**<br>Spatially Resolved Quantification of Diffusion Losses in a Segmented PEM Fuel Cell with adjustable Clamping Forces | **W. Bessler**<br>Operando SOC and SOH diagnosis with voltage-controlled models: Application to an LFP battery pack and to smart phone batteries |
| 12:50 | Lunch & Poster Session (Halle 37) | |

## *Thursday March 14th, Afternoon*

| | Session A<br>*Conversion Devices*<br>Room 36-3 | Session B<br>*Batteries*<br>Room 36-2 |
|---|---|---|
| 14:00 | Session A7: *Catalyst Layer*<br>Chair: J. Herranz | Session B7: *Lithium Transport*<br>Chair: O. Furat |
| 14:00 | Invited A7<br>**F.N. Büchi**<br>The Catalyst- and Porous Transport Layer Interface: Decisive for PEWE Performance | Invited B7<br>**N. Marzari**<br>What Electronic-structure Simulations Can Teach Us About Li-ion Batteries |
| 14:30 | **M.G. Justino Vaz**<br>Effect of Model Parameters on the Performance of a PEM Fuel Cell Using a Pore-scale Catalyst Layer Model | **F. Mendez-Corbacho**<br>Physics Informed Neural Network for solving Single Particle Model without using labeled data |
| 14:50 | **K. Gülicher**<br>Simulation of Oxygen Diffusion and Reduction Reaction in the Cathode Catalyst Layer of a PEM Fuel Cell using Lattice Boltzmann Modeling | **M. Cornish**<br>Modelling Dynamic Limitations of Lithium Transport in Lithium-Sulfur Batteries |
| 15:10 | **E. Tardy**<br>Modeling Oxygen Reduction Reaction kinetics in a Gas Diffusion Electrode | **R. Pakula**<br>Application and customization of Matlab Simscape framework for P2D simulation of batteries |
| 15:30 | **Y. Hou**<br>Machine Learning-Assisted Optimization of Proton Exchange Membrane Fuel Cell Catalyst Layer Production Recipe | **F. Röder**<br>Modeling of Path Dependency in Batteries |
| 15:50 | Short Break | |
| 16:00 | ModVal 2025 Announcement<br>Room 36-2 | |
| 16:15 | Poster Award & Farewell<br>Room 36-2 | |

# Oral Contributions

*Plenary Lectures*

*Invited Talks*

*Contributed Talks*

# Poster Contributions

| Nr. | Authors | Title | Page |
|---|---|---|---|
| P1 | (withdrawn) | | |
| P2 | D. Dvorak, H. Kapeller | The NextBMS Project: Improved Battery Models for Enhanced Utilization, Safety and Performance of Batteries | 86 |
| P3 | H. Lin, B. Lewerich, E. Knobbe, A. Latz | FEM-based Validation of Micro-Indentation to Characterize Mechanical Behaviour of Li-ion Battery Electrodes. | 87 |
| P4 | V. Siller, B. Lelotte, C.A.F. Vaz, C. Jordy, V. Pelé, M. El Kazzi | Probing the instable interface between solid electrolytes and high voltage cathodes with operando X-ray spectroscopy | 88 |
| P5 | (withdrawn) | | |
| P6 | H.S. Nguyen, A. Latz | An Effective Model for Sodium insertion in Hard Carbon | 90 |
| P7 | S.F. Gatti, A. Testino, S. Trabesinger | From theoretical prediction to real materials: hurdles and opportunities | 91 |
| P8 | Z. Han, T. Németh, M. Yandrasits, H. Ren, W. Bangay, L. Gubler | Influence of the testing protocol on the chemical durability of hydrocarbon proton exchange membranes for fuel cells | 92 |
| P9 | D. Dessiex, R. Fischer, T.W. Weng, F.N. Büchi, S. Haussener | Water Management in a Zero-gap $CO_2$ Electrolyzer Featuring a Bipolar Membrane in Forward Bias | 93 |
| P10 | B. Patel, A. Sorrentino, T. Vidakovic-Koch | Data-driven modeling of electrochemical processes through Loewner framework and symbolic regression | 94 |
| P11 | L. Jahn, P. Mößle, F. Röder, M.A. Danzer | A physically motivated voltage hysteresis model using a probability distributed equivalent circuit | 95 |
| P12 | (withdrawn) | | |
| P13 | L. Skarjan, P. Boillat, T.J. Schmidt, S. Trabesinger | Isotopes-based interfacial characterization using operando neutron imaging and Online electrochemical mass spectrometry | 97 |
| P14 | C. Fink, M. Mlakar | Detailed 3D CFD Simulation of PEM Electrolyzers | 98 |
| P15 | L. Liebl, A. Bardow, D. Roskosch | Identification of Working Fluids for Indirect Electrochemical Cooling | 99 |

| | | | |
|---|---|---|---|
| P16 | K. Manmi, F. Brosa Planella | Zero Dimensional Models for SEI Formation in Lithium-Ion Battery | 100 |
| P17 | R. Mühlpfort, L. Pfeifer, A. Heß, Th. Wetzel, P. Seegert | Analysis of crucial effective transport parameters of lithium-ion batteries within simulation studies based on Impedance Spectroscopy | 101 |
| P18 | L. Pfeifer, R. Mühlpfort, A. Heß, Th. Wetzel, P. Seegert | Investigation of different liquid electrolyte systems with lithium metal anodes and their influence on the performance and stability | 102 |
| P19 | A. Giudici, C. Please, J. Chapman | Mechanical stress-field in pouch cells due to lithium-induced swelling and gas formation. | 103 |
| P20 | M. Fath, C. Drechsler, B. Berkes, P. Heidebrecht, M. Kamlah | Strategic Approach for the Characterization of NCM Cathodes - Determining Kinetics, Transport and Thermodynamics | 104 |
| P21 | F. Schomburg, A. Schmidt, F. Röder | Identification and parametrization of SEI growth models for various electrolyte compositions using differential voltage analysis | 105 |
| P22 | D. Schmider, W.G. Bessler | Influence of intra-particle concentration gradients and lithium plating on the thickness change of a lithium-ion pouch cell | 106 |
| P23 | H. Kapeller, D. Dvorak | The XL-Connect Project: Quantitative Parametric Models for Assessing the Influence of V2X on Battery Degradation in Electric Vehicles | 107 |
| P24 | T. Nemeth, T. Nauser, L. Gubler | Effect of aromatic electron density on the durability of fluorine-free aromatic hydrocarbon-based proton-exchange membranes | 108 |
| P25 | A. Unni, J. Wagner-Henke, U. Krewer, P. Balbuena | KMC Simulation framework to study SEI formation in Li metal batteries | 109 |
| P26 | K. Braun, B. Rüppel, L. Weiß, M. Wensing | In-Situ Measurement Technique for Data Acquisition in Fuel Cells: Enabling Accurate Energy Balance Modeling | 110 |
| P27 | S. Ramasubramanian, C. Lechner, J.C. Wurzenberger, F. Röder | Modelling Battery Degradation using Neural Ordinary Differential Equations | 111 |
| P28 | C. Bieneck, L. von Kolzenberg, A. Latz | Matching micro- and mesoscale parametrization for electrochemical battery simulations | 112 |
| P29 | A. Pamperin, N. Ribic, O. Birkholz, V. Becker, M. Kamlah | Effective transport properties of granular cathode material in particle and pore space including intragranular cracks | 113 |

| | | | |
|---|---|---|---|
| P30 | P. O. Mmeka, M. Dubarry, W.G. Bessler | A physically-informed, aging-sensitive equivalent circuit model for predicting the “knee” in lithium-ion battery aging | 114 |
| P31 | P. Hadikhani | Investigating Bubble Nucleation and Flow in Membrane-less Water Electrolyzers | 115 |
| P32 | Y. Jiang, G. Offer, H. Wang | Modelling vent gas flow impact on thermal runaway propagation in battery modules/packs with varied void space dimensions | 116 |
| P33 | B. van Leer, L. Jiang, Z. Liu, L. Li | New method to characterize Li metal and SEI layer with Atomic resolution with inert gas transfer and Cryo-FIB | 117 |
| P34 | A.K. Jishnu, C. Burak, Y. Ugur, Z.F. Nessa, M. Zhuo, F.B. Planella, W.D. Widanage | Development and Validation of Physics-based Model for Lithium-Ion Battery Degradation Across Various Aging Conditions | 118 |
| P35 | S. Schneider, L. König, F. Wilhelm, J. Scholta | Model-based optimization of Gas Diffusion Layers material properties by CFD simulation | 119 |
| P36 | M. Schamel, M.A. Danzer | Simulating the current split between active material species in blend electrodes using a transmission line model | 120 |
| P37 | (withdrawn) | | |
| P38 | D. Baster, T. Schmitt, A.H. Clark, T.C. Asmara, Y. Wei, Z. Tao, J.B. Falqueto, M. El Kazzi | Quantifying the O-redox contribution to the charge compensation mechanism in $Na_{0.67}Mn_{0.62}Fe_{0.19}Al_{0.1}O_2$ - cathode material for Na-ion batteries | 122 |
| P39 | L. Fuchs, O. Furat, D.P. Finegan, P. Weddle | Stereological multi-scale modeling of anisotropic NMC particles, combining methods of spatial stochastics and generative neural networks | 123 |
| P40 | S. Zappe, F. Schomburg, F. Röder | Kinetic Monte Carlo simulation study on the influence of solubility on the initial SEI growth | 124 |
| P41 | B. Lelotte, V. Pelé, C. Jordy, C.A.F. Vaz, C.N. Borca, T. Huthwelker, L. Gubler, M. El Kazzi | Interface Evolution in the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ Solid-State Battery Cathodes During Cycling | 125 |
| P42 | J. Brucker, W.G. Bessler, R. Gasper | Grey-box modelling of lithium-ion batteries and their slow voltage dynamics with neural ordinary differential equations | 126 |
| P43 | (withdrawn) | | |
| P44 | (withdrawn) | | |

| | | | |
|---|---|---|---|
| P45 | P. Rieder, O. Furat, P. Weddle, J. Allen, D.P. Finegan, K. Smith, V. Schmidt | Methods of machine learning and stochastic modeling for the structural characterization of functional battery materials at various length scales | 129 |
| P46 | (reallocated to oral contribution B6.4) | | |
| P47 | M. Weichel, M. Reder, S. Daubner, D. Schneider, B. Nestler1 | Modeling of the battery electrode drying process | 131 |
| P48 | N. Erhardt, H. Nirschl | Replacing Microstructure Simulation with a Data-Driven Approach to Model Mechanical Degradation in Electrodes | 132 |
| P49 | Z. Zhang, A. Mühlmann, A. Testino, L. Gubler | Pt-Doped Ceria-Zirconia as a Bi-Functional Catalyst for Gas Recombination and Radical Scavenging in PEM Water Electrolysis Cells | 133 |
| P50 | (reallocated to oral contribution A6.4) | | |
| P51 | M. Röhe, R. Berndt, C. Bessai, G. Prietzsch, H. Ulmer, R. Wascheck | Multi-Level Model-Approach: Future Powertrain Topologies for Fuel Cell-based Commercial Vehicles | 135 |
| P52 | A. Durdel, J. Brehm, V. Elender, A. Aufschläger, M. Altmann, P. Kotter, A. Jossen | Modeling the Volume Change of Lithium-Ion Battery Cells due to Lithium Intercalation and External Pressure with Subsequent Porosity Changes | 136 |
| P53 | P. Lorson, S. Daubner, J. Naumann, R. Schoof, M. Kamlah | Phase-field study of intercalation processes in LFP-platelets | 137 |
| P54 | M. Scheller, A. Durdel, A. Frank, A. Jossen | Impact of Polymers on Hybrid Solid-State Battery Performance: Modeling and Simulation | 138 |
| P55 | J. Weinmiller, B. Kellers, T. Danner, A. Latz | Multiscale reaction modeling via a subgrid approach for the lattice Boltzmann method | 139 |
| P56 | P. Balestriere, A. Menard, D. Belin | Influence of partially constricted flow channels (Bottlenecks) on Polymer Electrolyte Fuel Cell performance | 140 |
| P57 | A.T. Anzaldo Grundler, A. Latz, T. Jahnke | Lattice Boltzmann Simulation of PEMFC Catalyst Degradation through Electrochemical Ostwald Ripening | 141 |
| P58 | C. Altenhofen, N. Fogla, J. How | PEM FCEV Cold Start Control Strategy Investigation of Digital Twin Based on Multi-Physics System Simulation | 142 |
| P59 | B. Dursun, Ö. Andersson | Improving heavy-duty FCEV efficiency by air system modeling | 143 |

| | | | |
|---|---|---|---|
| P60 | J. Hörmann, A. Agrawal, S. Hein, D. Kopljar, K.A. Friedrich, T. Danner, A. Latz | Characterization and Optimization of Lithium-Ion Battery Materials via Particle-Scale Measurements and Simulations | 144 |
| P61 | R. Fischer, M. Dessiex, F. Marone, F.N. Büchi | Bipolar Membranes for $CO_2$ Co-Electrolysis: Optimization and Characterization by X-ray Tomography | 145 |
| P62 | P. Neugebauer, P. Röse, U. Krewer | Dynamic Model-based Analysis of Mass Transfer Effects on Electroorganic Oxidation Processes | 146 |
| P63 | M. Bültel, A. Thüring, B. Ringeisen | Modelling Carbon Loss During Startup and Shutdown Operation of PEM Fuel Cells | 147 |
| P64 | S. Maaß, J. Fuhrmann, S. Ringe | Monolithic coupling of a CatMAP based microkinetic model for heterogeneous electrocatalysis to ion transport with finite ion sizes | 148 |
| P65 | A. Frank, A. Durdel, T. Roth, A. Jossen | Modeling In-plane Inhomogeneities of Lithium Iron Phosphate Battery Cells during Shallow Cycling | 149 |
| P66 | A. Singh, A. Ghosh, P. Nakhanivej, Y. Monaghan, S. Puravankara, M. Loveridge, A. Barai | Effect of thermal gradients on mechanistic model-based degradation diagnosis in Lithium-ion cells | 150 |
| P67 | S. Hoffmann, J. Haußmann | Novel flow structures for additive manufacturing of gas diffusion layers for PEM fuel cells | 151 |
| P68 | T. Dev, M. Spinola, T. Reichbauer, C. Weißinger | Multiscale-Multidomain modeling and validation of commercial 18650 cylindrical cells | 152 |
| P69 | N. Lindacher, L. Weiß, S. Rieß, M. Wensing | On the anode exhaust gas recirculation of PEM fuel cells using passive ejectors | 153 |
| P70 | (reallocated to oral contribution A5.3) | | |
| P71 | R. Wullich, L. Gubler, M. El Kazzi | Zero-Excess Lithium Metal Anodes in Next-Generation Sulfide-Based Solid-State Batteries | 155 |
| P72 | E. Tardy, P.X. Thivel, F. Druart, P. Kuntz, D. Devaux, Y. Bultel | Investigation of internal temperature distribution in lithium-ion battery cell and module using a 3D electrothermal model | 156 |
| P73 | (withdrawn) | | |
| P74 | (withdrawn) | | |
| P75 | F. Pichler, F. Feyersinger | A new distribution-based approach to modelling of hysteresis in electro chemical systems | 159 |
| P76 | (withdrawn) | | |

| | | | |
|---|---|---|---|
| P77 | W. Schrader, D. Müller, P. Hadikhani, A. Stroh | Numerical Investigation of bubble growth and detachment characteristics in electro-chemical systems | 161 |
| P78 | M. Benhamad, E. Tardy, K. Parfait Kamara, F. Druart, L. Svecova, J. Deseure | Numerical study of a hydrogen dilution effect on the performance of PEMFC fuel cell | 162 |
| P79 | M. Spinola, T. Dev, T. Reichbauer, C. Weißinger | Optimal control of a coupled electrical-thermal equivalent circuit model for Li-ion batteries with applications to fast charging | 163 |
| P80 | E. Olisa, M. Marinescu, M. Cornish | What is Missing from Current Li-S Models to Predict Coin-Cell Behaviour? | 164 |
| P81 | T. Dörenkamp, A. Zaccarelli, F.N. Büchi1, T.J. Schmidt, J. Eller | Development of 3D-Printed Gas Diffusion Layers for Enhanced Liquid Water Transport in Polymer Electrolyte Fuel Cells | 165 |
| P82 | V. Artemov | Aqueous Interfaces for Sustainable Electric Energy Storage | 166 |
| P83 | Z. Turtayeva, C.C. Weber, M. Ammann, F.N. Büchi | Preparation of Titanium Multilayer Porous Transport Layers (PTLs) for Polymer Electrolyte Water Electrolysis (PEWE) | 167 |
| P84 | N. Raue, J. Schall, D. Gerteisen | Advantage of spatially resolved 3D simulations for analysis of local effects and gradients along the channel in a PEM fuel cell | 168 |
| P85 | B. Galante, J. Herranz, F.N. Büchi, R. Gilardi, A. Guglielmi, B. Buades, J. Eller | Methods for cracks analysis in MPLs | 169 |
| P86 | A.N. Jacobsen, E. Mahravan, J. Catalano, P. Forooghi | Modeling of transport in alkaline electrolyzers using open-source computational fluid dynamics | 170 |
| P87 | T. Miličić, T.V. Hoang, K. Muthunayakage, L.A. Živković, T.K.S. Ritschel, T. Vidaković-Koch | Nonlinear Frequency Response Analysis for the Proton Exchange Membrane Water Electrolysis Model Validation | 171 |
| P88 | (withdrawn) | | |
| P89 | Y. Aymon, P. Caliandro | Parameters estimation fitting loop for enhanced physical based model | 173 |

# Abstracts for Oral Presentations

# Electrosynthesis: Modeling Processes at Electrodes

Ulrike Krewer, Philipp Röse, Inga Dorner, Niklas Oppel, Swantje Pauer
*Karlsruhe Institute of Technology, Institute for Applied Materials – Electrochemical Technologies*
*Adenauerring 20b, 76131 Karlsruhe, Germany*
*Ulrike.krewer@kit.edu*

To become more $CO_2$ neutral, Europe's energy supply system and its chemical industry are getting more and more electrified. $H_2$ is envisioned as a suitable long-term energy storage option, complementary to batteries for short-term storage in the range of minutes to hours. $H_2$ and further electrofuels can be produced with high efficiencies by electrolysis. Even so, there is presently no mass production of $H_2$ for this purpose. In contrast, the chemical industry has been using electrolysis for decades to produce chemicals like $Cl_2$ and organic chemicals. Yet, electrolysis processes account for only a small fraction of all chemical production processes. Over the next few decades, we expect to see a systematic and large-scale ramp-up of electrolysis for the production of various electrofuels and chemicals. Recent initiatives show the industry's enthusiasm: more than 15 companies team up with universities in the Cluster4future ETOS (Electrifying Technical Organic Synthesis) for the large-scale application of electro-organic synthesis processes [1].

A prerequisite for establishing competitive electrolysis processes is a thorough, quantitative understanding and debottlenecking of the processes from surface to system level. This comprises identifying suitable electrolysis models, and especially, the model-based analysis and optimisation from electrode to cell level [2]. To date, there are only few continuum-level models that comprise reasonable reaction kinetics to describe electrochemical performance as well as product selectivity.

This talk shows how to identify suitable kinetic models and model parameters for a wide range of electrosynthesis processes: PEM water electrolysis [3], $O_2$ depolarized cathodes for $Cl_2$ electrolysis [4], $CO_2$ reduction in aqueous [5] vs. organic electrolyte, and electrosynthesis of fine chemicals. In some of these applications, electrochemical reactions and electrochemical side reactions are shown to play a large role, whereas others suffer from carbonation reactions in the electrolyte, gas/phase equilibria, or slow transport processes.

Dynamic measurements, such as cyclic voltammetry, impedance spectroscopy, and chronoamperometry/potentiometry, are well reproduced by the models, and the underlying processes causing a characteristic dynamic response are revealed. Crucially, the models are then used to identify the performance-limiting processes among the various reaction and transport processes, and measures are suggested and evaluated to improve the performance of the electrodes. The kinetic models are essential tools and building blocks for model-assisted design and optimisation and state diagnosis of electrolysis cells.

References:

1. https://www.clusters4future.de/die-zukunftscluster/die-zukunftscluster-der-zweiten-wettbewerbsrunde/etos
2. B. J. M. Etzold, U. Krewer, S. Thiele, A. Dreizler, E. Klemm, T. Turek, *Chem. Eng. J.* **424** (2021), 130501.
3. J. Geppert, P. Röse, S. Czioska, D. Escalera-López, A. Boubnov, E. Saraçi, S. Cherevko, J.-D. Grunwaldt, U. Krewer, *J. Am. Chem. Soc.*, **144** (2022), 13205.
4. M. Röhe, F. Kubannek, U. Krewer. *ChemSusChem,* **12** (2019), 2373.
5. I. Dorner, P. Röse, U. Krewer, *ChemElectroChem*, **10** (2023), e2023003.

# Battery Design by Modeling and Simulation: From Particle over Electrode Structure to Cell Performance

Arnulf Latz
*German Aerospace Center (DLR) and Helmholtz Institute Ulm, Germany*
*University of Ulm, Germany*
*Arnulf.Latz@dlr.de*

Improving the design of batteries to achieve higher power density, energy density, safety and longevity is a complex task. It requires not only optimizing materials but equally important optimizing function and interplay of materials as well as reducing side reactions during the operation of the battery. The function of the material during operation is determined by electrode and cell design. The interplay of the materials influences structure of double layers and emergence of interphases (e.g. the solid electrolyte interphase or SEI) which may affect dramatically reaction kinetics and overpotentials. Side reactions as e.g. plating are initiated on a very local nanometer to micrometer scale and therefore strongly depend on the local overpotential distribution, which is influenced by the design of the active particle shape or morphology and local fluctuations in the SEI thickness. To capture all these phenomena within a rational design approach for batteries using modelling and simulations, detailed models on particle, electrode and cell scales including side reaction and transport in interphases and the binder domain need to be developed and solved within a coupled numerical framework.

In the presentation an overview is given about our recent theoretical developments on microstructure resolved particle, electrode and solid electrolyte models. In particles and solid electrolytes the impact of grain boundaries on the performance are captured within microstructure resolved simulations [1]. Electrode models include the impact of the binder – carbon black domain and composite electrodes on cell performance and degradation [2,3,4]. Our new models for SEI formation and growth coupled with microstructure resolved simulations predict thickness fluctuations of the SEI on electrode scale and different growth regimes depending on the operating conditions and mechanical properties of the SEI [5,6]. SEI properties and particle shape influence the local onset of plating. As a consequence the classical porous electrode theory has been generalized to capture the impact of particle shape and surface accessibility on SEI growth and plating [7].

References:

1. Ates, T., Neumann, A., Danner, T., Latz, A., Zarrabeitia, M., Stepien, D., Varzi, A., & Passerini, S. (2022). *Advanced Science*, 2105234. https://doi.org/10.1002/advs.202105234
2. Hein, S., Danner, T., Westhoff, D., Prifling, B., Scurtu, R., Kremer, L., Hoffmann, A., Hilger, A., Osenberg, M., Manke, I., Wohlfahrt-Mehrens, M., Schmidt, V., & Latz, A. (2020). *Journal of The Electrochemical Society*, *167*(1), 013546. https://doi.org/10.1149/1945-7111/ab6b1d
3. de Lauri, V., Krumbein, L., Hein, S., Prifling, B., Schmidt, V., Danner, T., & Latz, A. (2021). *ACS Applied Energy Materials*, *4*(12), 13847-13859. https://doi.org/10.1021/acsaem.1c02621
4. Randau, S., Walther, F., Neumann, A., Schneider, Y., Negi, R. S., Mogwitz, B., Sann, J., Becker-Steinberger, K., Danner, T., Hein, S., Latz, A., Richter, F. H., & Janek, J. (2021). *Chemistry of Materials*, *33*(4), 1380-1393. https://doi.org/10.1021/acs.chemmater.0c04454
5. von Kolzenberg, L., Latz, A., & Horstmann, B. (2022). *Batteries and Supercaps*, *5*(2), 1-11. https://doi.org/10.1002/batt.202100216
6. Bolay, L. J., Schmitt, T., Hein, S., Mendoza-Hernandez, O. S., Hosono, E., Asakura, D., Kinoshita, K., Matsuda, H., Umeda, M., Sone, Y., Latz, A., & Horstmann, B. (2022). *Journal of Power Sources Advances*, *14*(November 2021), 100083. https://doi.org/10.1016/j.powera.2022.100083
7. Traskunov, I., & Latz, A. (2021). *Electrochimica Acta*, *379*, 138144. https://doi.org/10.1016/j.electacta.2021.138144

# Liquid water formation and transport in Membrane Electrode Assembly of PEMFC: liquid injection, vapor condensation and mixed scenario

Joël Pauchet
Université Grenoble Alpes, CEA, LITEN, 38054 Grenoble, France
*joel.pauchet@cea.fr*

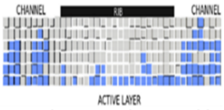
The improvement of water management in a PEMFC is a major challenge to increase performance and durability (avoid drying and flooding) and reduce cost (better use of the catalyst); Gas Diffusion Layer (GDL) is a key component on water management.
Based on specific in-operando experiments (X-ray, Neutron, optical, μ-sensors…) and ex-situ GDL characterizations (HRTEM, E-SEM, anisotropy, wettability, durability…) that gave general guidelines and/or validation, Pore Network Modeling (PNM) has been put in place to better understand liquid water formation and transport in Membrane Electrode Assembly (MEA) and especially in GDL. GDL is a thin porous medium for which PNM is of interest to model two-phase flows.

This experimental/modeling approach has allowed highlighting different water management scenarii: injection (liquid water enters the GDL), condensation (vapor water enters the GDL then condenses) and mixed scenario (combining injection and condensation).

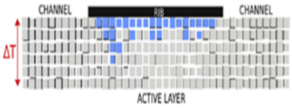
Some outcomes are discussed: GDL is a complex porous medium (multiscale, anisotropic, mixed wettability, thin…); the water management scenario depends on the local operating conditions and components' properties; existence and location of liquid droplets (breakthrough points) at the GDL/rib-channel interfaces; influence of the adjacent layers (two-phase filtering effect), mixed wettability distribution, temperature gradient… on the liquid distribution, gas diffusion and cell performance; conventional macro-homogeneous models (Leverett, relative gas diffusion…) can lead to incorrect saturation profile, overestimated gas diffusion, and underestimated flooding; condensation, mainly below the rib, contributes to non-uniform local current density distribution at the rib-channel scale; PTFE loss in the GDL contributes to cell performance loss with huge non-linearity (percolation threshold); concept of condensation diagram; influence of rib-channel dimensions; 3D image-based two-phase modeling; application of PNM to the cathodic active layer…

Experimental and modeling perspectives are discussed as a step towards design tools.

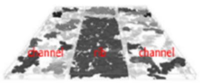

Optical visu of droplets on the GDL/channel interface



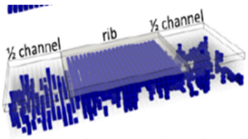
Liquid injection (water in blue, GDL in grey) (PNM)



Vapor condensation (PNM)



3D X-ray visualisation (PSI)



Mixed scenario (PNM)

# Computational Workflows for an Accelerated Design of Novel Materials and Interfaces

Ivano E. Castelli
*Department of Energy Conversion and Storage, Technical University of Denmark*
*Anker Engelundsvej 411, DK-2800 Kgs. Lyngby, Denmark*
*ivca@dtu.dk*

The development of automated computational tools is required to accelerate the discovery of new functional materials, to speed up the transition to a sustainable future. Here, I address this topic by designing new electrodes with controlled interfaces for different applications which accelerate the transition to a sustainable future. These workflows are implemented in the framework of Density Functional Theory, using MyQueue and the Atomistic Simulation Environment (ASE). In the first part, I describe a fully autonomous workflow, which identifies materials to be used as intercalation electrodes in batteries, based on thermodynamic and kinetic descriptors like adsorption energies and diffusion barriers [1]. A substantial acceleration for the calculations of the kinetic properties has been obtained due to a recent implementation of the Nudged Elastic Bands (NEB) method, which takes into consideration the symmetries of the system to reduce the number of images to calculate. Moreover, we have established a surrogate model to identify the transition states, which can further reduce the computational cost to at least one order of magnitude [2, 3]. We have applied this workflow to discover new cathode materials for Mg batteries as well as solid state electrolytes for Li, Na, and Mg all-solid-state batteries [1, 3]. In the second part of my talk, I discuss how engineering the interface can positively impact surface properties. I show this concept using two examples. In the first one, I nanostructure materials to increase the Li-storage capacity in C-anodes or to adjust the change in volume during charge/discharge in Si-anodes for Li-ion batteries [4]. In the second example, I apply strain engineering and external stimuli to switch material's polarization to decrease the reaction overpotential in oxynitride materials for the oxygen evolution reaction [5, 6].

References:

1. F. T. Bölle, N. R. Mathiesen, A. J. Nielsen, T. Vegge, J. M. García-Lastra, and I. E. Castelli, *Batteries & Supercaps* **3**, 488 (2020).
2. F. T. Bölle, A. Bhowmik, T. Vegge, J. M. García-Lastra, and I. E. Castelli, *Batteries & Supercaps* **4**, 1516 (2021).
3. B. H. Sjølin, P. B. Jørgensen, A. Fedrigucci, T. Vegge, A. Bhowmik, and I. E. Castelli, *Batteries & Supercaps* **2023**, e202300041 (2023).
4. S. B. Oliva, F. T. Bölle, A. T. Las, X. Xia, and I. E. Castelli, *J. Mater. Chem. A*, **11**, 21036 (2023).
5. Z. Lan, D. R. Småbråten, C. Xiao, T. Vegge, U. Aschauer, and I. E. Castelli, *ACS Catal* **11**, 12692 (2021).
6. C. Spezzati, Z. Lan, and I. E. Castelli, *Journal of Catalysis* **413**, 720 (2022).

# The Catalyst- and Porous Transport Layer Interface: Decisive for PEWE Performance

Felix N. Büchi[1], Cesar C. Weber[1], Tobias Schuler[1,2], Jacob Wrubel[2], Jens Eller[1]
[1] *Electrochemistry Laboratory, Paul Scherrer Institut*
*CH-5232 Villigen PSI, Switzerland*
[2] *National Renewable Energy Laboratory*
*Golden, CO 80401, USA*
*felix.buechi@psi.ch*

The need to develop polymer electrolyte water electrolyzers with minimum amounts of precious materials, in particular those from the platinum metal group, but conserving high performance needs development and optimization of many materials and components.

The interface between the catalyst- and porous transport layers (PTL) [1-3] is in this respect particularly important as it seems to have a strong influence on the current density distribution, the $IrO_2$ catalyst utilization and its mass activity. For low loading anodes two factors seem important, the surface should be least corrugated [4] and a noble metal interface layer helps to increase catalyst utilization [5].

The presentation reviews the effects of Catalyst layer and PTL structures on the decisive limitations and explains improvements.

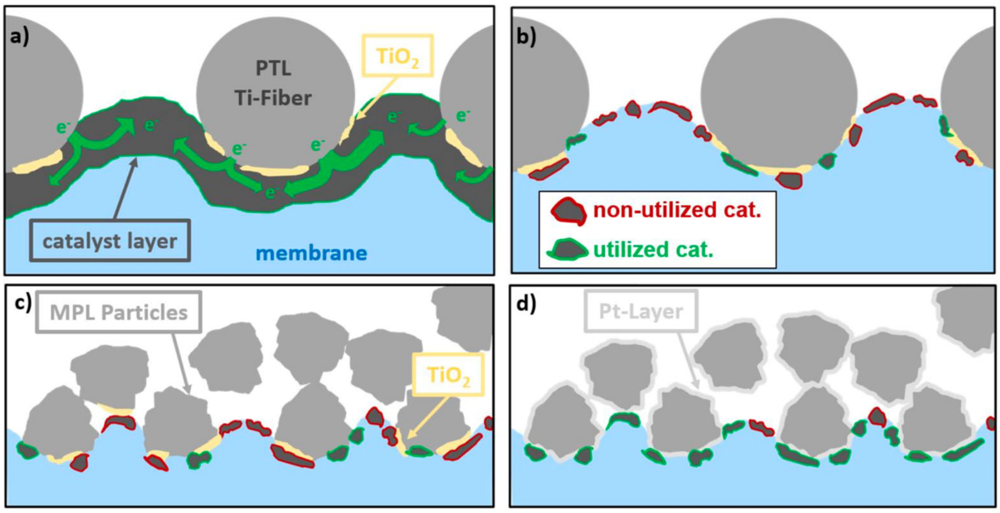


Figure 1: Schematic illustrations showing the effects of MPL and Pt-interlayer at the anode of a PEWE cell; a) PTL in contact with a CL with high catalyst loading, b) PTL with low catalyst loading, c) MPL without Pt-interlayer with low catalyst loading, and d) MPL with Pt-layer and low catalyst loading. Figure from Ref. [5].

References:
1. T. Schuler, T.J. Schmidt, and F.N. Büchi, *J. Electrochem. Soc.*, **166,** F555-F565 (2019)
2. C.C. Weber, J.A. Wrubel, L. Gubler, G. Bender, S. De Angelis, and F.N. Büchi, *ACS Applied Materials & Interfaces*, **15,** 34750-34763 (2023)
3. T. Schuler, J.M. Ciccone, B. Krentscher, F. Marone, C. Peter, T.J. Schmidt, and F.N. Büchi, *Advanced Energy Materials*, **10,** 1903216 (2020)
4. T. Schuler, C.C. Weber, J.A. Wrubel, L. Gubler, B. Pivovar, F.N. Büchi, and G. Bender, *Advanced Energy Materials*, **14,** 2302786 (2024)
5. C.C. Weber, S. De Angelis, R. Meinert, C. Appel, M. Holler, M. Guizar-Sicairos, L. Gubler, F.N. Büchi, *EES Catalysis*, **2**, 585-602 (2024)

# What Electronic-structure Simulations Can Teach Us About Li-ion Batteries

Nicola Marzari
*EPFL and PSI*
*EPFL STI IMX THEOS, Station 9, Lausanne, Swtizerland*
*Laboratory of Materials Simulations (LMS), Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
*nicola.marzari@epfl.ch*

Electronic-structure simulations can be powerful tools in understanding the energetics, thermodynamics, and kinetics of battery materials. I'll provide an overview on what is possible nowadays for cathodes or for solid-state electrolytes. In particular, I'll focus on accurate and predictive description of the redox energetics in Li-ion cathodes, where standard approaches based on density-functional theory perform poorly, due to the self-interaction errors inherent in most approximations to the exchange-correlation potential. I'll highlight how extended Hubbard functionals, on the other hand, provide very accurate predictions of cathode voltages, and a faithful description of redox reactions in mixed-valence states [1].

A second topic will be on materials design and discovery, highlighting how we can screen thousands of Li-containing materials for optimal solid-state electrolytes [2,3], and how we can use machine-learning models to capture the Li-ion kinetics both in the bulk materials and in polymer-inorganics blends [4].

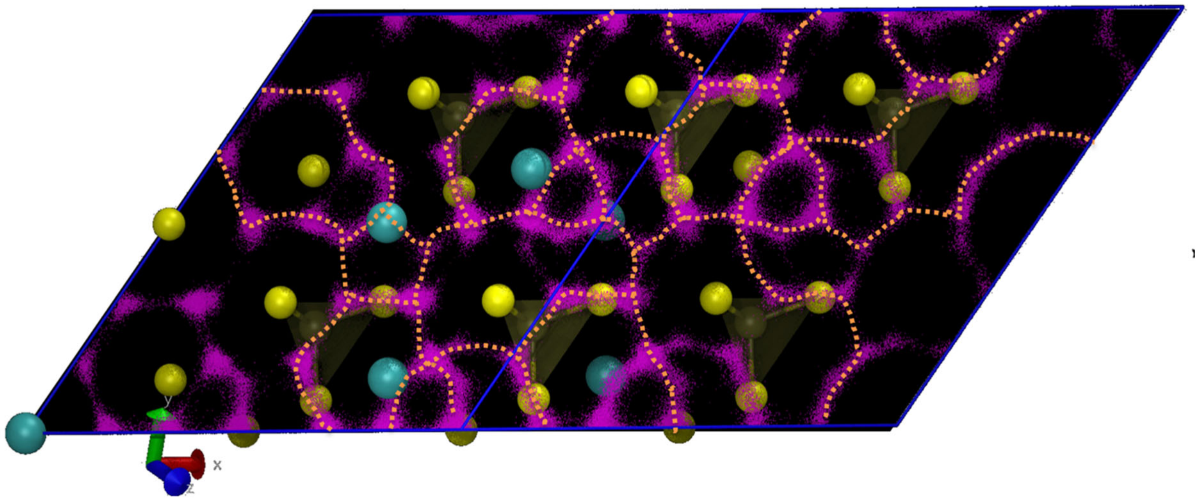


Figure 1: Optimal doping/co-doping of a Li-ion argyrodite solid-state conductor.

References:
1. I. Timrov, F. Aquilante, M. Cococcioni, and N. Marzari, *PRX Energy* **1**, 033003 (2022).
2. L. Kahle, A. Marcolongo, and N. Marzari, *Energy and Environmental Science* **13** (2020), 928-948.
3. T. Thakur, L. Kahle, and N. Marzari, *in preparation* (2024).
4. S. Muy and N. Marzari, *in preparation* (2024).

# Unraveling the Influence of Ionomer on Catalyst Layer Degradation in Proton Exchange Membrane Fuel Cells: A Hierarchical Modeling Approach

Jannik Heitz[1,2], Thomas Kadyk[1,2], Michael Eikerling[1,2,3]
[1] *Theory and Computation of Energy Materials (IEK-13), Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*
[2] *Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany*
[3] *Jülich Aachen Research Alliance, JARA Energy, 52425 Jülich, Germany*
*j.heitz@fz-juelich.de*

Electrochemical energy conversion technologies play a crucial and increasing role in the transition towards a sustainable global energy economy. For mobile applications, proton exchange membrane fuel cells (PEMFC) have reached a high level of maturity and entered commercialization. Since applications in heavy duty vehicles (HDV) place higher demands on operation life (30'000 h), reducing degradation in PEMFCs is one of the foremost challenges to increase their economic viability. The main contribution to degradation stems from microstructural changes in the electrodes. However, the degradation mechanisms encompassing Ostwald ripening, particle coagulation and dissolution and the influence of material properties on them are not yet fully understood.

This work uses a hierarchical model to link microstructural changes to the evolution of materials properties and, ultimately, to the transformation of performance over the lifetime of the cell [1,2]. On particle level, the size of the Pt particles is influenced by degradation mechanisms. In this work, the focus is on the Ostwald ripening mechanism, i.e. the dissolution of catalyst particles and the redeposition of dissolved particles. Since small particles are less stable, they dissolve faster. Large particles grow due to their enhanced rate of redeposition. Overall, the surface excess energy drives particle growth towards larger radii, which reduces the overall electrochemical surface area (ECSA).

This particle degradation is influenced by the local reaction conditions, especially the pH on the particle surface. The ionomer in the catalyst layer influences these local reaction conditions and thus the local degradation rates. We examine the influence of ionomer on catalyst degradation by dividing the Pt particle population into two distinct groups: particles covered by ionomer and those without ionomer coverage. This represents the agglomerate structure shown in Figure 1, in which catalyst particles can sit on the surface of the carbon agglomerate and are covered by ionomer, or particles can be inside the agglomerate, not in contact with ionomer. We analyse the impact of ionomer coverage, and thus proton density, on the degradation of Pt particles. We will demonstrate capabilities to deconvolute and quantify the influence of ionomer on performance degradation, providing guidance for materials development and cell fabrication.

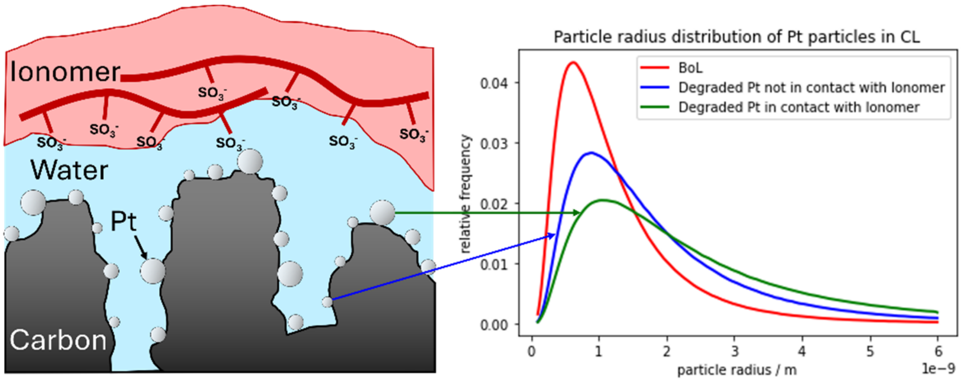


**Figure 1: Structure of catalyst layer and its influence on the degradation of the Pt particles**

References:
1. P. Urchaga, T. Kadyk, S.G. Rinaldo, et al., *Electrochimica Acta* **176** (2015) 1500-1510.
2. A. A. Kulikovsky, *J. Electrochem. Soc.* **161**(3) (2014) F263-F270.

# Bootcamp for Neural Networks: Boost Neural Network Training using Physical Simulation Models and Transfer Learning for Fuel Cell Operation Monitoring

L. Klass, L. Holz, L. König, A. Kabza, F. Sehnke, K. Strecker, M. Hölzle
*Centre for Solar Energy and Hydrogen Research Baden-Württemberg,*
*Lise-Meitner-Str. 24, 89081 Ulm, Germany*
*lukas.klass@zsw-bw.de*

Fuel cells are a promising technology contributing to the decarbonisation of the transportation sector. The development of fuel cells requires extensive testing on test stations to investigate new designs and especially to verify lifetime and durability. Today's requirements for fuel cells in heavy duty transportation applications e.g. 25,000 h, as announced by the U.S. Department of Energy, pose a huge challenge for both the development but also for the testing and operation of fuel cells.

Performance Monitoring supports the achievement of the durability goals by detecting and preventing harmful events in a very early stage.

A monitoring approach using a digital twin based on machine learning (ML) models was presented in [1]. However, owing to the strong correlation and cyclic repetition of the operating conditions used for training the network, adjusting the ML model for new stacks or load cycles is only possible to a limited extent and requires extensive retraining. Furthermore, the definition of a constant alarm threshold prevented an adaptive monitoring based on the ML model's confidence.

We now present a new adaptable ML model for the probabilistic prediction of the stationary cell voltage of a fuel cell stack based on the operating conditions. The ML model consists of a feed forward neural network with a Gaussian output layer that enables the prediction of both the expected cell voltage level as well as the corresponding prediction confidence. The operating conditions of the fuel cell (current, pressure, temperature, humidity, stoichiometry) serve as input features for the ML model.

To circumvent the aforementioned operating condition correlation issue of the previous model, the ML model was pre-trained using simulated data. A 1.5 D fuel cell model developed at ZSW [2] was used to generate the training data by randomly sampling data from the simulation model within a predefined window of operating conditions. This proceeding allows the model to learn the characteristics of a fuel cell and the most important correlations between input and output from the simulation model. Afterwards, transfer learning allows adapting the preconditioned ML model to the characteristics of a real fuel cell using real data from a test bench. However, in contrast to the previous ML model generation, this proceeding requires considerably less test bench data and handles correlations in the input data much better.

To demonstrate the precision and robustness of the machine learning model, a ML model is trained using transfer learning on a small subset for each of the different test bench data sets. Afterwards the performance of the different models is assessed using the remaining data points.

In the next step, the stationary ML model will be complemented with a degradation model to enable the cell voltage monitoring during the whole lifetime of the fuel cell.

References:

1. L. Klass, A. Kabza, F. Sehnke, K. Strecker, M. Hölzle, Lifelong Performance Monitoring of PEM Fuel Cells Using Machine Learning Models, *Journal of Power Sources.* **580** (2023), 233308
2. T. Wagner, Experimental and Model Based Analysis of LT PEM Fuel Cells Exposed to Gaseous Impurities and Development of a Simulation Software, *PhD Thesis, University of Ulm*, July 2023, in press

# Investigating the Impact of Air Pollutants on Fuel Cell Performance and Durability: Experimental and Modelling Approaches

A. Abd El Kader[1,2], M. Marchand[2], P. Affonso Nobrega[1], C. Beauger[1]
*[1] Mines Paris, PSL University, Centre for processes, renewable energy and energy systems (PERSEE), 06904 Sophia Antipolis, France.*
*[2] Ampere France, Renault Group, 78084 Guyancourt, France.*
*[3] Mines Paris, PSL University, Centre for processes, renewable energy and energy systems (PERSEE), 06904 Sophia Antipolis, France.*
*ahmad.abd-el-kader@minesparis.psl.eu*

Fuel cells hold immense promise as efficient and sustainable power sources for transportation and stationary applications. However, their operation can be severely impacted by air pollutants, particularly sulfur dioxide ($SO_2$) and nitrogen oxides ($NO_x$). These pollutants can adsorb onto the platinum catalyst, leading to a decrease in fuel cell performance and durability.

In this study, we investigate the impact of $SO_2$ and $NO_2$ on PEM fuel cell performance and durability. The contamination tests were carried out at a constant current density of 0.5 $A.cm^{-2}$ and consisted of four steps: a pre-poisoning step to evaluate initial performance (16 h), poisoning step (50 h), self-recovery in a pure air stream (20 h) and a driven CV-induced recovery. Electrochemical characterizations were carried out at the end of each step (Polarization curve, Electrochemical Impedance Spectroscopy, Cyclic Voltammetry and $H_2$ Crossover). Figure 1 shows the effect of contaminating a single fuel cell with a low concentration of 0.5 ppm of sulfur dioxide ($SO_2$). Remarkably, this resulted in a 29% decrease in cell voltage. Building on this foundation, our ongoing research aims to delve deeper into the impact of individual pollutant concentrations ($SO_2$ and $NO_2$) and their combined effects, considering varying temperatures and current densities to simulate real-world conditions.

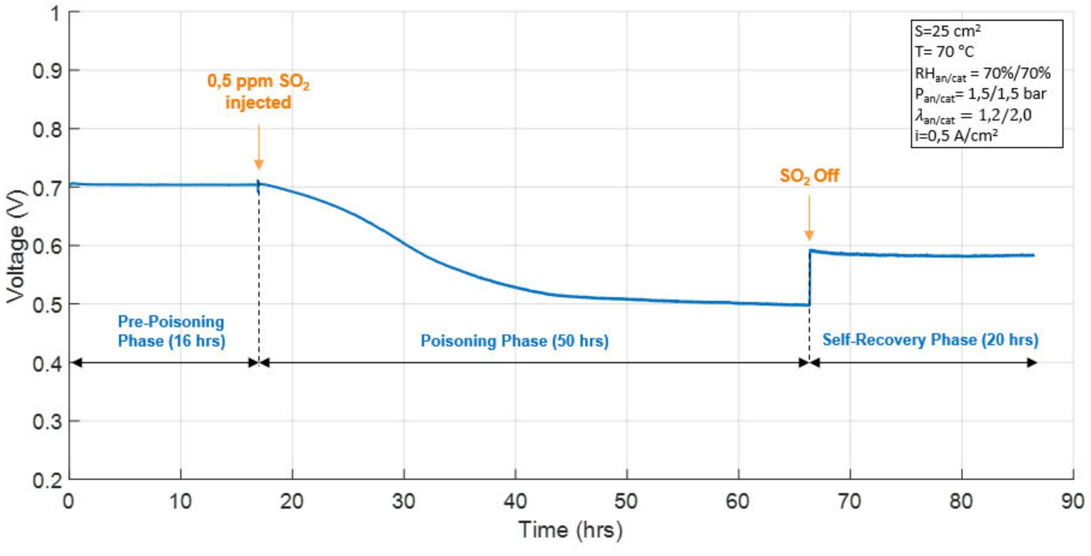


Figure 1: Cell Voltage under Contamination with 0.5 ppm of $SO_2$ for 50 hours followed by Recovery with Pure Air for 20 hours ($T$ = 70 °C and $i$ = 0.5 $A/cm^2$)

Simultaneously, a comprehensive model is being developed using Simscape in Matlab. The model accounts for the pollutants either as single-component gases or as a mixture. For single-component gas adsorption, the Langmuir Isotherm model is employed. To capture the competitive adsorption of $SO_2$ and $NO_2$ on platinum in gas mixtures, we are testing the Modified Competitive Langmuir Isotherm Model. The model will further be calibrated and validated using the experimental results.

This combined experimental and modelling approach will provide a comprehensive understanding of the impact of air pollutants on fuel cell performance and durability. The insights gained from this study can inform the development of mitigation strategies and enhance the robustness of fuel cells in real-world applications as well as the sizing of a filter to reduce the effect of these pollutants.

# Multiphase-field Simulation studies on Coarsening in FIB-SEM reconstructed Ni/CGO SOFC Anodes

R. K. Jeela[1], M. Ahmad[1], D. Schneider[1,4], Y. Liu[5], M. Juckel[6], N. H. Menzler[6], A. Weber[5],
M. Wieler[3], B. Nestler[1,2,4]
[1] Institute of Digital Materials Science (IDM), Karlsruhe University of Applied Sciences, Karlsruhe, Germany
[2] Institute for Applied Materials (IAM-MMS), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[3] Computational Materials Engineering (CR/ATC1), Robert Bosch GmbH, Renningen, Germany
[4] Institute of Nanotechnology (INT-MSS), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[5] Institute for Applied Materials (IAM-ET), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
[6] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, Materials Synthesis and Processing (IEK-1), Jülich, Germany
*ravi.jeela@partner.kit.edu*

Due to their potential to generate clean and efficient power, Solid oxide fuel cells (SOFC) are anticipated to play a key role in future green energy production. In this regard, the long-term degradation of the functional materials presents an ongoing challenge. Due to the mixed electronic-ionic conductivity of the gadolinium doped ceria (CGO) phase, Nickel-gadolinium doped ceria (Ni/CGO) cermet anode is gaining increasing attention over time as an alternative electrode, providing enhanced reaction sites and improved electro-chemical performance. Compared to Nickel-Yttria stabilized zirconia (Ni/YSZ), Evolution of the microstructure is found to be different in Ni/CGO cermet, and the exact nature of the processes is not yet known.

To increase the lifetime of SOFCs, it is necessary to deepen the understanding of degradation-mechanisms over the lifetime. Coarsening of Nickel and CGO particles is considered to be one of the major contributors to microstructural degradation of Ni/CGO anode. To model the coarsening of nickel and CGO, a multiphase-field model is deployed. The model is based on a grand potential functional [1] and a recent extension to delimit surface self-diffusion from bulk diffusion [2]. The model facilitates the precise inclusion of measured surface diffusivities.

In this work, multiphase-field simulation studies are presented on nickel and CGO coarsening in a FIB-SEM reconstructed pristine Ni/CGO anode after aging at 900°C for 1000 hours. Effective properties of the microstructure such as particle size distributions, mean particle diameters, tortuosities, three-phase boundary lengths (TPBL) and specific surface areas are considered as indicators of possible degradation. These simulation studies and results assist in further investigations of finding optimal microstructures for Ni/CGO anodes by varying the volume fractions of nickel and CGO as well as particle size ratios.

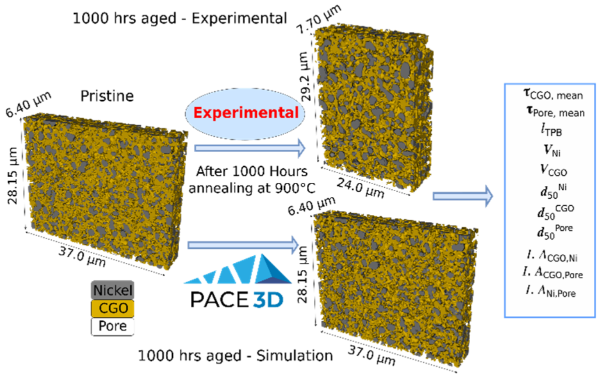


Figure 1: Multiphase-field simulations of Ni and CGO coarsening in a FIB-SEM reconstructed SOFC anode microstructure and Comparison with experimental

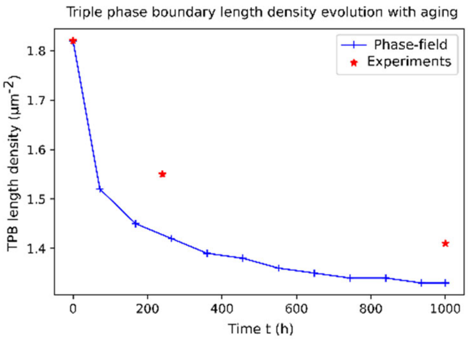


Figure 2: Ni/CGO anode effective properties evolution over time

1. Choudhury, Abhik, and Britta Nestler: Physical Review E 85(2) (2012) 021602
2. Hoffrogge, Paul W., et al.: Physical Review E 103(3) (2021) 033307

Acknowledgements: Funded by the Federal Ministry of Education and Research (BMBF, 03SF0622A) and supported by the state of Baden-Württemberg through bwHPC

# Impedance model for SOFC stacks

Sadhana Golani, André Weber
*Karlsruhe Institute of Technology (KIT), Institute for Applied Materials – Electrochemical Technologies (IAM-ET), 76131-Karlsruhe, Germany*
*sadhana.golani@kit.edu*

Operando diagnosis of stacks is one of the crucial aspects required for target-oriented development and commercialization of solid oxide fuel cell (SOFC) systems. Impedance spectroscopy is considered to be a powerful tool for such analysis. However, evolution of the losses at the stack level is complicated as the loss mechanisms over the entire stack volume strongly vary and critical local phenomena might be averaged out. Hence, for reliable quantification and thorough interpretation of the processes, electrolyte supported cells (ESC) with a small active area of 1 cm², ensuring homogeneous operating conditions, were monitored by Current-Voltage (CV) curves and electrochemical impedance spectroscopy (EIS) measurements. The impact of several operating parameters such as temperature, fuel composition and current density was studied in the whole range of technically relevant operating conditions. These experimental single cell EIS data sets were subsequently evaluated by (i) a distribution of relaxation times (DRT) analysis followed by (ii) a complex non-linear square (CNLS) fit of a physiochemically meaningful equivalent circuit model (ECM) [1].

In this study, a parameter map is derived using these measurements and a static model is developed to predict the local electrochemical losses at the stack level [1]. This model provides thorough information about the current density distribution and fuel utilization along the gas channel. Using this approach, a calculation of the stack impedance at relevant operation voltages and fuel gas compositions becomes feasible.

Reference:

1. D. Klotz, A. Leonide, A. Weber, E. Ivers-Tiffée, International Journal of Hydrogen Energy, 39 (2014), 20844-20849

# Towards SOFC modeling with the Lattice Boltzmann method

Nilesh Sawant, Ilya Karlin
*CKG, IEPE, D-MAVT ETH Zurich*
*LEO D8, Leonhardstrasse 27, 8092 Zürich, Switzerland*
*sawantn@ethz.ch*

In this project, we explore the possibility of building lattice Boltzmann models having multicomponent diffusion, detailed mass action reaction kinetics for electrochemistry and heterogeneous adsorption with an aim to perform transient thermal computational fluid dynamics simulations of single phase fuel cells such as the Solid Oxide Fuel Cells (SOFC).

The lattice Boltzmann method (LBM) [1] for Computational Fluid Dynamics (CFD) solves a discrete realization of the Boltzmann transport equation at the mesoscale such that the Navier Stokes equations are recovered at the macroscale. The LBM can simulate a variety of flows including but not limited to transitional flows, flows in complex moving geometries, compressible flows, multiphase flows, multicomponent flows, rarefied gases, nanoflows etc. The recent developments in the LBM for multicomponent [2] and reactive [3] flows and the innate ability of the method to capture Knudsen effects due to its kinetic nature make it an excellent fit for modeling fuel cells. The work involves development of a Dusty Gas Model from the Stefan-Maxwell model within the kinetic framework of the LBM, development of porous media non-isothermal hydrodynamics models, implementation of detailed chemistry models for adsorption-desorption and electrochemistry at the triple phase boundary, etc. for full cell multicomponent Direct Numerical Simulations (DNS) with averaged electrode microstructure. The polarization curves shown in Figure 1 have been obtained from the LBM model in development, compared with experimental results [4]. Extension of the model to account for variable porosity factors is currently underway.

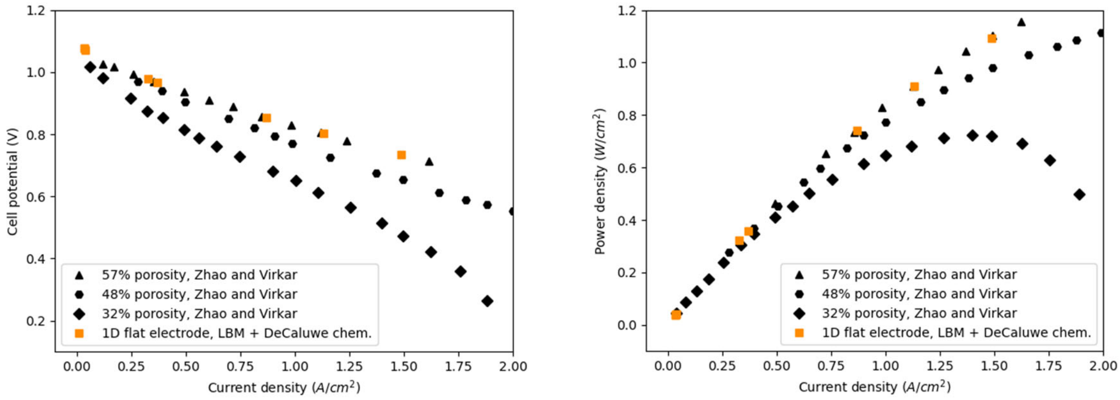


Figure 1: Polarization curve for LBM simulations of a a one-dimensional flat electrode SOFC. Left: Cell potential v/s current density. Right: Power density v/s current density.

References:
1. F. J. Higuera, S. Succi, and R. Benzi, "Lattice gas dynamics with enhanced collisions", Europhysics Letters 9(4) (1989), 345-349.
2. N. Sawant, B. Dorschner, and I. V. Karlin, "Consistent lattice Boltzmann model for multicomponent mixtures", Journal of Fluid Mechanics 909 (Feb. 25, 2021), A1
3. N. Sawant, B. Dorschner, and I. Karlin, "Consistent lattice Boltzmann model for reactive mixtures", Journal of Fluid Mechanics 941 (June 25, 2022), A62
4. F Zhao and A Virkar, "Dependence of polarization in anode-supportedsolid oxide fuel cells on various cell parameters", Journal of Power Sources 141(1) (Feb. 16, 2005), 79-95.

# Effect of liquid saturation transients on electrochemical impedance of PEM fuel cell

Ying Sun[1,2], Thomas Kadyk[1,3], Andrei Kulikovsky[1], Michael Eikerling[1,2,3]
[1]*Forschungszentrum Jülich GmbH, Theory and Computation of Energy Materials (IEK-13) Institute of Energy and Climate Research, 52425 Jülich, Germany*
[2]*Chair of Theory and Computation of Energy Materials, Faculty of Georecources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany*
[3]*JARA Energy, Jülich Aachen Research Alliance, 52425 Jülich, Germany*
*y.sun@fz-juelich.de*

Electrochemical impedance spectroscopy (EIS) is a vital and widely used tool for studying proton exchange membrane (PEM) fuel cells. The capabilities of EIS measurements to reveal the influence of transport and kinetic processes on fuel cell performance and deconvolute them have been extensively demonstrated. One enigmatic feature often observed in Nyquist plots is a low-frequency (LF) inductive loop [1]. At frequencies from $10^{-3}$ Hz to $10^{-1}$ Hz, the related process is notably slower than typical oxygen transport processes in porous layers [2]. A process in this dynamic range is oxygen transport in the channel, but it lacks inductive behavior [2] and thus cannot resolve the mystery. Hypotheses for the LF loop's origin include slow ORR intermediates [3], hydrogen peroxide formation, or platinum dissolution [4], Pt oxidation [5], CO poisoning [6], and proton conductivity variations [7].

While for different operating conditions, different mechanisms may come into play to a different extend, our research explores how liquid water dynamics affect proton and oxygen transport in the cathode catalyst layer of a PEM fuel cell. We introduce a novel impedance model for the PEM fuel cell cathode that incorporates liquid water transport, resulting in the formation of a low-frequency loop. We analyze the LF loop's formation and its dependence on the relaxation behavior of the proton conductivity. We emphasize the crucial role of the water retention behavior of the CL, particularly in the context of the relationship between liquid saturation and capillary pressure. When the saturation is assumed to be independent of the capillary pressure, the LF loop vanishes. Our research enhances the understanding of the impedance behavior observed for PEM fuel cells. It sheds light on the origin of the LF loop, connecting its formation with water dynamics and transport processes within the cell [8].

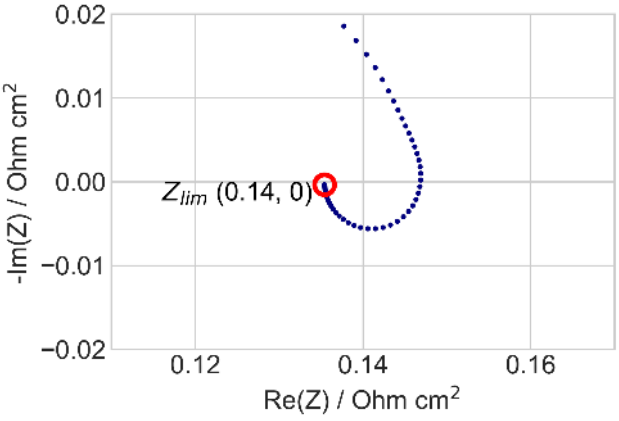


Figure 1: Low-frequency part of Nyquist EIS spectra of PEMFC; the red circle indicates the low frequency limit impedance, $Z_{lim}$.

References:
1. A. Kulikovsky, *J. Electrochem. Soc.*, **166** (2019), F306-F311.
2. A. Kulikovsky, *J. Electrochem. Soc.*, **168** (2021), 114520.
3. O. Antoine, Y. Bultel, R. Durand, *J. Electroanal. Chem.*, **499** (2001), 85-94.
4. S. K. Roy, M. E. Orazem, B. Tribollet, *J. Electrochem. Soc.*, **154** (2007), B1378-B1388.
5. B. P. Setzler, Th. F. Fuller, *J. Electrochem. Soc.*, **162** (2015), F519-F530.
6. N. Wagner, E. Gülzow, *J. Power Sources*, **127** (2004), 341-347.
7. A. Kulikovsky, *Electrochem. Comm.*, **140** (2022), 107340.
8. Y. Sun, T. Kadyk, A. Kulikovsky, M. Eikerling, (in preparation).

# Empirical PEMFC model for local performance and resistance prediction

Philipp Oppek, André Weber
*Institute for Applied Materials (IAM-ET), Karlsruhe Institute of Technology (KIT),*
*Karlsruhe, Germany*
*philipp.oppek@kit.edu*

PEMFC cell and stack performance is controlled by interdependent, non-linear multi-physical processes. The operation of large-scale cells leads to significant spatial gradients in operating conditions and performance.

To predict and optimize the operating behaviour, different types of modeling approaches can be applied [1,2,3]. Due to the tremendous variety of influencing factors for PEMFCs, an enormous amount of experimental effort is required to set up a model that considers the effects of all factors and their interactions in a spatially resolved way.

The commonly used one-factor-at-a-time testing (OFAT) is not only insufficient in terms of experimental effort, but also fails due to the one-dimensional variation in the resolution of interactions between influencing factors. [4] Since, multi-physical and interdependent non-linear complex processes occur in PEMFC the OFAT approach is inefficient and insufficient. To overcome this approach, a suitable methodology is required.

Therefore, we transfer a methodology using design of experiments (DoE) [5] on a segmented cell to establish an empirical model, while keeping the experimental effort low. In this cell not only the local performance, but also the resistance distribution can be determined by applying electrochemical impedance spectroscopy (EIS) on each segment.

The local operating conditions that govern resistance and performance distribution along the cell can be investigated by setting up an appropriate experimental design. Mathematical-statistical methods [5] are used to identify the significant main effects and interactions and to establish the empirical model. Using the model, the local performance and the resistance distribution can be predicted as a function of operating conditions.

In this contribution the development and verification of an empirical model using DoE for a segmented PEMFC will be presented. Based on the influence of the operating conditions on the local performance and the resistance distribution, consequences for the further development of the cell will be discussed.

References:

1. G.A. Futter, P. Gazdzicki, A.K. Friedrich, A. Latz, T. Jahnke, J. Power Sources 391 (2018), 148-161
2. M. Heinzmann, A. Weber, E. Ivers-Tiffée, J. Power Sources 402 (2018), 24-33
3. Kim, S.-M. Lee, S. Srinivasan, C.E. Chamberlin, J. Electrochem. Soc. 142 (1995), 2670-2674
4. R. Leardi, Analytica Chimica Acta 652 (2009), 161-172
5. R.H. Myers, D.C. Montgomery, *Design and Analysis of Experiments*, John Wiley & Sons, New York, 2009

# Predicting the performance of real fuel cells with a fast MATLAB model

L. König, L. Klass, F. Wilhelm, J. Scholta
*Centre for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW)*
*Lise-Meitner-Straße 24, 89081 Ulm, Germany*
*Lukas.Koenig@zsw-bw.de*

Depending on the intended purpose, there are several ways to appropriately simulate polymer electrolyte membrane fuel cells (PEMFCs). For high accuracy in combination with detailed local resolution, one way is a full three-dimensional CFD model including a sophisticated description of all relevant physical and chemical processes. However, for many applications this level of detail is not required, whereas on the other hand, the computational effort required for the simulation may be an important aspect. In such cases, more coarse-grained, semi-empirical and fast 1-D models can constitute valuable tools. The MATLAB model [1, 2] presented here is able to deliver accurate and fast predictions on cell voltage and efficiency. This is demonstrated within this contribution by validation with test bench data. The model uses a segmented approach that resolves the anode and cathode side in co- or counter-flow configurations.

The experimental validation data for the tool employed here was measured with two different fuel cell stacks. The first data set (126 samples + 5 pole curve points) stems from an automotive stack that was operated with typical PEMFC operating conditions. The second data set (270 samples + 17 pole curve points) was generated using a different automotive design. This stack was tested employing a randomly generated set of operating conditions (with a bias towards extreme values) to validate the model over a wider range for more atypical scenarios. For each test case, the model was fitted to an experimental begin of test pole curve. For the first test, the model shows very good accuracy with a root mean square error (rmse) of cell voltage prediction of 5.26 mV. For the second test, the rmse amounts to a higher value of 31.32 mV. This apparently higher deviation is mainly due to the very atypical operating points that would usually not be expected in normal operation. The worst predictions occur only at very low humidity. This demonstrates that the model is already really accurate for the relevant operating window, but still especially the membrane water model could be improved to better cover extreme situations. The Springer model [3] used here does not work very well for such conditions.

Overall, the model is capable to obtain accurate results for PEMFC under typical operating conditions. Another important feature is the computational efficiency of the model, calculating 300 sample points takes about 1 minute of simulation time on one recent CPU core.

Next steps envisaged for further development of the model are the introduction of a more realistic membrane model and the inclusion of an aging (degradation) model.

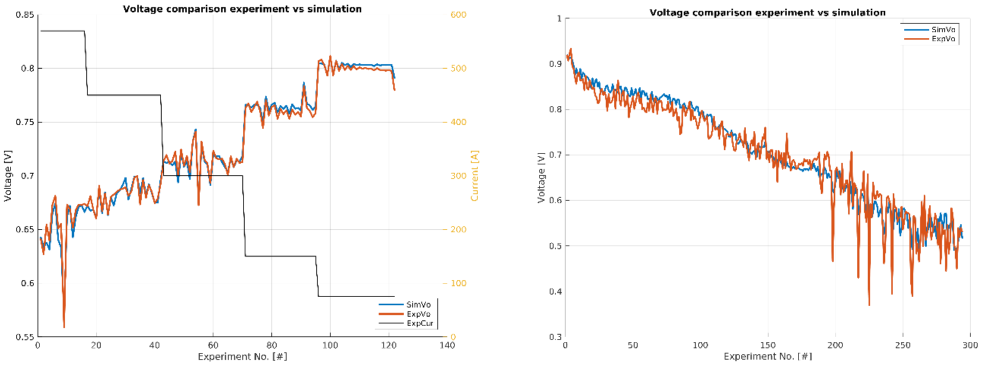


Figure 1: experimental vs. simulated voltage, left for experiment one, right side for experiment two.

References:
1. A. Kabza, "Fuel cell formulary" *Kabza, Ed* (2021). https://pemfc.de/FCF_A4.pdf
2. T. Wagner. Experimental and Model Based Analysis of LT PEM Fuel Cells Exposed to Gaseous Impurities and Development of a Simulation Software. PhD thesis, University of Ulm, July 2023.
3. T.E. Springer, T.A. Zawodzinski, and S. Gottesfeld. "Polymer electrolyte fuel cell model." *Journal of the Electrochemical Society* 138(8) (1991) 2334.

# Model-assisted Analysis of Carbon-free Silver Gas Diffusion Electrode Designs for Performance Enhancement in Electrochemical $CO_2$ Reduction

Inga Dorner[a], Jens Osiewacz[b], Philipp Röse[a], Barbara Ellendorff[b], Thomas Turek[b], Ulrike Krewer[a]
*[a]Karlsruhe Institute of Technology, Institute for Applied Materials – Electrochemical Technologies,*
*Adenauerring 20b, 76131 Karlsruhe, Germany*
*[b]Clausthal University of Technology, Institute of Chemical and Electrochemical Process Engineering,*
*Leibnizstraße 17, 38678 Clausthal-Zellerfeld, Germany*
*inga.dorner@kit.edu*

Electrochemical $CO_2$ reduction represents a promising technology for recycling $CO_2$ from air or emissions, converting it into valuable chemicals. Achieving industrially relevant conversion rates in electrochemical $CO_2$ reduction relies on the use of gas diffusion electrodes to ensure high $CO_2$ availability. However, challenges in optimization arise due to the complex and insufficiently understood characteristics of electrolyte intrusion and distribution within carbon-free silver electrodes, influencing active area and transport losses. [1] In this study, we combine experimental variations of electrode and operational parameters with physicochemical modelling to elucidate the key factors for achieving high Faradaic efficiency and low overpotentials. The comprehensive model illuminates the interaction of gas and liquid transport, electrochemical and electrolyte reaction kinetics, gas/liquid interface phase transitions, and current transfer. [2] Our investigations underscore the importance of a robust gas-liquid interface for carbon-free electrodes, achieved by operating at a high overpressure of 100 mbar to attain elevated local $CO_2$ concentrations. This practice results in a twofold increase in Faradaic efficiency from 20 to 42% for CO at high current densities of 200 $mAcm^{-2}$ particularly. Thin electrodes with a thickness of 200 μm prove to be a favourable design, exhibiting higher CO selectivity. The improvement is enabled by enhanced transport of $CO_2$ and fresh electrolyte within these electrodes, leading to reduced local pH levels. The optimization of PTFE content aids in preventing the masking of electrochemically active surface area while stabilizing the gas-liquid boundary. Beyond facilitating the optimization of electrode and operation parameters, our insights reveal the interplay of species transport and reaction processes within these electrodes. The identified crucial processes determining electrode performance are also relevant for other electrode designs and concepts. This offers valuable insights for broader application in electrochemical systems.

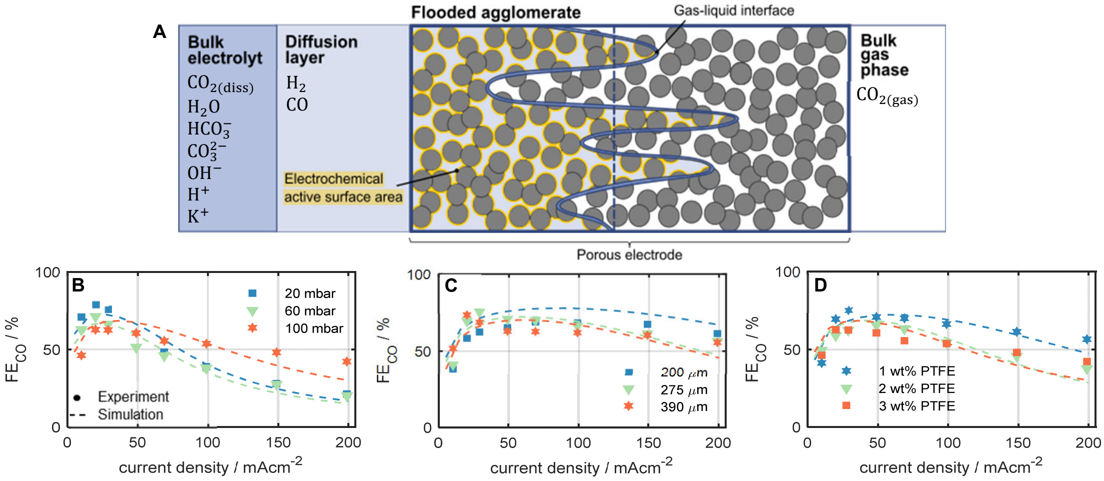


Figure 1: (A) Scheme of gas diffusion electrode model for $CO_2$ reduction and experimental and simulated Faradaic efficiency of carbon monoxide product ($FE_{CO}$) for the variation of (B) differential pressure, (C) electrode thickness, and (D) PTFE mass fraction.

References:
1. M. Löffelholz, J. Osiewacz, A. Lüken, K. Perrey, A. Bulan, T. Turek, *Chem. Eng. J.* **436** (2022), 134920.
2. I. Dorner, P. Röse, U. Krewer, *ChemElectroChem* **10** (2023), e202300387.

# Modeling the Interface between Transport and Catalyst Layer and its Influence on Water Electrolysis Performance

T.-C. Ma[1,2], A. Hutzler[1,2], B. Bensmann[3], R. Hanke-Rauschenbach[3], S. Thiele[1,2]
*[1]Forschungszentrum Jülich GmbH, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IEK-11), 91058 Erlangen, Germany*
*[2]Department of Chemical and Biological Engineering Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany*
*[3]Institute of Electric Power Systems, Leibniz University Hannover, 30167 Hannover, Germany*
*t.ma@fz-juelich.de*

Optimizing the structure of the porous transport layer (PTL) is crucial for improving the performance of proton exchange membrane water electrolysis (PEMWE), particularly for cells with low anode catalyst loadings. A growing number of studies reveal that catalysts are often not entirely utilized in PEMWE, and the degree of catalyst utilization strongly depends on the structure of the anode catalyst layer (aCL)/PTL interface. As the oxygen evolution reaction (OER) at the anode is the limiting reaction step in PEMWE, inefficient use of the aCL would result in higher activation losses and, thus, cause a waste of unused catalysts [1–3]. This phenomenon becomes more serious when the catalyst loading is reduced to meet the eco-friendly requirement of \$2 per $kg_{H2}$ while conserving noble material resources [4].
In our contribution, we implement an in-plane physical model as shown in Figure 1, combining with tomographic data presented in literature [5] to investigate the aCL/PTL interface and catalyst utilization. Our simulation results are in good agreement with literature, enabling the prediction of activation overpotentials corresponding to the PTL structure at aCL/PTL interface. Moreover, our results illustrate the local aCL behavior, which can be used to optimize the porous structure at the aCL/PTL interface, maximizing catalyst utilization. With our model, we aim to screen for an optimum PTL structure for a given aCL, allowing us to improve PEMWE cell performance by minimization of activation losses.

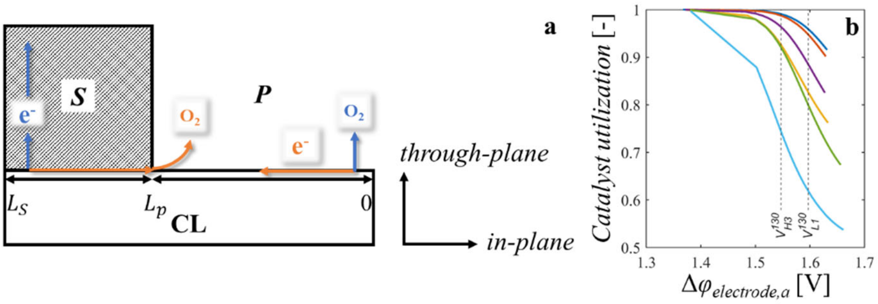


Figure 1: (a) Illustration of the in-plane physical model and (b) modeled catalyst utilization of different aCL/PTL interface formed cells.

References:

1. T. Schuler, T. J. Schmidt, F. N. Büchi, *J. Electrochem. Soc.* 166, 2019, F555-F565.
2. X. Peng, P. Satjaritanun, Z. Taie, L. Wiles, A. Keane, C. Capuano, I. V. Zenyuk, N. Danilovic, *Adv. Sci.* 8, 2021, 2102950.
3. Z. Kang, J. Mo, G. Yang, Y. Li, D. A. Talley, B. Han, F.-Y. Zhang, *Electrochim. Acta* 255, 2017, 405-416.
4. D. Kulkarni, A. Huynh, P. Satjaritanun, M. O'Brien, S. Shimpalee, D. Parkinson, P. Shevchenko, F. DeCarlo, N. Danilovic, K. E. Ayers, C. Capuano, I. V. Zenyuk, *Appl. Catal. B* 308, 2022, 121213.
5. T. Schuler, R. D. Bruycker, T. J. Schmidt, F. N. Büchi, *J. Electrochem. Soc.* 166, 2019, F270-F281.

# Numerical and Experimental Analysis of Two-phase Flow in Porous Transport Layers in Water-Electrolysis Processes

S. Erdogan[1], L. Feierabend[1], F.Durmus[1], M. Pilaski[1], H. E. Hoster[1,2]
[1] *The Hydrogen and Fuel Cell Center ZBT GmbH, 47057 Duisburg, Germany*
[2] *University of Duisburg-Essen, 47057 Duisburg, Germany*
*l.feierabend@zbt.de*

The Polymer Electrolyte Water Electrolysis (PEM-WE) is a well-established process for hydrogen production. The Porous Transport Layer (PTL) is crucial in facilitating water transport to the catalyst sites and removal of the produced hydrogen and oxygen ($O_2$), thereby enhancing the mass transport efficiency of the WE process. Various properties of the PTL, such as fibre structure and wettability, influence the transport of generated gases and the accessibility of water to active sites required for the electrochemical process. Experimental techniques (e.g. 3D X-ray microscopy) to visualize the two-phase flow within the porous PTLs are expensive and not readily available. Therefore, we use numerical methodology and employ the Lattice Boltzmann Method (LBM) [1, 2] to investigate the two-phase flow through two different types of industrial PTLs, a structured fabric and an unstructured one made of sintered fibres (Fig. 1), with regard to their mass transport properties under electrolysis-relevant flow conditions. As expected, the analysis of the gas distribution in the porous domain shows that PTLs with a hydrophilic surface, whether structured or unstructured, have a lower total $O_2$ saturation than PTLs with a hydrophobic surface. From a fluidic perspective, the structured fabric PTL has advantages over the unstructured sintered fibre PTL due to its lower breakthrough pressure and lower hold-up for the gas phase, especially for the hydrophilic case ($\theta = 70°$). Moreover, the mass transport properties of the PTL types are investigated via Electrochemical Impedance Spectroscopy (EIS) measurements in an electrolysis cell under high current operating conditions to further support the numerical findings and evaluate the overall performance of the PTLs.

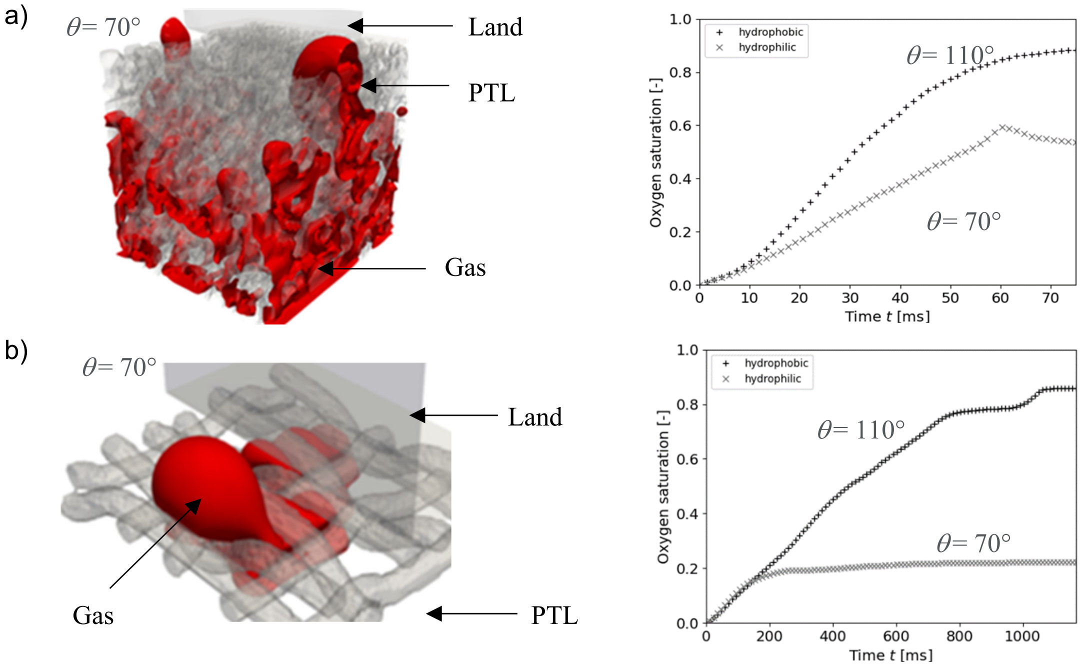


Figure 1: Gas (red) invasion (left) and $O_2$ saturation (right) for the PTLs with different morphology: a) unstructured sintered fibre; b) structured fabric.

Reference:

1. Sukop, M.C. and Thorne, D.T., JR. Lattice Boltzmann modeling: An introduction for geoscientists and engineers, 2006 Springer, Berlin, New York
2. Shan, X.; Chen, H. Phys. Rev. E., 1993 47 (3), 1815-1819.

# Two-phase flow simulation in gas diffusion layers: effect of fiber curvature

Danan Yang, Himani Garg, Martin Andersson
*Department of Energy Sciences, Faculty of Engineering, Lund University, P.O. Box 118, Lund, SE-221 00, Sweden*
*danan.yang@energy.lth.se*

There are various types of gas diffusion layers (GDLs) in various applications, which are different in porosity, thickness, wettability and binder treatment, as well as the shape of the basic component carbon fiber. The dynamics of two-phase flow within the cathode of a proton exchange membrane fuel cell, particularly in GDLs with varying fiber curvatures, are hardly explored. Using a periodic surface model, we stochastically reconstruct three GDL types with different fiber curvatures, incorporating the parameters extracted from a physical GDL [1]. Considering the randomness in reconstruction, the structure generation process is iterated four times for each type, enabling an ensemble average analysis. Pore network models are adopted to reveal disparities in these GDL porous structures. The subsequent two-phase simulations are conducted to explore liquid transport through these GDLs and interface. Time-varying total- and local water saturation, as well as capillary pressure are investigated. Results show that stochastic reconstructions exhibit similar frequency peak values in pore and throat diameters, and coordination numbers, but diverge from those of the physical GDL. Larger fiber curvature tends to enhance the pore network connectivity by increasing the number of smaller pores, leading to higher water saturation and capillary pressure. Straight-fiber GDLs, compared to curved-fiber GDLs, show a greater potential proximity to the physical GDL in terms of overall water saturation and capillary pressure but are also accompanied by increased uncertainty. Despite of adopting similar layer and bulk porosity, water saturation is different among four samples. Water breakthrough and detachment at the interface of gas channel and GDL can induce significant water saturation instability at the interface. Detached droplets in gas channels connected with straight-fiber GDLs exhibit larger sizes and slower movement than those in channels assembled with curved-fiber GDLs. These findings can be utilized in future design and optimization.

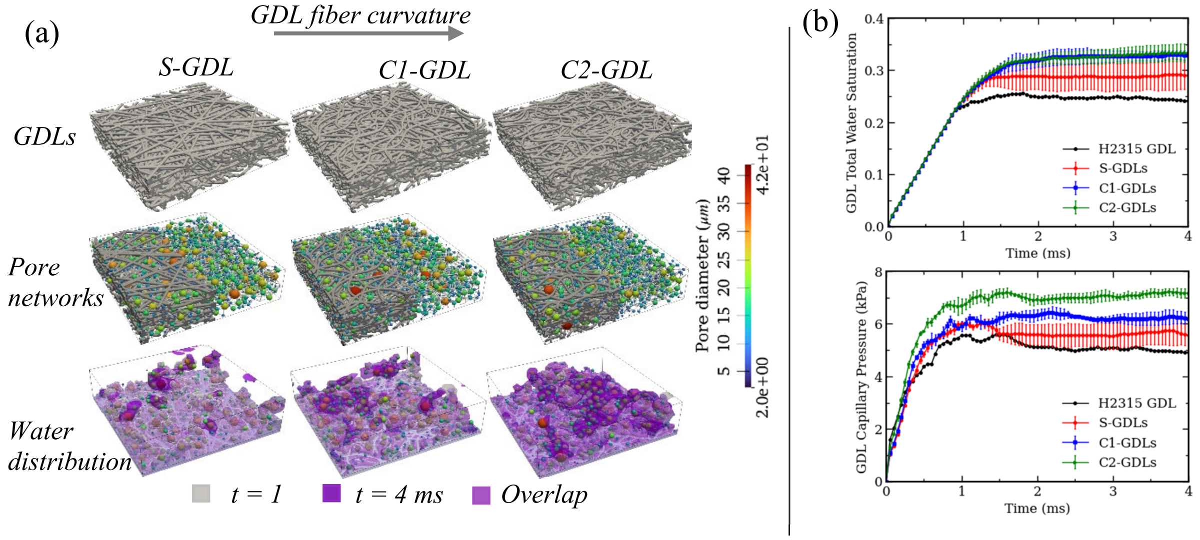


Figure 1: (a) GDL configuration with three different fiber curvature, and the corresponding pore networks, and the combination of filtered pores and GDL water distribution state at 1 ms (gray surface) and 4 ms (purple surface). The gray color, dark purple color, and light purple color represent the water saturation at 1 ms, the water saturation at 4 ms, and the overlap water distribution at two timesteps, respectively. The pores are colored with the pore diameter size (see left color bar). (b) The resemble water saturation and capillary pressure of four samples in each type of GDL.

References:

1. S.B. Beale, M. Andersson, N. Weber, H. Marschall, W. Lehnert, *ECS Trans.* 98(2020), 9, 305

# Topology optimization of porous electrodes for redox flow batteries using the finite element method

Mojtaba Barzegari, Martin de Waal, Pedro Carvalho, Antoni Forner-Cuenca
*Electrochemical Materials and Systems, Department of Chemical Engineering and Chemistry*
*Eindhoven University of Technology (TU/e), Eindhoven, The Netherlands*
*m.barzegari.shankil@tue.nl*

Redox flow batteries (RFBs) are a class of rechargeable electrochemical systems that are particularly promising for grid-level electricity storage, leveraging electroactive species dissolved or suspended in liquid electrolytes that are pumped to an electrochemical reactor where they undergo electrochemical reactions on the surface of porous electrodes to charge and discharge the battery [1].

To increase the cost-competitiveness of the technology, one strategy is to design electrochemical reactors with higher power density and, in this perspective, the optimization of the cell components (e.g. electrodes, flow fields, membranes) is essential. In RFBs, porous electrodes are performance-defining components affecting the thermodynamics, kinetics, and transport, where the flow distribution, surface area, and transport of species are critical for obtaining high power and electrochemical performance [2]. Traditionally, electrodes are engineered by empirical methodologies which necessitate large amount resources and time. On the contrary, computational techniques have the potential to provide a unique perspective to guide the design of porous electrodes, an example of which is predictive inverse design algorithms such as topology optimization (TO). Rather than evaluating the performance of a proposed setup, this method involves setting a performance target and iterating over permissible architectures to meet such a target [3, 4].

In this project, we have developed a high-performance TO framework for two- and three-dimensional porous electrodes in RFBs integrated with multi-physics computational models of transport processes correlating how reactor design influences RFB performance. This was achieved by numerically solving transport and kinetics equations using the finite element method implemented in the open-source code Firedrake. The macroscale TO problem was formulated to maximize electrochemical performance under a controllable pumping power loss, in which the porous electrode was considered as a macroscopic porosity-variable block in a half-cell of a redox flow cell (Fig 1-A).

The resulting designs (Fig 1-B) may seem non-intuitive, but their performance is higher than electrodes with uniform porosity. Specifically, the computed electrode geometries provide reduced ohmic, kinetics, and pumping power losses of RFBs across various operating conditions. The porosity-variable electrodes can be converted to cellular architectures and triply periodic minimal surface structures to be manufactured using stereolithography 3D printing followed by carbonization, the output of which will be used to assess the performance of the inversely designed electrodes in a real setup.

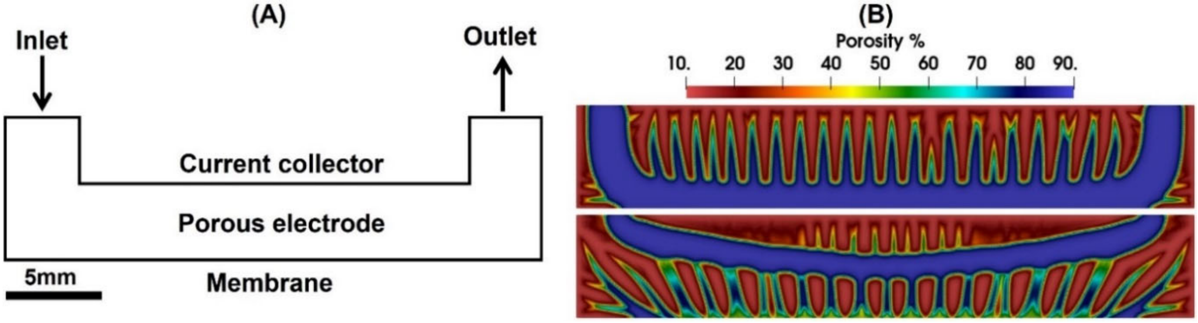


Figure 1: A) Schematic computational domain of the TO process, representing a half-cell of an RFB-like setup, B) Sample results of the TO framework showing the optimized porosity field across the porous electrode. Higher current density and electrolyte conductivity were applied in the top simulation.

References:

1. Alotto et al. *Renew. Sustain. Energy Rev.* **29**, 325-335 (2014).
2. B. K. Chakrabarti et al., *Sustainable Energy & Fuels.* **4**, 5433-5468 (2020).
3. Roy et al. *Struct. Multidiscip. Optim.* **65** (2022).
4. Beck et al. *J. Power Sources* **512**, 230453 (2021).

# An Open-source Model for High-throughput Flow Battery Cell Performance Predictions

R. P. Schärer, J. O. Schumacher
*ZHAW, ICP, Electrochemical Cells & Energy Systems*
*Technikumstrasse 71, 8400 Winterthur*
*scsl@zhaw.ch*

Flow batteries are a promising technology for large-scale energy storage of intermittent renewable energy provided by photovoltaic systems and wind farms. Recently, different organic redox active species have been investigated and proposed for next-generation sustainable flow battery systems.

The European research project SONAR has set the aim to develop a multiscale simulation framework from the atomistic to the techno-economic scale for assessing the suitability of redox active species for flow battery applications. To connect the lower-scale atomistic predictions with key cell performance values, such as cell voltage and power density, we developed a macrohomogeneous model, named RfbScFVM, for single flow battery cells. The model solves for the spatially resolved profiles of species concentrations, electric and ionic potentials, pressure, and temperature. The transport equations are discretised with a Voronoi FV scheme [1] in the through-plane direction of the cell assembly (horizontal axis in Fig. 1). The model is flexible with respect to the number and types of redox active species and electrochemical reactions, which allows for a simple adaption of the model to other types of flow battery cells. The model has been validated for a lab-sized cell using the all-organic methyl viologen / TEMPTMA system [2] showing good agreement with experimental measurements. In contrast to more reduced models, such as simplified 0D flow cell models [3], the RfbScFVM model allows for good performance predictions also at large current densities. To facilitate the integration of the cell model into the high-throughput pipeline of SONAR, model input and output parameters are provided via JSON configuration files, which allows for a good interoperability with other models.

The model has been published on GitHub under the permissive MIT license [4], allowing other research groups to use and adapt the model to their needs.

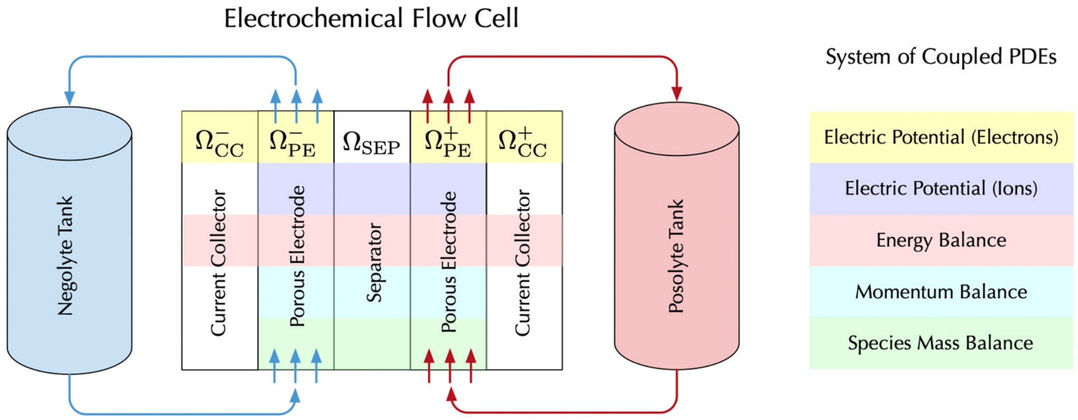


Figure 1: Subdomains of a flow battery cell with a simplified geometry.

References:

1. J. Fuhrmann, D. Abdel, J. Weidner, A. Seiler, P. Farrell, and M. Liero, “VoronoiFVM.jl - Finite volume solver for coupled nonlinear partial differential equations.” Weierstrass Institute Berlin. [Online]. Available: https://github.com/j-fu/VoronoiFVM.jl
2. T. Janoschka, N. Martin, M. D. Hager, and U. S. Schubert, Angew. Chem. Int. Ed., **55**, (2016)
3. G. Mourouga, R. P. Schaerer, X. Yang, T. Janoschka, T. J. Schmidt, and J. O. Schumacher, *Electrochimica Acta*, **415** (2022)
4. R. P. Schaerer, “RfbScFVM” (2023) [Online]. Available: https://github.com/Isomorph-Electrochemical-Cells/RfbScFVM

# Tracking $CO_2$ Bubble Flow in a Direct Formic Acid Fuel Cell, Numerical and Experimental Investigation

Monika Jałowiecka[1], Arkadiusz Antonowicz[1,2], Łukasz Makowski[1]
*[1]Faculty of Chemical and Process Engineering, Warsaw University of Technology, Waryńskiego 1, 00-645 Warsaw, Poland*
*[2]Eurotek International Sp.z o.o., Skrzetuskiego 6, 02-726 Warsaw, Poland*
*monika.jalowiecka.dokt@pw.edu.pl*

In contemporary times, substantial pressure exists to transition from conventional fossil fuels to hydrogen fuel, harnessing renewable energy sources. In response to this overarching shift, the present research aims to advance direct formic acid fuel cells (DFAFCs). Formic acid, as a liquid hydrogen carrier, exhibits the potential to facilitate the deployment of fuel cells. It can be integrated into the existing fuel infrastructure and exhibits lower transportation costs [1].

The research methodology encompasses a numerical analysis of multiphase reactant flow on the anode side of a DFAFC, executed by applying computational fluid dynamics and the volume of fluid method within the ANSYS Fluent software. To validate the numerical calculations, a transparent DFAFC prototype was fabricated using 3D printing technology, which was stereolithography. During experiments, comprehensive documentation was undertaken, capturing images detailing the successive stages of $CO_2$ bubble morphology and their flow trajectory within the interconnector channels.

The integration of numerical simulations and experimental investigations yields valuable insights into the dynamics of gas bubble flow within the interconnect channels. This knowledge is crucial in refining the channel geometry of the distribution system, with the overarching objective of minimising gas phase retention at the electrode surface. Subsequently, this optimisation process can significantly mitigate mass transport resistances in fuel cells and electrolysers. The analogous construction of these electrochemical devices, characterised by a two-phase flow with a gas-dispersed phase, underscores the potential applicability of findings across both systems.

Reference:

1. Eppinger, J., Huang, K.-W., 2017. Formic Acid as a Hydrogen Energy Carrier. ACS Energy Lett. 2, 188–195

Acknowledgements:

The research was funded by the Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme

# Experimental and simulative analysis of the dependence between liquid water amount and mass transfer in a planar membrane humidifier

S. Mull, L. Weiß, M. Wensing
*Professorship for Fluidsystemtechnology*
*Cauerstraße 4, 91058 Erlangen, Germany*
*sophie.mull@fau.de*

In the field of polymer electrolyte membrane fuel cell systems (PEMFCS), the literature currently distinguishes between two different operating modes for membrane humidifiers with perfluorosulfonic acid (PFSA) membranes. The first operating mode is the vapour transferred from gaseous stream to another, which is mainly used in automotive applications. The other operating mode is the exchange of water from a liquid to a gaseous aggregate state, which is mainly used in stationary test benches. Intermediate states of the humidifier, in which the membrane is partially covered or fully covered with a thin film of liquid water, are presently not part of the literature. These mixed states already occur in mobile PEMFCS in current applications, depending on the operating point and the architecture of the system, among other things. Fundamentally, due to the so-called Schröder's paradox, water transport through PFSA membranes is strongly improved if the water originates from the liquid state instead of the gaseous state [1]. Investigations by the author have recently indicated [2] that the humidifier can achieve maximum water transport at much lower water quantities compared to the boundary conditions currently used in stationary operation. Complete wetting of the membrane with a thin layer of water seems to be sufficient to maximize the performance of the humidifier. This means that the performance of the membrane humidifier can be optimized with the system water management enabling a more efficient use of water and thus a more efficient fuel cell system. This effect has been investigated using a specially developed, optically accessible single channel humidifier test stand. In addition, the author has already developed a simulation model in previous work, which is able to simulate these intermediate operating modes of the humidifier [2]. The investigations focus on the dependence of the minimum amount of liquid water required for the described effect on the possible thermodynamic boundary conditions of a humidifier for automotive PEMFCS, such as the temperature, the air and water flow rates and the pressure. Figure 1 shows an exemplary measurement in which the operating case of complete flooding by a water column is compared with an operating mode with a thin film of water on the membrane surface. The gas mass flow rate of the dry side is varied. Both operating modes achieve almost the same water transfer and therefore similar relative humidities (RH) at the outlet of the dry flow. This shows the effect described above that significantly less water is sufficient for the maximum water transfer ratio and therefore the maximum humidifier performance.

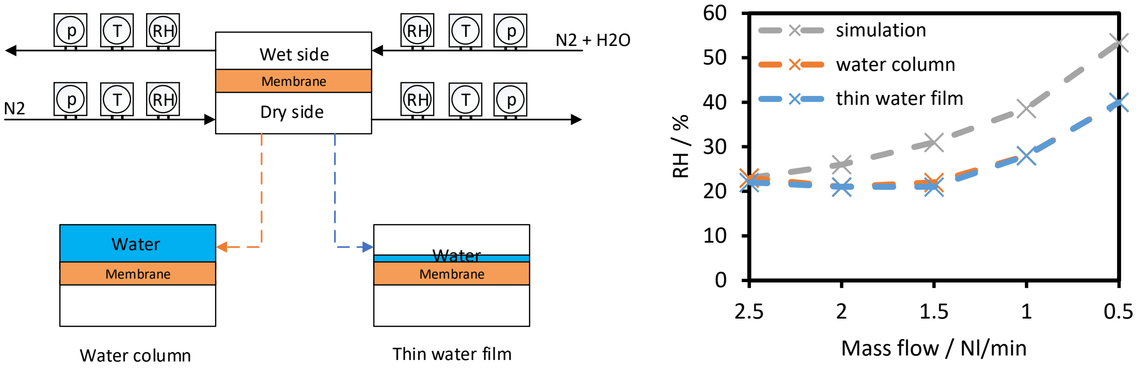


Figure 1: Comparison of the simulation to the experimental data from the operating state flooded with a water column to flooded by a thin layer of water with variation of the flow rate

References:
1. A. Kusoglu, A. Z. Weber, *Chem. Rev.* 2017, 117, 987-1104
2. S. Mull, L. Weiß, M. Wensing, Membrane humidifier model for PEM fuel cell systems, *European Fuel Cell Forum* 2023, Lucerne

# Model-based design of a strategy for switching stacks in a multi-stack PEM fuel cell system

S. Nicolay[1], G. Luisoni[1], S. Armanini[2]
[1] *MTU Aero Engines AG, Munich, Germany*
[2] *Technical University of Munich, Assistant Professorship of eAviation, Ottobrunn*
*sebastian.nicolay@mtu.de*

Proton-exchange membrane fuel cell stacks are limited in size both in terms of cell area and number of cells [1]. Large power applications such as a fuel cell electric aircraft propulsion systems hence require an electrical connection of several fuel cell stacks. Both serial and parallel electric connection is conceivable. A parallel connection however offers the possibility to switch individual stacks on and off depending on the power requirement. This way, the operating point of the individual stacks can be kept within a narrow band throughout a large range of power demands. Eventually, switching stacks on and off requires a suitable operating strategy which enables dynamic load changes while minimising the risk of accelerated degradation.

The shutdown of an individual stack within a parallel arrangement can be accomplished via stopping the air supply of the stack under consideration [2], making a high-power physical switch obsolete. The resulting oxygen starvation will keep the stack from generating electric current while the remaining stacks take over the entire current. The hydrogen supply remains active when switching off a stack.

In this study, a strategy for switching stacks on and off individually is developed based on a 1D physical and semi-empirical fuel cell system model. Hereby, the switching on and off of stacks is done during a transient load change. In the example shown in Fig. 1, the electric current load of a scaled fuel cell system is doubled and, later on, halved. At the same time, the number of active stacks is switched from one to two and back to one. As can be seen in Fig. 1 (a), the actual current is applied with a time delay, as the system waits for the air supply of stack 2 to overcome a stoichiometry threshold.

The final system voltage is equal to the initial voltage before the switching (cf. Fig. 1 (b)). During the switching procedure itself, the voltage shows a positive and a negative deviation. This study will present approaches to keep the system voltage as flat as possible during the switching process. As can be seen in Fig. 1 (c), the electric currents of the two stacks take a while to equalize after switching on stack 2. Approaches to balance the current distribution between the two stacks will also be discussed.

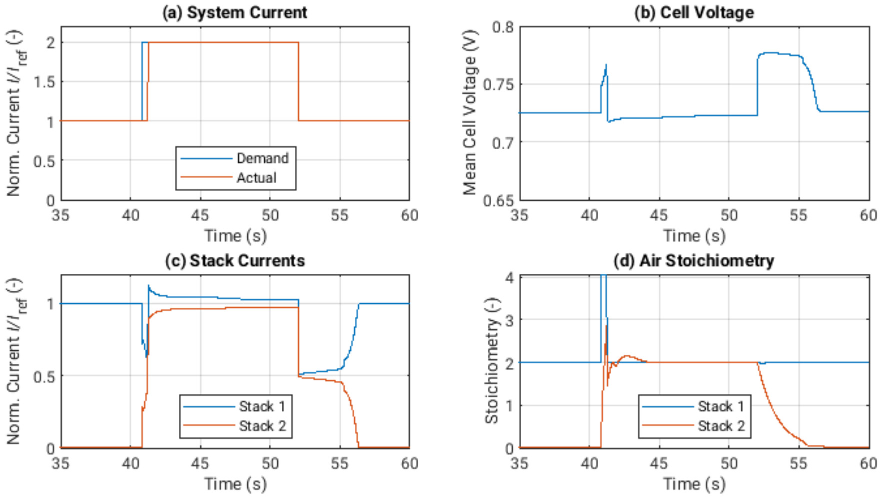


Figure 1: Voltage and currents of two stacks during the switch-on and switch-off of stack 2.

References:

1. Barbir, F.: “CHAPTER 6 - Stack Design”. In: PEM Fuel Cells. Ed. by Barbir, F. Burlington: Academic Press, 2005, pp. 147–206. DOI: https://doi.org/10.1016/B978-012078142-3/50007-0.
2. Nicolay, S.; Fritsche, L.; et al. (2023): Development and Evaluation of Strategies for Parallel Operation of Fuel Cell Stacks. Deutsche Gesellschaft für Luft- und Raumfahrt - Lilienthal-Oberth e.V., https://doi.org/10.25967/570412.

# Thermal Management Design and Optimization for Hydrogen-Powered Fuel Cell Systems in Aviation

Elisa Revello, Andrea Bronzino, Alessandro H. A. Monteverde
*Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.*
*elisa.revello@polito.it, alessandro.monteverdevidela@polito.it*

Aviation is currently responsible for approximately 2% of global $CO_2$ transport-related emissions. To reach the net zero emissions (NZE) scenario by 2050, the aviation industry should adopt technical strategies related to aircrafts electrification, encouraging sustainable aviation fuels (SAF), and demand containment measures. [1] The most promising solution for next-generation aircrafts is the hydrogen-powered fuel cell (FC) system, as it could meet the aeronautic requirements of compactness and lightness. However, thermal management system (TMS) of such systems is crucial, as they produce a large amount of heat to be removed to prevent overheating. Therefore, cooling system design affect the overall energy consumption and have a direct impact on achieving durability, cost, and performance targets required for an effective electrified aircraft.

The present work is focused on the sizing and optimization of the cooling network of an $H_2$-powered proton exchange membrane (PEM) FC. Particularly, the TMS architecture consists of a low temperature cooling (LTC) subsystem and a high temperature cooling (HTC) subsystem. [2] The increase in fuel cell performances involved an overall weight reduction of 30%. Preliminary results shown in Figure 1 revealed that the main contributors to the overall weight are the fuel cell system and the hydrogen storage tank, representing 37% and 30% of the total system weight, respectively. LTC system constitutes 6% by weight, while the HTC system accounts for 12% of the total system. Optimization on the exchanger network, material lightening and potential thermal integration will be part of the future work.

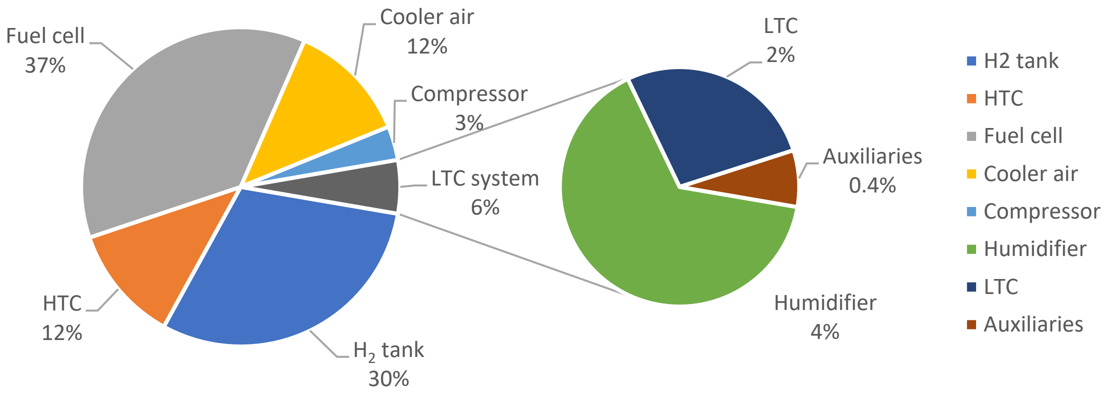


Figure 1: Weight distribution of the overall $H_2$-powered PEMFC system.

References:
1. IEA, “Tracking Clean Energy Progress 2023.” Accessed: Jan. 09, 2024. [Online]. Available: https://www.iea.org/energy-system/transport/aviation#tracking
2. A. Datta, A. Gessow, and R. Center, “PEM Fuel Cell MODEL for Conceptual Design of Hydrogen eVTOL Aircraft,” 2021. [Online]. Available: http://www.sti.nasa.gov

# Spatially Resolved Quantification of Diffusion Losses in a Segmented PEM Fuel Cell with adjustable Clamping Forces

Yannick Fischer[1,2], Philipp Oppek[1], Sebastian Raab[1], André Weber[1]
*[1]Institute for Applied Materials (IAM-ET), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
*[2]GFS Fuel Cells GmbH, Saarbrücken, Germany*
yannick.fischer@student.kit.edu

Polymer electrolyte membrane fuel cells (PEMFCs) are particularly promising for heavy-duty applications. However, this requires large-scale cells that are operated under high loads, where mass transport becomes a performance-limiting factor. The oxygen transport takes place via different transport processes such as Knudsen, molecular and ionomer diffusion. These are influenced to varying degrees by the operating conditions in the gas channel as well as its geometry and the properties of the porous media. In particular the spatial clamping force distribution has a significant influence on the compression of the porous layers and thus the oxygen transport resistance.

Due to the size of the cells, operation inevitably leads to significant spatial gradients along the gas channels. The different operating conditions result in a spatially varying diffusion resistance, which strongly affects the local performance.

In order to enable targeted optimization of the operating strategy and component design for operation under high loads, a quantification and separation of the local diffusion processes and their dependencies is essential.

This requires a measurement setup that allows the precise adjustment of the operating conditions and clamping forces along the gas channel, as well as a method that locally identifies and quantifies the mass transport processes.

For this purpose, we apply limiting current measurements on a segmented cell and determine the local oxygen transport resistance by means of a limiting current density distribution. [1,2] In this measurement setup, the clamping force for each segment is adjusted and continuously recorded. Based on this, the oxygen transport resistance can be quantified as a function of the local operating conditions and the clamping force. In addition, different inert gases as $N_2$ and He allow a separation of gas phase and ionomer diffusion.

In this contribution a method to determine the local oxygen mass transport resistance and its separation into gas and ionomer contributions will be presented. The impact of selected operating conditions and the clamping force on the oxygen transport resistance and its distribution along the gas channel will be discussed. Furthermore, it is demonstrated how the overall cell performance can be optimized by adjusting the clamping force distribution along the gas channel.

References:
1. M. A. Rahman, M. Sarker, F. Mojica, P.-Y.A. Chuang, Electrochimica Acta 320 (2019), 134601
2. T. V. Reshetenko, J. St-Pierre, J. Electrochem. Soc. 161 (2014), 10, F1089-F1089

# Effect of Model Parameters on the Performance of a PEM Fuel Cell Using a Pore-scale Catalyst Layer Model

M. G. J. Vaz[1], C. Fink[1], D. Gerteisen[2]
[1]*AVL List GmbH, München, Germany*
[2]*Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany*
*gabriela.vaz@avl.com*

The catalyst layer is one of the most important components of the fuel cell and over the past decades, models with different level of accuracy have been developed to cover their structure and transport process. These models can be mainly classified into three groups: interface model, homogeneous model, and agglomerate model [1-2]. The current work proposes the incorporation of structure-property relationships to improves the realistic representation of the catalyst layer structure. The model is based on the correlation of the platinum (Pt) specific particles size distribution and its position on the carbon support: Pt inside the primary pore or Pt sitting on the surface of the carbon particle, as shown in Figure 1(a). Thus, their placement leads to different reactivity due to local transport resistances surrounding the Pt-particles as for example the thin film diffusion, proton accessibility in the pores, $SO_3^-$ poisoning and oxygen blockage. In addition, the oxygen and protons accessibility are based on the capillary condensation of the pore, which it can assume two statuses: dry or flooded with water.
The model is composed of twelve parameters and was implemented on the commercial software AVL FIRE M [3]. To understand the impact of those parameters, a sensitivity analysis was performed on a straight channel cell. Based on the polarization curve calculations, it was possible to identify the parameters that have a very low or neutral impact on the calibration process, in the range explored in this work, and those that act directly in each "classic regime": activation loss, ohmic loss and concentration loss. In complement, the model was compared to the experimental data of a commercial three-serpentine channel PEM fuel cell with an active area of 25 cm². Figure 1(b) shows the polarization curve (full line), and the individual contribution of outer current density (double dotted line) and inner current density (dotted line) for the reference case. For this case, the simulation presented a good agreement with the experimental data, with a maximum relative error of 2,01% at 0,8 A/cm². Figure 1(c) shows the inner and outer contribution on the reaction current density in the middle of the cathode catalyst layer at 0,8 A/cm².

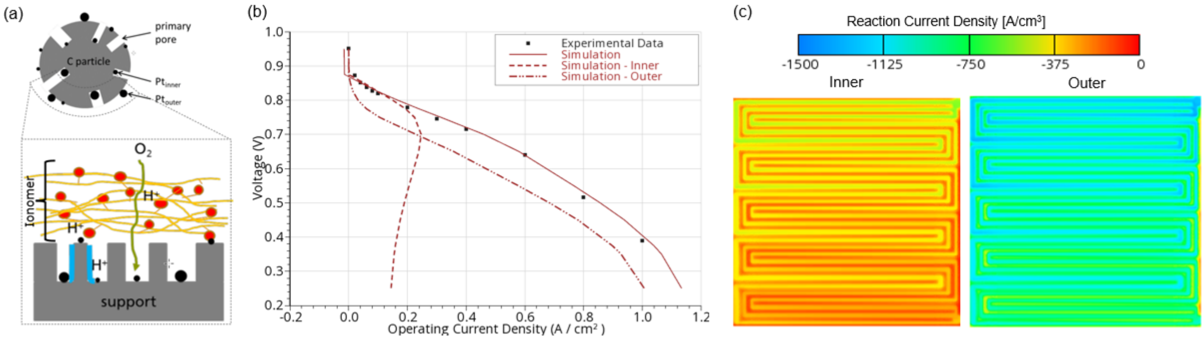


Figure 1: (a) schematic of the Pt size and location on the carbon support where the primary pore is dry or filled with water. The red circles represent the $SO_3^-$ groups. (b) Polarization curve for the reference case, in detail the influence of the outer current density and inner current density. (c) Reaction current density in the middle of the catalyst layer at 0,8 A/cm².

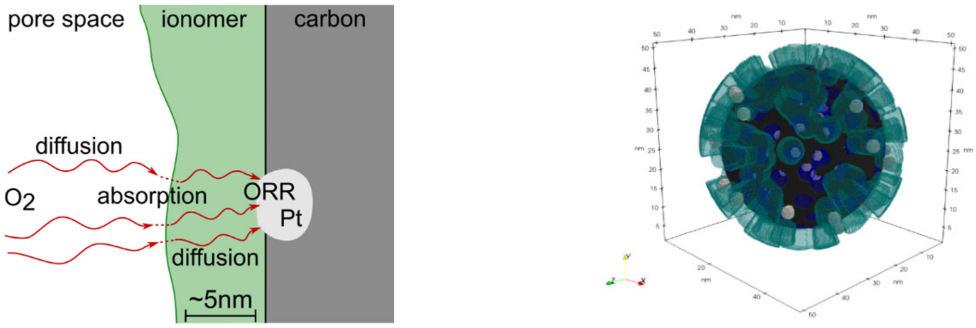
References:
1. S. Li, J. Yuan, G. Xie, B. Sundén, *Int. J. of Hydrogen Energy*, 8 (2018), 8451-8463
2. P. Barnoon, D. Toghraie, B. Mehmandoust, M. Fazilati, S. Eftekhari, *Energy Reports*, 8 (2022), 11343-11362
3. AVL List GmbH, *FIRE™ M User Manual 2023 R2*, 2023

# Simulation of Oxygen Diffusion and Reduction Reaction in the Cathode Catalyst Layer of a PEM Fuel Cell using Lattice Boltzmann Modeling

K. Gülicher[1], A. Latz[1,2], T. Jahnke[1]
*[1] German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany*
*[2] Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Albert-Einstein-Allee 11, 89081 Ulm, Germany*
*Konrad.Guelicher@dlr.de*

The Polymer Electrolyte Membrane Fuel Cell (PEMFC) could be a competitive, environmentally friendly replacement of the combustion engine if the necessary amount of platinum used as catalyst and therefore the price can be further reduced. Yet, for low platinum loadings, additional performance losses arise and the reasons for these losses are not well understood so far. In order to shed some light on the limiting processes taking place in the cathode catalyst layer (CCL) of a PEMFC on the sub-µm scale, we are developing a Lattice Boltzmann Model of the oxygen transport in the CCL as depicted in figure 1(a). For this purpose, we are combining a multi-relaxation-time model [1], simulating diffusion and interface absorption, with a modified Bounce-Back boundary condition [2], simulating oxygen reduction at the surface of platinum nano-particles. Implementations are done using the Palabos framework [3]. With the simulation, we have investigated self-created, idealized CCL geometries, see figure 1(b). In addition, the simulation can also be applied for reconstructions of real microstructures. Our study focuses on the influence of microstructural properties on the limiting current such as ionomer distribution or shape of micro pores. We investigate the influence of the resistance, provided by the various interfaces of the ionomer film, on the transport process. Here, we found an interaction between platinum nano-particles affecting the limiting current which varies with the distance between the particles and the resistances provided by the different interfaces. We also compare the contribution of platinum particles in water-filled micro pores to the limiting current with the contribution of platinum which is deposited on the surface of a primary carbon particle in order to see where transport limitations are arising.

*This project FURTHER-FC [4] has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No* ***875025****. This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation program, Hydrogen Europe and Hydrogen Europe Research.*



(a) (b)

Figure 1: Schematic depiction of oxygen transport on the sub-µm scale inside the cathode catalyst layer (a). Self-created, idealized geometry of a primary carbon particle (black) with platinum particles (white), water-filled micro pores (blue) and partially covering ionomer thin film (cyan) on top (b).

References:
1. L. Chen, R. Zhang, Q. Kang, W.Q. Tao, Chemical Engineering Journal, **391** (2020), 123590
2. G.R. Molaeimanesh, M.H. Akbari, International Journal of Hydrogen Energy, **40** (2015), 5169
3. J. Latt, et al, Computers & Mathematics with Applications, **81** (2021), 334
4. https://further-fc.eu/

# Modeling Oxygen Reduction Reaction kinetics in a Gas Diffusion Electrode

Erwan Tardy[1], Raphaël Riasse[1], Florent Vandenberghe[1], Florence Druart[1], Antoine Bonnefont[1],
Marian Chatenet[1], Yann Bultel[1], Melaine Guillou[2], Benoit Latour[2]

[1]*Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI,*
*F-38000 Grenoble, France*
[2]*Manufacture Française des Pneumatiques Michelin, 23, Place des Carmes,*
*63040 Clermont-Ferrand, France*
*erwan.tardy@grenoble-inp.fr*

Proton exchange membrane fuel cells (PEMFCs) are advanced electrochemical systems that have benefited from intense research for decades. They are considered as promising zero-emission technology to produce electricity from green hydrogen through a highly efficient conversion process and provide high energy density. However, they rely on scarce and expensive platinum group metal-based electrocatalysts, especially for the cathodic oxygen reduction reaction (ORR) [1]. Indeed, due to the sluggish ORR kinetics, a significant amount of catalyst has to be used at the cathode. This implies that the precise evaluation of the intrinsic activity of ORR electrocatalysts is crucial, in particular under relevant conditions for PEMFC operation.

A gas diffusion electrode (GDE – Fig. 1a) is currently a good compromise between rotating disk electrode (RDE) and differential cell (DC) setups for studying the ORR activity. Indeed, GDE enables high current density measurements with a small amount of electrocatalyst [2]. The combination of experimental measurements with numerical simulations is a promising approach to understand the factors affecting the performance of an electrocatalyst. In this study, a 3D multiphysics and multicomponent model is developed on the commercial software COMSOL Multiphysics® to study the ORR kinetics in a GDE considering an acidic electrolyte. The model includes mass, species and momentum transports, as well as the Butler-Volmer's law for the electrochemical reaction, current distribution and transport of charged ions. The numerical results are then compared to the experimental data for three different widely used ORR electrocatalysts: Pt/Vulcan carbon, PtCo/Vulcan carbon and Pt/graphitized carbon (Fig. 1b). These results will be discussed. This work is supported by Manufacture Française des Pneumatiques Michelin.

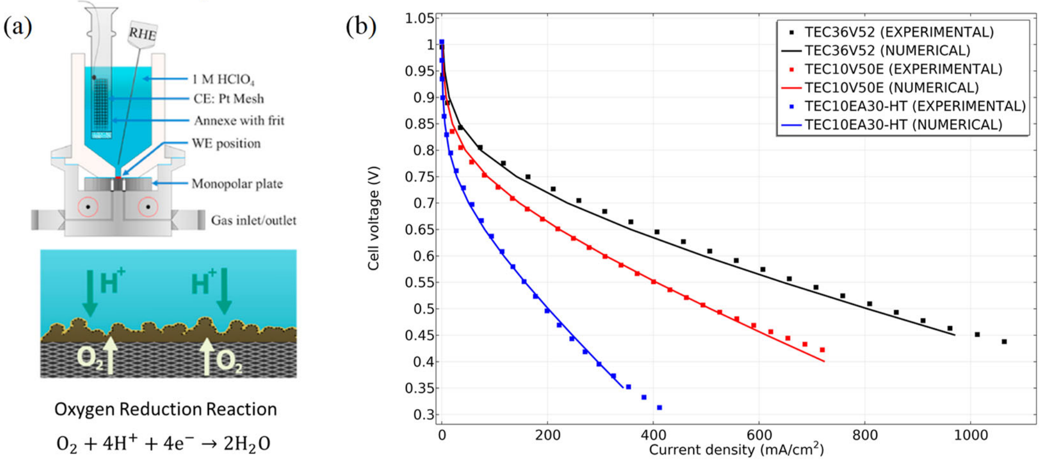


Figure 1. (a) Schematic of the GDE setup [2] and (b) comparison between experimental and numerical polarization curves for three different ORR electrocatalysts.

References:

1. Huimin Tang, Zhiwei Peng, Ran Tian, Lei Ye, Jian Zhang, Mingjun Rao, Guanghui Li, Journal of Environmental Chemical Engineering 11(5), 2023, 110237, ISSN 2213-3437, https://doi.org/10.1016/j.jece.2023.110237.
2. Raphaël Riasse, Clémence Lafforgue, Florent Vandenberghe, Fabrice Micoud, Arnaud Morin, Matthias Arenz, Julien Durst, Marian Chatenet, Journal of Power Sources 556, 2023, 232491, ISSN 0378-7753, https://doi.org/10.1016/j.jpowsour.2022.232491.

# Machine Learning-Assisted Optimization of Proton Exchange Membrane Fuel Cell Catalyst Layer Production Recipe

Yuze Hou, Patrick David Schneider, Linda Ney, Nada Zamel
*Fraunhofer Institute for Solar Energy Systems ISE*
*Heidenhofstraße 2, 79110 Freiburg im Breisgau, Germany*
*yuze.hou@ise.fraunhofer.de*

Proton exchange membrane (PEM) fuel cell is one of the most promising energy conversion devices [1]. The performance of a PEM fuel cell is predominantly influenced by the membrane electrode assembly (MEA), where electrochemical reactions are catalyzed by precious platinum (Pt) particles. The MEA typically consists of a PEM sandwiched between two catalyst layers (CLs) and the production recipe of a CL can be succinctly described by Pt loading, ionomer/carbon (I/C) ratio and Pt/carbon (Pt/C) ratio [2]. The amount of each substance within CL must be meticulously balanced to attain optimal performance [3]. However, this subject can be quite challenging, as the production and characterization of MEAs with various recipe combinations are inherently demanding in terms of both time and resources. Thanks to the exceptional efforts of our production and characterization teams [4], a robust fuel cell database is established, which encompasses information spanning the production process, characterization results, and even degradation data. Leveraging this wealth of information, an Artificial Neural Network (ANN) is developed to forecast the performance of a PEM fuel cell based on its cathode CL substance parameters, namely Pt loading, I/C ratio and Pt/C ratio. Through extensive fine-tuning of network structure and hyperparameters, the ANN shows excellent predictive capabilities, offering reliable and accurate estimations of PEM fuel cell behavior. The effect of each individual parameter on performance is investigated. Furthermore, the trained ANN exhibits the capability to recommend optimal CL production recipes tailored to specific operating conditions. This research underscores the immense potential of machine learning in the optimization of MEA production processes.

References:

1. Y. Hou, J. Schall, S. Dietze, T. Kurz, D. Gerteisen. (2024) Journal of Power Sources, 591, 233780
2. L. Ney, J. Hog, R. Singh, N. Göttlicher, P. Schneider, S. Tepner, U. Groos. (2023) Journal of Coatings Technology and Research, 20(1), 73-86.
3. Y. Hou, H. Deng, F. Pan, W. Chen, Q. Du, K. Jiao. (2019). Applied Energy, 253, 113561.
4. P. Schneider, A. C. Scherzer, B. D. Storey, M. Klingele, N. Zamel, D. Gerteisen. (2023). Journal of The Electrochemical Society, 170(10), 104505.

# A model for Solvation in Battery Electrolytes and analysis of Electrochemical Double Layer differential capacitance

Constantin Schwetlick, Max Schammer, Arnulf Latz, Birger Horstmann
*Ulm University, German Aerospace Centre, Helmholtz Institute Ulm*
*Wilhelm-Runge-Straße 10, 89081 Ulm*
*Constantin.schwetlick@dlr.de*

Accurately modelling complete batteries provides a path to improved chemistries [1]. In recent years, research has identified highly concentrated electrolytes as promising constituents for battery cells with high energy density [2]. These are, however, complex systems, where the bulk electrolyte concentration and external electric potential significantly influences the electrochemical double layer (EDL) structure. It is challenging to model the behaviour of highly concentrated electrolytes near a charged surface.

We present a continuum transport theory for these highly concentrated electrolytes. The model is made to conform with the second law of thermodynamics by enforcing positive entropy production. The key thermodynamic contributions to entropy production can be used to extrapolate a consistent from of the free energy, which constitutes the transport equations [3,4]. Our continuum model can describe both static and dynamic systems of highly concentrated electrolytes. To analyse the EDL, static simulations have proven effective due to their very low computation cost. Using this method, we are able to achieve concentration profiles at EDL length scales; when adding nonlocal contributions [4] even oscillatory behaviour can be recreated.

Solvation is a key effect to consider when modelling reactions at the electrode surface or intercalation. The desolvation at the electrode surface constitutes an energy barrier, which must be overcome. For this a local solvation model is needed, enabling a description of the electric forces removing the solvation shell in the EDL.

Solvation is added to the free energy of the system by modifying the statistics which determine the entropic contribution, rather than using a probabilistic approach [5]. Additionally, we include a term to represent the ion-solvent interaction energy. Thus, two novel parameters are used to define the interaction – the maximum number of solvent molecules binding to a single ion, and the binding energy. We supplement our analytic discussion by numerical double layer simulations of an electrolyte consisting of an IL with a solvent, neutral or charged. Analysing the differential EDL capacitance, we can both reproduce known effects, as the shift from a “camel”-shape curve to a “bell”-shape for larger salt concentrations [6], and previously not described effects, like the effect of ion size asymmetry on the capacitance minimum. We find that desolvation can also be seen in differential capacitance plots in some cases, as our model predicts the solvation shell stripping to coincide with an increased capacitance. We present here studies on which electrolyte properties influence the solvation behaviour, the most important ones being salt concentration, solvent binding energy and ion size asymmetry.

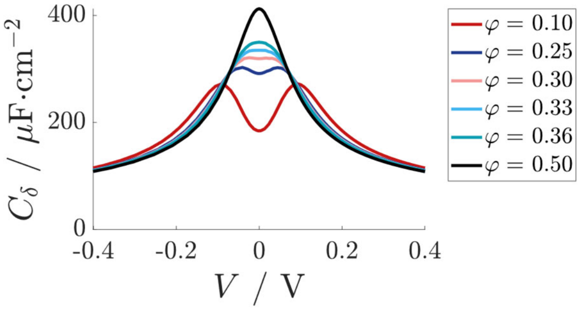


Figure 1: Differential capacitance of a symmetric salt with an equal size solvent molecule at different salt concentrations. $\varphi$ denotes the volume fraction taken by the salt, so $\varphi = 1$ would denote an ionic liquid. The transition from a double peak (“camel”-shape) to a single peak (“bell”-shape) is evident.

References:
1. Armand, M.; Tarascon, J.-M. Nature 2008 451, 652.
2. Giffin, G.A., Nat Commun 2022 13, 5250.
3. Schammer, M. et al. J. Electrochem. Soc. 2021, 168, 026511.
4. Schammer, M. et al. J. Phys. Chem. B 2022, 126, 14, 2761-2776.
5. Goodwin, Z., et al. PRX Energy 2023, 2, 013007
6. Kornyshev, A. J. Phys. Chem. B 2007, 111, 618, 5545

# Ab initio study of the thermodynamic properties of the $Li_6PS_5Cl$ solid electrolyte

T. Ayadi, M. Nastar and F. Bruneval
*Université Paris-Saclay, CEA, Service de recherche en Corrosion*
*et Comportement des Matériaux, SRMP*
*91191 Gif-sur-Yvette, France.*
*tarek.ayadi@cea.fr*

In recent years, solid-state batteries have attracted considerable interest. They do not suffer from leaks and degradation as compared to existing technologies that use liquid electrolytes. The $Li_6PS_5Cl$ electrolyte used in solid-state batteries has several advantages, including increased safety and significant energy density [1, 2, 3]. However, solid-state batteries based on this electrolyte are still in their early stages. Some issues persist, such as challenges with chemical stability at the solid-solid interfaces.

In this study, we have performed DFT static and dynamic simulations to investigate the structural and the thermodynamic properties of the $Li_6PS_5Cl$ solid electrolyte. An in-depth analysis of the structural properties of $Li_6PS_5Cl$ reveals that this material presents a non-uniform distribution of Li ions around S and Cl atoms. This specific short-range order of Li has a significant impact on the energetic stability of $Li_6PS_5Cl$ at 0 K. Moreover, new crystallographic sites of Li ions are highlighted which align favourably with a recently published experimental paper [2]. Then, the heat capacity $C_p$ was calculated using the ab initio molecular dynamics simulations (AIMD) combined with the temperature remapping approximation (TRA) [4] to include quantum effect in the nuclear degrees of freedom. To the best of our knowledge, there exists no experimental or theoretical $C_p$ value for $Li_6PS_5Cl$ in the literature, despite the importance of this thermodynamic quantity. To check the thermodynamic stability of this material, the Gibbs free energy was calculated from the $C_p$ value. We show that $Li_6PS_5Cl$ is stable above 700 K which is consistent with the reported temperature of synthesis of 823K [1]. Our results offer a comprehensive and detailed analysis aimed at understanding the thermodynamic stability of $Li_6PS_5Cl$ and elucidating the mismatch between experimental and theoretical outcomes.

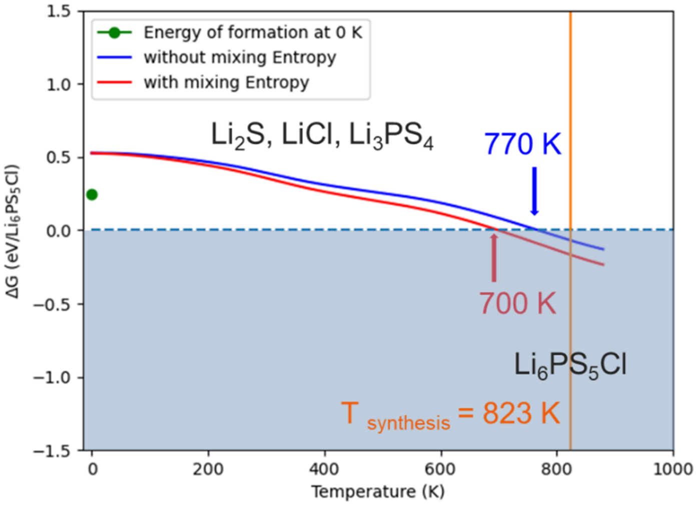


Figure 1: Gibbs free energy as a function of temperature.

References:
1. M. A. Kraft, *et al.*, J. Am. Chem. Soc. **139**, 10909, (2017).
2. R. Schlenker, *et al.*, Chem. Mater. **32**, 8420, (2020).
3. T. Das, *et al.*, J. Mater. Chem. A, **10**, 16319, (2022).
4. R. Dsouza *et al.*, Phy. Rev. B **105**, 184111 (2022).

# Extracting Ion Density and Mobility - Transient Current Method Revisited

S. Jenatsch[1], M. H. Futscher[2], A. Schiller[1], B. Blülle[1], Y. E. Romanyuk[2], B. Ruhstaller[1]
[1] *Fluxim AG, Katharina-Sulzer-Platz 2, 8400 Winterthur, Switzerland*
[2] *Laboratory for Thin Films and Photovoltaics, Empa, Überlandstr. 129, 8600 Dübendorf, Switzerland*
*beat.ruhstaller@fluxim.com*

Solid-state batteries (SSBs) are among the most promising candidates for next-generation energy storage due to their high-energy and high-rate electrochemical storage capabilities. An essential component in a SSB is the solid-state electrolyte (SSE), in which a key parameter is the ionic conductivity, defined as a product of ion density and mobility. As pointed out recently, the main cost driver for SSBs is the lithium ion density.[1] It is thus essential to distinguish between these two parameters and characterise them reliably. A popular technique to determine ionic conductivities is electrochemical impedance spectroscopy in combination with equivalent circuit fitting.[2] While this technique is fairly established, it does not allow to separate between ionic mobility and density. Therefore, the transient current method has been proposed which is performed on a simple device consisting of an SSE sandwiched between two electrodes.[2] Upon pre-biasing the device with a constant voltage, the current response to an opposite voltage step is measured. While the time-integral of the current $J$ provides the mobile ion density $N_{\text{ion}}$, the transition point is used to determine the mobility $\mu_{\text{ion}}$. Figure 1(a) shows a typical current transient and the used analytical formulas.

Here, $q$ is the elementary charge, $V_{\text{step}}$ is the voltage step height, $\tau_{\text{transit}}$ is the transit time which is here defined as the time at which the current has the highest first derivative and $d$ is the SSE layer thickness. To analyse the accuracy of determining $N_{\text{ion}}$ and $\mu_{\text{ion}}$ from transient current measurements, we use the electrical device simulation software Setfos [3] to generate synthetic data on which the analytical formulas are applied. If only mobile cations ($Li^+$) are assumed in simulations, we find that the ion density is underestimated significantly. Thus, ways to reduce the discrepancy are analysed, e.g. the use of the electric double layer width ($d_{\text{EDL}}$) instead of $d$ in the analytical formulas. However, for measured data this results in values of $N_{\text{ion}}$ significantly exceeding the theoretical lithium concentration in LiPON.[4] The discrepancy can be resolved if in addition to the cations, also the anions are considered mobile. As shown in Figure 1(b), we find a good agreement between simulation input value and calculated $N_{\text{ion}}$ using the SSE layer thickness $d$. We analyse in more detail how other factors (*e.g.* SSE thickness, extraction voltage, metal plating) affect the validity of calculated $N_{\text{ion}}$ and $\mu_{\text{ion}}$ values and thereby assess under which conditions the transient current method can be applied reliably.

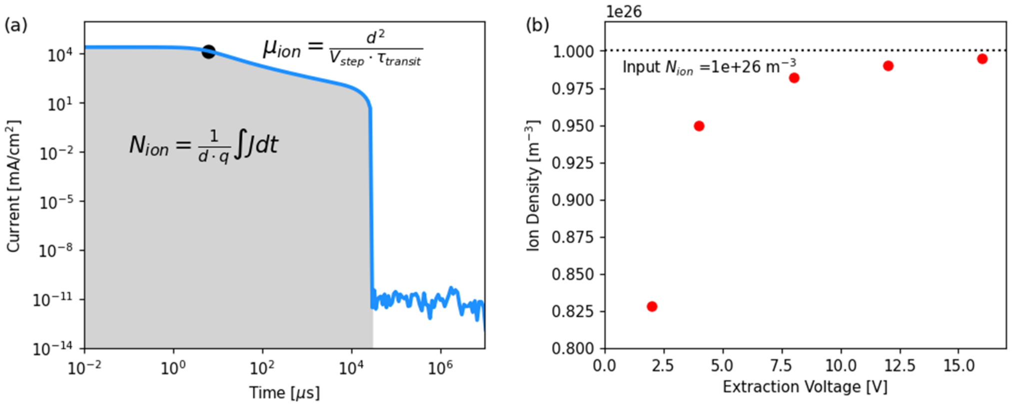


Figure 1: Simulation with two mobile ionic species. (a) Typical simulated current transient from which $N_{\text{ion}}$ and $\mu_{\text{ion}}$ are extracted. (b) Input (dashed line) vs. calculated $N_{\text{ion}}$ (red circles) for varying $V_{\text{step}}$.

References:
1. J. Janek, W. G. Zeier, *Nat. Energy* **8** **(**2023), 3, 230-240.
2. J. Sastre, M. H. Futscher, L. Pompizi, A. Aribia, A. Priebe, J. Overbeck, M. Stiefel, A. N. Tiwari, Y. E. Romanyuk, *Commun. Mater.* **2** (2021), 1, 76.
3. Simulation software Setfos, by Fluxim AG, Switzerland, www.fluxim.com/setfos-intro
4. L. Le Van-Jodin, F. Ducroquet, F. Sabary, I. Chevalier, *Solid State Ionics* **253** (2013), 151-156.

# Systematic Workflow for Efficient Identification of Local Representative Elementary Volumes

Benjamin Kellers, Martin P. Lautenschlaeger, Nireas Rigos, Julius Weinmiller,
Timo Danner, Arnulf Latz
*German Aerospace Center (DLR) at the Helmholtz Institute Ulm (HIU)*
*Wilhelm-Runge-Str. 10, 89081 Ulm, GERMANY*
*benjamin.kellers@dlr.de*

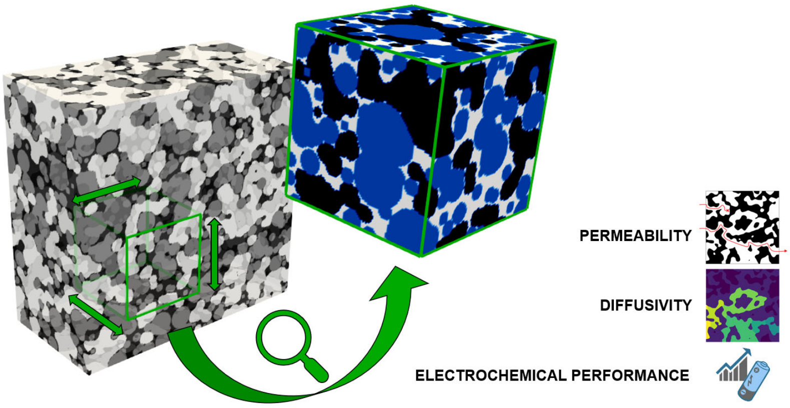


Figure 1: Schematic representation of the presented local REV workflow.

Many aspects of battery chemistry, operation, and manufacturing, including degradation mechanisms, electrochemical performance [2], or calendaring and electrolyte filling [1], are modeled using images of porous media resolving its microstructure. A typical and key question is if the cutout of the microstructure represents the key morphological properties of the porous media. Moreover, due to limitations of the software and/or the computational resources, one is often faced with the task of choosing a smaller subdomain to represent the full image. In both cases one seeks a so-called representative elementary volume (REV). There exist different definitions of REVs and methods to choose a REV in the literature. Most of them share common problems: they usually overestimate the size and most often focus on a single property only.

However, the right choice of a REV is key for relating pore-scale simulations to continuum properties of a given porous medium. To achieve this, we present a novel type of REV workflow [3] that is capable of identifying the so-called *local REV*: a REV of minimal size tuned to be representative for multiple properties at the same time. The algorithm is based on pore networks, ensuring memory efficiency and performance. It is showcased using a selection of battery-related simulations, such as charging and discharging of battery cells, electrolyte filling of electrodes, and Lithium-plating during fast charging.

Our results show that the concept of a local REV captures all relevant physical behaviors, while keeping the selected sub-volume as small as possible. Through a right choice of selection criteria, the algorithm can be applied to a large variety of problems, ensuring representativeness with respect to the investigated physical properties. This alleviates many of the downsides of other known REV concepts and allows high-quality results at an efficient usage of computational resources. This enables larger parameter studies in general or specific memory intensive applications, such as cycling simulations on the microstructure scale.

References:
1. M.P. Lautenschlaeger, B. Prifling, B. Kellers, J. Weinmiller, T. Danner, V. Schmidt, A. Latz, *Batteries & Supercaps* **5** (2022), e202200090
2. A. Latz and J. Zausch, *J. Power Sources* **196** (2011), 3296-3302
3. B. Kellers, M.P. Lautenschlaeger, N. Rigos, J. Weinmiller, T. Danner, A. Latz, *Batteries* **9** (2023), 7, 390

# Influence of Passive Material Distribution and its Structural Properties on Cathode Performance

Mrudula Prasad[a,b], Simon Hein[a,b], Matthias Neumann[c], Benedikt Prifling[c], Rares Scurtu[d], Alice Hoffmann[d], André Hilger[e], Markus Osenberg[e], Ingo Manke[e], Margret Wohlfahrt-Mehrens[d], Volker Schmidt[c], Timo Danner[a,b], and Arnulf Latz[a,b,f]
*[a] German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Stuttgart, Germany*
*[b] Helmholtz Institute Ulm (HIU) for Electrochemical Energy Storage, Ulm, Germany*
*[c] Ulm University (UUlm), Institute of Stochastics, Ulm, Germany*
*[d] ZSW-Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Ulm, Germany*
*[e] Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany*
*[f] Ulm University (UUlm), Institute of Electrochemistry, Ulm, Germany*
*mrudula.prasad@dlr.de*

As the requirements for batteries with a high energy density are constantly growing, the need to optimize the electrode microstructure has become increasingly critical. Passive materials are an essential component of lithium-ion battery electrodes and enhance the electrical connectivity and mechanical stability within an electrode matrix. The spatial distribution of the passive materials, namely, the conductive additive and binder domain (CBD), and its internal structure, have a major effect on battery performance. However, disentangling different transport processes in the electrodes and their impact on electrode performance is non-trivial. Combining microstructure-resolved simulations [1] with advanced imaging and electrochemical characterization techniques, such as electrochemical impedance spectroscopy (EIS) on symmetric cells and half-cell discharge experiments, provides a powerful methodology to characterize the lithium-ion transport in the electrode pore space.

In the standard simulations, the CBD is treated as a homogenized phase with effective transport parameters, not resolving its internal nano-structure. To develop an improved model with increased predictive power, we need to characterize and understand the properties of the CBD on the nano-scale. In the present contribution, high-resolution 3D FIB-SEM data [2] is used to obtain further geometric information on the porous networks within the CBD, shedding light on its average effective ionic conductivity and its dependence on the porosity. This information is then fed-back to the model, allowing us to account for the local porosity-dependent tortuosity on the nano-scale in the CBD domain.

In our contribution we present the results of our analysis of the CBD, and advanced electrochemical simulations on an electrode scale. The results highlight the importance of the CBD distribution and we address future design strategies on electrode and material level.

References:

1. Hein, S. *et al.* (2020) ‘Influence of conductive additives and binder on the impedance of lithium-ion battery electrodes: Effect of morphology’, *Journal of The Electrochemical Society*, 167(1), 013546. doi:10.1149/1945-7111/ab6b1d.
2. Prifling, B. *et al.* (2022) ‘Quantitative comparison of different approaches for reconstructing the carbon-binder domain from tomographic image data of cathodes in lithium-ion batteries and its influence on electrochemical properties’, *Energy Technology*, 11(5). doi:10.1002/ente.202200784.

# Modeling Li-ion battery electrodes accounting for microstructure properties: The Newman's model revisited

G. Lenne[1], E. Woillez[1], T. David[2], M. Chandesris[1]
[1]*Univ. Grenoble Alpes, CEA, LITEN/DEHT/SAMA/LMP, Grenoble, France*
[2]*Univ. Grenoble Alpes, CEA, LITEN/DTNM/STDC/LCAE, Grenoble, France*
*guillaume.lenne@cea.fr*

Volume-averaged treatment of microscopic transport and reaction equations is performed to obtain a model in which the solid and fluid phases are conceived as a pseudo-continuum. The most established porous-based model is the Newman's pseudo-two-dimensional (P2D) model used to reduce the computational cost of numerical simulations. However, the classical formulation of the P2D model does not capture the microstructure heterogeneities and does not allow resolving their influence. In particular, the local fluctuations of physical fields become significant at high C-rate and are responsible of deviations between the microstructure model and the P2D model. In this work, we revisit the P2D model by applying the method of volume averaging [1] to mass and charge transport equations of a Lion-Ion Battery (LIB) microstructure model. The closure problems are explicitly expressed for the mass and charge transport equations and solved on real 2D microstructure by asymptotic expansion. In this way, for non-negligible Thiele modulus/Damköhler number [2] (i.e. for non-negligible diffusion relative to reaction rates), a non-classical homogenized model is obtained where the effective properties do not depend only on the geometry but are shown to be a function of the reaction rate through the dimensionless Thiele modulus. The result strongly improve the predictions of the P2D model especially at high C-rate for a complex geometry.

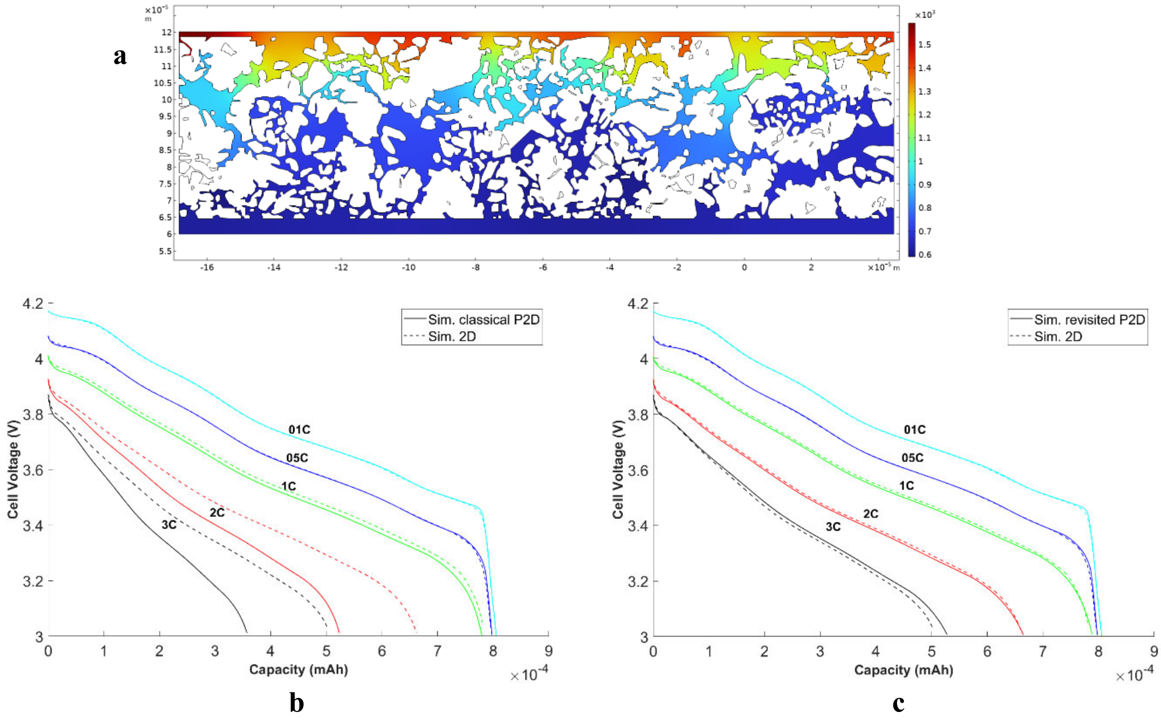


Figure 1: (a) Lithium concentration in the electrolyte during lithiation from a simulation on a real 2D microstructure of NMC. The simulations results at various C-rate are compared to the classical P2D (b) and the revisited P2D (c).

References:
1. S. Whitaker, *The method of Volume Averaging*, Springer Netherlands, Dordrecht, 1999
2. F. J. Valdés-Parada, D. Lasseux, S. Whitaker, International Journal of Chemical Reactor Engineering, 2017, 15

# Quantifying the impact of operating conditions on particle cracking in Li-ion battery cathodes, using super-resolution of SEM images and stereology

Orkun Furat[1], Donal P. Finegan[2], Jeffery Allen[2], Peter Weddle[2], Kandler Smith[2], Volker Schmidt[1]
[1]*Ulm University, Helmholtzstraße 18, 89069 Ulm, Germany*
[2]*National Renewable Energy Laboratory, 15013 Denver W Parkway, Golden, CO 80401, USA*
*orkun.furat@uni-ulm.de*

Quantitative relationships that link the effect of repeated cycling of Li-ion batteries on the structural degradation of cathode particles are not yet well established. In this presentation, we propose a computational method for quantifying cracks within cathode particles from scanning electron microscopy (SEM) image data of cross-sectioned NMC 532 electrodes, see Figure 1. More precisely, a generative adversarial network (GAN) is trained to super-resolve SEM images, i.e., the trained network can increase the resolution of lowly resolved SEM images—allowing for a more reliable quantification of fine features such as cracks, while leveraging the statistically representative field of view of the lowly resolved image data [1]. Then, a second neural network and further image processing steps are deployed to segment the super-resolved image data into back-ground, particles and cracks, such that crack statistics on particle porosity or crack size/width/length distributions can be computed [2]. Additionally, a stereological method has been developed to investigate the local particle porosity as a function of distance to the particle center. The proposed computational methods have been deployed for the crack quantification of cathodes that have been cycled with various charge rates (1C, 6C, 9C) and cycle numbers (25, 225 and 600 cycles). We observed that the crack sizes increase co-monotonously both with the number of cycles and with the charge rate, where the former has a more significant effect on the crack length, whereas the latter influences the crack width. Additionally, the computed crack statistics have been compared to electrochemical data from full and half cells of NMC532 cathodes [2]. This comparison indicated that the capacity fade correlates strongly with the structural degradation within the first 25 cycles, however, for larger numbers of cycles this correlation decreased. In addition to the study performed for cathodes cycled with different numbers of cycles and charge rates, the developed methods have been applied to characterize the structural degradation of cathodes which have been cycled at different operating temperatures (20°C, 30°C, 40°C, 50°C) [3]. Thus, the presented methods can be applied for a wide range of scenarios to quantify particle cracking in batteries and thereby to provide useful parameters for the calibration of battery models.

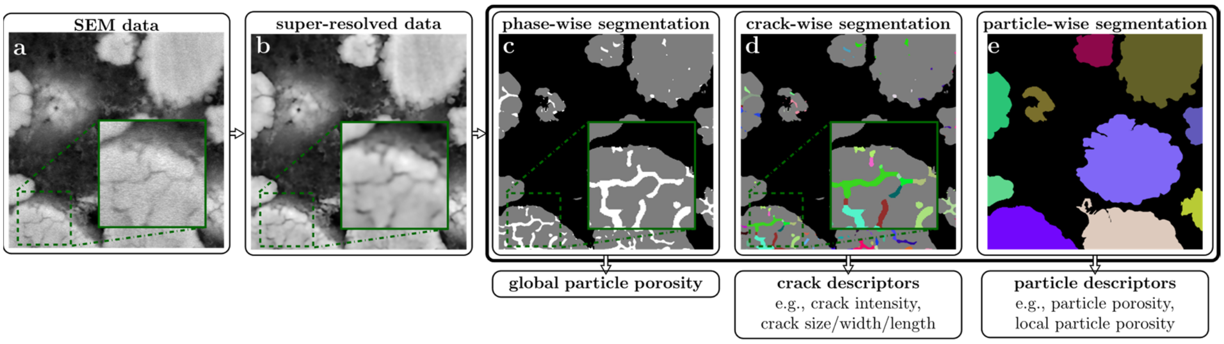


Figure 1: Work flow for quantifying structural degradation. First, SEM image data (a) is super-resolved (b). Then, phase-wise (c), crack-wise (d) and particle-wise (e) segmentations are computed, from which various descriptors for characterizing particle cracking can be determined [3].

References:

1. O. Furat, D.P. Finegan, Z. Yang, T. Kirstein, K. Smith, V. Schmidt, *npj Comput. Mater.* **8** (2022), 68
2. O. Furat, D.P. Finegan, Z. Yang, T.R. Tanim, K. Smith, V. Schmidt, *J. Electrochem. Soc.* **169** (2022), 100541
3. O. Furat, D.P. Finegan, Z. Yang, M. Neumann, T.R. Tanim, K. Smith, V. Schmidt, *Energy Storage Mater.* **64** (2024), 103036

# Investigation of nano-porous cathode particles for battery cell simulations

Simon Daubner[1], Daniel Schneider[1,2] and Britta Nestler[1,2]
*[1] Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology (INT-MSS),*
*Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
*[2]Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-MMS),*
*Kaiserstraße 12, 76131 Karlsruhe, Germany*
*simon.daubner@kit.edu*

The research of new electrode materials such as sodium ion intercalation compounds is key to meet the challenges of future demands of sustainable energy storage. Many commercial as well as promising electrode materials exhibit strongly anisotropic properties and are synthesized as polycrystalline agglomerates. These two factors lead to a strong correlation between the hierarchical particle morphology and effective ion transport in the host material. Simultaneously, the microscale interactions of chemical, electrical, and mechanical forces determine the intercalation dynamics and, consequently, exert a substantial influence on the overall cell performance.

In the realm of computational simulations, a gap exists between the atomistic understanding of intercalation and diffusion in a perfect crystal and the effective reaction-diffusion kinetics of secondary particles. Fast computational models for battery state-of-charge prediction, however, strongly depend on a homogenized description of the microscale. A suitable tool to bridge this gap by studying the ion transport in complex battery microstructures, is the multiphase-field method. Our previous work [1] highlights the capability to simulate polycrystalline battery materials in the micrometer range including phase transformations and heterogeneous nucleation at existing grain boundaries. Furthermore, the grain orientations and respective material diffusion anisotropy can be considered in simulation studies to reveal the connection between particle microstructure and apparent diffusivity [2]. Our previous work is extended to cover nano-porous agglomerates and arbitrary complex microstructures. We discuss how pixelated image data from FIB-SEM can be directly included into simulations to compute effective properties such as tortuosity, active surface area and apparent diffusivity. By combining the multiphase-field approach with a smooth boundary description of intercalation fluxes, the ion distribution in these microstructures can be simulated for various (dis-)charge conditions. These investigations pave the way for a multi-scale investigation of battery materials from nano-sized single crystals to a porous electrode consisting of hierarchical secondary agglomerates and, thus, hold the potential to guide research towards batteries with longer lifetime and improved rate performance.

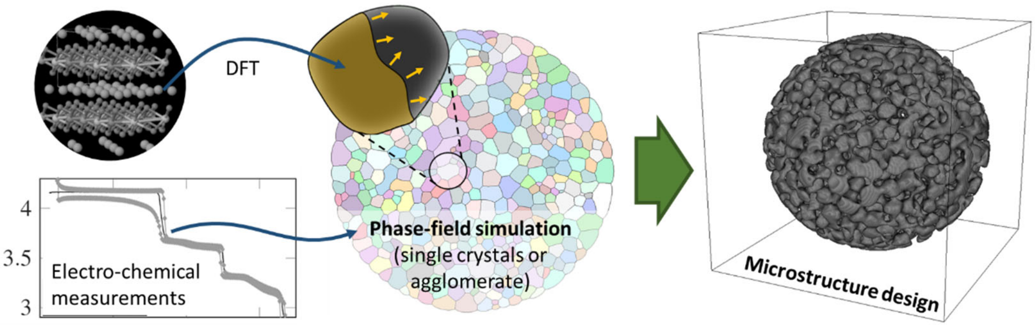


Figure 1: Based on ab-initio computations and/or experimental input (left), the phase-field method can be employed for electro-chemo-mechanical simulations (middle) to guide microstructure design (right).

References:
1. S. Daubner, M. Weichel, D. Schneider, and B. Nestler. Modeling intercalation in cathode materials with phase-field methods: Assumptions and implications using the example of $LiFePO_4$. Electrochim. Acta 421 (2022) 140516.
2. S. Daubner, M.Weichel, D. Schneider, and B. Nestler. Modeling anisotropic transport in poly-crystalline battery materials. Batteries 9(6) (2023) 310.

# Understanding the effect of hierarchically structured cathode morphology on the performance of intercalation battery cells

J. Naumann[1], N. Bohn[1], O. Birkholz[2], M. Neumann[3], M. Müller[1], J. R. Binder[1], M. Kamlah[1]
*[1]Institute for Applied Materials, Karlsruhe Institute of Technology, Germany*
*[2]APL Automobil-Prüftechnik Landau GmbH, Germany*
*[3]Institute of Stochastics, Ulm University, Germany*
*johanna.naumann@kit.edu*

Hierarchical structuring of the cathode can improve the rate capability of battery cells. In this case, the secondary active material particles possess a designed inner porosity, so the electrolyte directly contacts the smaller primary particles. The resulting short transport paths for solid diffusion in the active material have shown to increase the specific capacity especially at high insertion and extraction rates compared to dense secondary particles [1, 2]. The performance of the cell depends on the morphology of the hierarchically structured cathode including the microstructure of the secondary particles [3]. We combined a Doyle-Fuller-Newman-type cell modelling framework [4] with discharge experiments to show that different physical processes in the battery cell influence its performance depending on the morphology and material properties of the hierarchically structured cathode [5].

For the investigated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) cathodes, electronic transport in the secondary particles was the dominant process which determined the rate capability. Due to the low electronic conductivity of the active material, the transport of electrons to the primary particle surfaces where the electrochemical reaction takes place was insufficient. Despite the main electronic transport taking place via conductive additives surrounding the secondary particles and comparatively short electronic transport paths within the secondary particles, the latter played a dominant role since the electronic conductivity of additives and active material differ several orders of magnitude. A low secondary particle porosity and a small secondary particle size reduced the limitations due to electronic conductivity.

Even though hierarchical structuring was found to mitigate the reduction of rate capability associated with a low diffusivity in NMC, limiting effects remained within large primary particles. Film thickness affected hierarchically structured cathodes in a similar way as classical granular cathodes consisting of dense secondary particles. Namely, with increasing thickness, depletion of the electrolyte reduced the rate capability of the cell. While transport proved to be limiting, the cell performance was insensitive to the experimentally achievable variation of electrochemically active surface area for hierarchically structured cathodes.

Including the effect of varying material properties, we deduced general recommendations for the design of hierarchically structured cathodes. To increase the rate capability, a good electronic conductivity within the secondary particles of at least $10^{-4}$ $Sm^{-1}$ is crucial. For active materials with a low electronic conductivity, conductive additives inside the secondary particle are therefore necessary. In addition, if the diffusivity in the active material lies below $10^{-15}$ $m^2s^{-1}$, a small primary particle radius below 100 nm fully exploits the advantage of short diffusion paths in hierarchically structured cathodes. Ultrafast applications require thin cathodes, at most 70µm, or electrolytes with a high ion mobility.

References:
1. Z. Chen, J. Wang, D. Chao, T. Baikie, L. Bai, S. Chen, Y. Zhao, T. C. Sum, J. Lin, Z. Shen, *Sci. Rep.* **6** (2016), 1
2. M. Müller, L. Schneider, N. Bohn, J. R. Binder, W. Bauer, *ACS Appl. Energ. Mater.* **4** (2021), 1993
3. A. C. Wagner, N. Bohn, H. Geßwein, M. Neumann, M. Osenberg, A. Hilger, I. Manke, V. Schmidt, J. R. Binder, *ACS Appl. Energ. Mater.* **3** (2020), 12565
4. O. Birkholz, M. Kamlah, *Energy Technol.* **9** (2021), 2000910
5. J. Naumann, N. Bohn, O. Birkholz, M. Neumann, M. Müller, J. R. Binder, M. Kamlah, *Batteries Supercaps* **6** (2023), e202300

# Improving the Relationship between State of Charge, Charge History and Voltage Hysteresis Evolution in First Order Differential Equation Voltage Hysteresis Models

E. Hagopian, D. Howey, C.W. Monroe
*Department of Engineering Science, University of Oxford, Oxford, United Kingdom*
*emmanuelle.hagopian@eng.ox.ac.uk*

Voltage hysteresis in batteries needs to be modelled effectively for accurate state of charge estimation in battery management systems, particularly in battery systems that experience a voltage plateau in their OCV profile, such as lithium-ion batteries with lithium iron phosphate (LFP) cathodes.

Plett's voltage hysteresis model is a first order differential equation which effectively describes the normalised hysteresis state [1]. Initial pseudo OCV experiments show that Plett's model can be improved by further considering the state of charge and charge history hysteresis dependence. The shape of voltage hysteresis evolution is not accurately modelled by an exponential at states of charge where graphite changes stage, reflected by bumps in the OCV profile [2][3]. This is exemplified in the 20% loop in Figure 1b) where hysteresis does not evolve exponentially while experiencing two graphite stage transitions (2L and 3L) (demonstrated in Figure 1a)).

The dependence of hysteresis evolution on state of charge and charge history needs to be accounted for in the hysteresis model. Subsequent research explores the relationship between hysteresis and state of charge and charge history through further experiments.

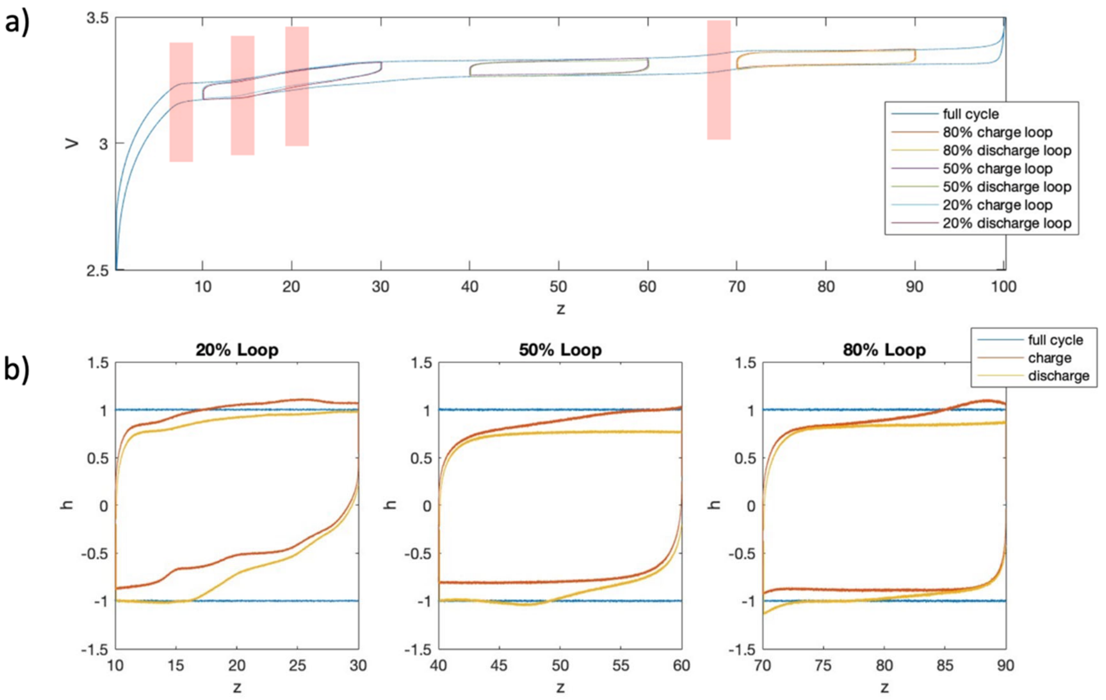


Figure 1: Pseudo OCV at 1/24 C rate on NX energies LFP/graphite 18650 cells. a) Loops around 20%, 50% and 80% state of charge (z) starting from charge and discharge. The red bands highlight graphite stage transitions. b) Normalised hysteresis (h) evolution for loops around 20%, 50% and 80% z.

References:
1. Plett, Gregory L. Battery management systems, Volume II: Equivalent-circuit methods. Artech House, 2015.
2. Mercer, Michael Peter, et al. "Voltage hysteresis during lithiation/delithiation of graphite associated with meta-stable carbon stackings." *Journal of Materials Chemistry A* 9(1) (2021) 492.
3. Ovejas, V. J., and A. Cuadras. "Effects of cycling on lithium-ion battery hysteresis and overvoltage." *Scientific Reports* 9(1) (2019) 14875.

# Optimization and Parameterization of Electrochemical Systems in BattMo, the Battery Modeling Toolbox

Xavier Raynaud[1], August Johansson[1], Halvor Nilsen[1], Simon Clark[2], Eibar Flores[2]
*[1] SINTEF Digital, PB 124 Blindern, 0314 Oslo, Norway*
*[2] SINTEF Industry, PB 4760 Torgarden, 7465 Trondheim, Norway*
*xavier.raynaud@sintef.no*

Optimization and parameterization are two important procedures in computational modelling and design of electrochemical systems. In this contribution we illustrate how this is performed in BattMo [1], a comprehensive solution for modelling of electrochemical devices. BattMo has been primarily developed for PxD (x=2,3,4) models of Li-ion batteries but has also been used for electrolysis and other electrochemical systems. Thanks to the general, chemistry-agnostic design based on continuum models (aka physics-based models), optimization and parameterization can be performed for all the electrochemical systems in the same manner. BattMo is developed in MATLAB [2] and has a high-performance Julia version (BattMo.jl) [3].

Being based continuum models, optimization and parameterization are similar from a mathematical perspective and can be performed with the same algorithms. Also, since the models are both large and nonlinear, they can be quite costly to evaluate. To reduce this cost, we propose the use of gradient-based methods where the gradients are computed by solving an adjoint problem. This means that the optimization or parameterization can be done with a cost independent on the number of parameters to be optimized or fitted. The adjoint problem is derived automatically using automatic differentiation (AD). Automatic differentiation also means that sensitivities of output quantities with respect to any underlying parameter can be calculated. We will present results from the parameterization of a novel SiGr – LNMO battery, optimized to maximize energy output.

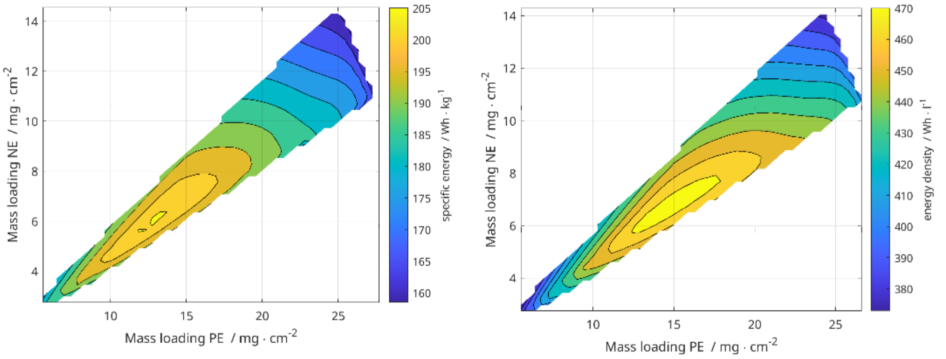


Figure 1: Isocurves of specific energies (left) and energy densities (right) as function of mass loadings of the electrodes, optimized under the constraint of NP being in the range [1.0, 1.5].

References:

1. https://batterymodel.com/ (accessed Jan 15, 2024)
2. https://github.com/BattMoTeam/BattMo (accessed Jan 15, 2024)
3. https://github.com/BattMoTeam/BattMo.jl (accessed Jan 15, 2024)

# Parametrization of a Thermochemical-Kinetic Model for Gas Analysis of Lithium-ion Batteries

J. Valenzuela, L. Schmidt, J. Wagner-Henke, U. Krewer
[1]*Karlsruhe Institute for Technology, Institute of Applied Materials – Electrochemical Technologies*
*Adenauerring 20b, Building 50.40, 76131 Karlsruhe, Germany*
*jorge.leon@kit.edu*

The high demand for electric vehicles has steadily increased the prevalence of lithium-ion batteries with high energy densities in everyday life. This prevalence has generated a commensurate increase in safety concerns since high-performing batteries often tend to degrade faster, which can lead – in rare cases - to thermal runaway. Calculating kinetic parameters and their relationship with the properties of the electrolyte components provides a fundamental understanding of the process that gives rise to thermal runaway in lithium-ion batteries [1, 2]. A commonly used technique for degradation analysis is Online Electrochemical Mass Spectrometry (OEMS), which provides insights into the gas evolution during the operation of lithium-ion batteries. Figure 1 shows a simplified scheme of an OEMS system, indicating gas flows with arrows. In the past, investigations with OEMS focused solely on the SEI formation or overcharging of the battery. Recently, we presented a novel variant of the method, which can heat cells to 132°C with in-situ gas analysis to better understand thermal degradation [3]. Due to the high complexity of the reactions and gas/liquid phase changes, especially of the electrolyte solvents, the interpretation of the measurements is challenging.

This work presents a model that is capable of reproducing the results obtained from OEMS measurements of a Li-ion battery heated from room temperature to 132°C and back. It is used to identify a proper reaction scheme and to elucidate the complex phenomena that occur during thermal degradation. The model considers phase equilibrium to address the evaporation and solubility phenomena inside the cell and a power law kinetic model to represent the generation and consumption of chemical compounds.

We successfully reproduce the evaporation of DMC considering its interaction with the carrier gas, and we also reproduce in an acceptable level the production of the salt degradation product $POF_3$ during thermal abused (Fig. 2). The talk will elucidate the underlying network, processes and limitations. It reveals the importance of the thermochemical properties of electrolytes' chemical components and their impact on lithium-ion batteries during thermal degradation processes.

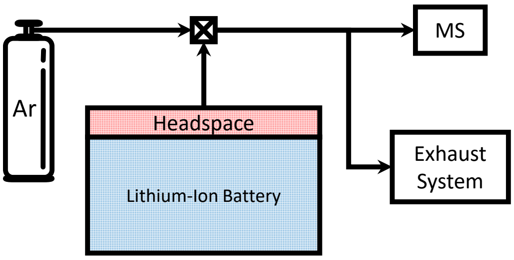


Figure 1: Simplified OEMS setup scheme.

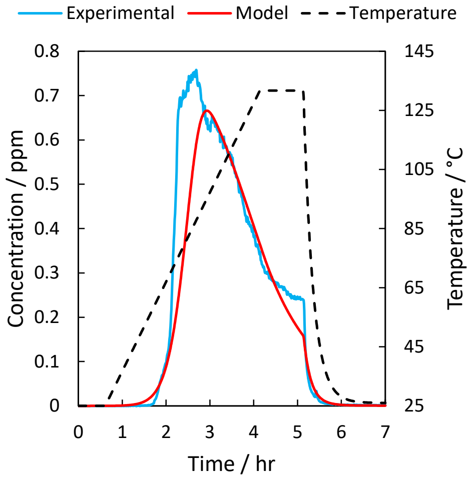


Figure 2: $POF_3$ concentration profile during thermal decomposition.

References:

1. F. Baakes, M. Lüthe, M. Gerasimov, V. Laue, F. Röder, P. B. Balbuena, U. Krewer, *J. Power Sources* **522** (2022)
2. F. Baakes, D. Witt, U. Krewer, *Chem. Sci.* **47** (2023), 14, 13783–13798
3. L. Bläubaum, P. Röse, F. Baakes, U. Krewer, *Batter. Supercaps*, accepted

# Characterising diffusion in lithium-ion batteries from operando impedance measurements during relaxation

Noël Hallemans, Emmanuelle Hagopian, David Howey, Stephen Duncan
*Department of Engineering Science, University of Oxford, Oxford, UK*
*The Faraday Institution, Didcot, UK*
*noel.hallemans@eng.ox.ac.uk*

Determining battery diffusion timescales from measurements is a long-lasting problem. Typically, the galvanostatic intermittent titration technique is used, and the diffusion constant is estimated by fitting data to known equations such as current pulses and relaxation curves [1]. However, results are often inconsistent due to various flaws of the technique (e.g. assuming a planar one-dimensional semi-infinite system) [2]. An alternative approach is to estimate diffusion parameters by fitting a physics-based model—for instance the single-particle model (SPM) [3]—to electrochemical impedance spectroscopy (EIS) data [4]. This works well when sufficiently low frequencies are measured, corresponding to long measurement times.

In this research, we tackle the determination of diffusion timescales by merging both techniques: we measure the nonstationary impedance [5] of the battery *during* relaxation. This is achieved using a recently developed operando EIS technique with multisine excitation [6]. We also fit the impedance data to the SPM (including diffusion and charge transfer kinetics). The advantage of measuring impedance—instead of voltage—during relaxation is that different processes (e.g. diffusion and charge transfer) can be monitored, distinguishable by their characteristic timescales, from the shape *and* time-evolution of the impedance. Hence, more information is inferred than is possible with only stationary impedance data or only voltage relaxation data.

This method is promising for characterising batteries and other electrochemical devices and can be performed—up to a limited frequency—with a traditional potentiostat/cycler. It also provides information on how long it takes a device to reach steady state. Moreover, it can potentially be utilised for detecting lithium plating.

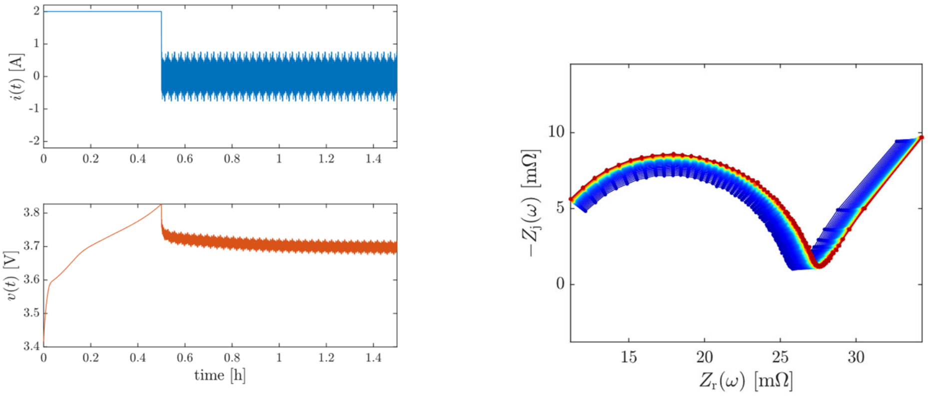


Figure 1: Left: current and voltage data during charge and multisine relaxation. Right: time-varying impedance (time increases from blue to red).

References:
1. W.R.A.H. Weppner, R.A. Huggins, *Journal of The Electrochemical Society*, 1977, 124(10), 1569.
2. S.D. Kang, W.C. Chueh, *Journal of The Electrochemical Society*, 2021, 168(12), 120504.
3. M. Guo, G. Sikha, R.E. White, *Journal of The Electrochemical Society*, 2010, 158(2), A122.
4. A.M. Bizeray, J.H. Kim, S.R. Duncan, D.A. Howey, *IEEE Transactions on Control Systems Technology*, 2018, 27(5), 1862-1877.
5. N. Hallemans, D. Howey, D., A. Battistel, N.F. Saniee, F. Scarpioni, B. Wouters, F. La Mantia, A. Hubin, W.D. Widanage, J. Lataire, *Electrochimica Acta*, 2023, 142939.
6. N. Hallemans, W.D. Widanage, X. Zhu, S. Moharana, M. Rashid, A. Hubin, J. Lataire, *Journal of Power Sources*, 2022, 232005.

# The $\Delta Q$-Method: State of Health and Degradation Mode Estimation for Lithium-Ion Batteries Using a Mechanistic Model with Relaxed Voltage Points

Tobias Hofman[1,2], Jiahao Li[2], Julian Raith[2], Simon Erhard[2], Jan Philipp Schmidt[1]
*[1]Chair of Systems Engineering for Electrical Energy Storage, University of Bayreuth, Weiherstraße 26, 95448 Bayreuth Bayreuth, Germany*
*[2]BMW Group, Petuelring 130, 80809 Munich, Germany*
*tobias.th.hofmann@bmw.de*

Lithium-ion batteries exhibit path-dependent aging behavior. Degradation mode (DM) estimation is a first step towards accurate state of health (SOH) representations by clustering degradation mechanisms. Mechanistic models shift and scale pristine half-cell open-circuit potential (OCP) curves of both electrodes to reconstruct the open-circuit voltage (OCV) curve by minimizing the difference between measured and reconstructed OCV. Alignment parameters describe the shift and scaling of the OCPs and can be used to estimate SOH and DMs. In this study, we introduce the novel $\Delta Q$-method that exclusively relies on relaxed voltage points and the accumulated charge between these points, rather than charging events at low current-rates. It is therefore independent of the applied current during charging or driving and rather is applicable to relaxed voltage points and the accumulated charge between these points after almost every event. It does not require a fixed reference voltage and thus eases the application to sparse data. The optimization problem is formulated to minimize the deviation between the measured and reconstructed $\Delta Q$, utilizing a nonlinear least-squares solver. The method is developed with an automotive cell dataset from laboratory measurements. The resulting algorithm is finally adopted for real-world vehicle data and validated with a dataset from the BMW i3 fleet. The accuracy of DM estimation is confirmed by first validating it with simulation data and subsequently verifying it using an automotive cell dataset. The labels for the latter are generated from a reference model. The $\Delta Q$-method demonstrates its applicability to existing battery electric vehicle fleets, achieving a mean absolute SOH estimation error of $2.52\ \%$ and a mean absolute OCV reconstruction error of $7.19\ \mathrm{mV}$. Reliable estimations are guaranteed by predefined filters, which allow only data from the last 25 to 40 days and check for at least 10 existing relaxed voltage points. The inclusion of these filters enables 59 % of the evaluated vehicles to be used for estimation. Even with a restricted state of charge window from 30 to 75 % or just three data points, the method maintains SOH errors below 3 %. A sensitivity analysis demonstrates the robustness of the method against variations in input data, choice of solver, and optimization settings. Convergence to the most likely solution is improved by constraining the solution space. This study demonstrates the applicability of the $\Delta Q$-method for SOH estimation exemplary on real world fleet data extending over 8 years.

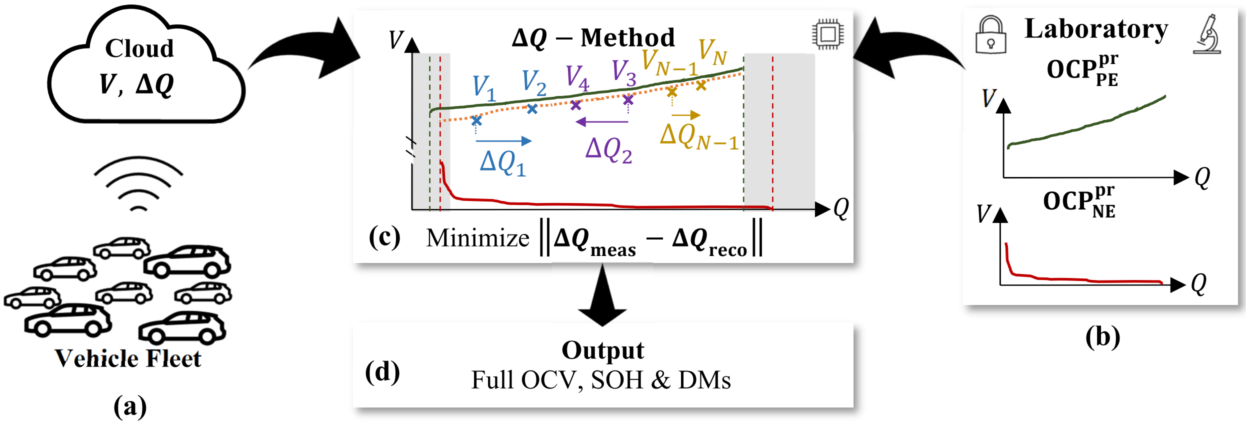


Figure 1: Overview of the novel $\Delta Q$-method: (a) Data, including relaxed voltage points and the accumulated charge between these points, is gathered from the cloud. (b) The OCPs are captured from laboratory measurements in pristine state. (c) The method minimizes the error between measured and reconstructed $\Delta Q$-vectors and (d) finally outputs the SOH, full OCV curve and DMs.

# Predicting failure behaviors in lithium-ion batteries subjected to thermal abuse following long-term degradation

Xinlei Gao[1,2], Gregory J. Offer[1,2], Huizhi Wang[1,2]
*[1]Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, U.K.*
*[2]The Faraday Institution, Harwell Science and Innovation Campus, Didcot OX11 0RA, U.K.*
*x.gao22@imperial.ac.uk, gregory.offer@imperial.ac.uk, huizhi.wang@imperial.ac.uk*

With the increasing availability and extensive utilization of lithium-ion batteries (LIBs) in diverse applications, safety always holds the highest priority in the current battery industry. However, battery safety performance evolves with battery usage, as accumulated degradation can change the internal physico-chemical states, thereby affecting the battery failure behaviours once triggered. Due to the complex degradation mechanisms and insufficient understanding of degradation-safety interface, predicting the failure behaviour evolution throughout battery cycle life remains challenging. In this study, to link the battery degradation to failure behaviours, a joint degradation-failure model is developed, which includes coupled degradation and failure sub-models. The model can be used to evaluate the safety performance such as thermal stability and thermal runaway (TR) hazard at different ageing states with different degradation paths.

In our previous study[1], several high-energy 21700 cylindrical cells were degraded to end of life (EoL) under three ambient temperatures. Identical virtual experiments were conducted to evaluate the severity of each degradation mechanism. Despite of the similar capacity fade curves for 25 °C and 40 °C ageing, the capacity losses due to solid electrolyte interphase (SEI) growth and irreversible lithium (Li) plating substantially differ. It was found that high temperature significantly facilitates SEI growth with the least Li plating severity, and the solvent concentration also substantially decreases. For 25 °C ageing, Li plating aggregates a little and SEI growth loss is alleviated. Low temperature of 10 °C clearly slows down the ion transport and promote irreversible Li plating with the highest amount of metallic dead Li. Failure behaviours after long-term degradation under 25 °C are further analysed. The maximum temperature for the aged cell during failure is substantially reduced as each heat source decreases except for the additional heat source from the reaction between plated Li and electrolyte. Electrolyte dry-out tends to decrease the reactant concentrations for both the anode-electrolyte reaction and electrolyte decomposition, leading to reduced heat generation from those reactions. The anode-electrolyte reaction is slowed down due to the diffusion limit from the thickened SEI layer, hindering the intercalated Li from reacting with electrolyte. The additional reaction between plated Li and electrolyte preferentially initializes below 100 °C, which is responsible for the decreased self-heating and TR onset temperature. This study improves the understanding of the effects of degradation on battery safety.

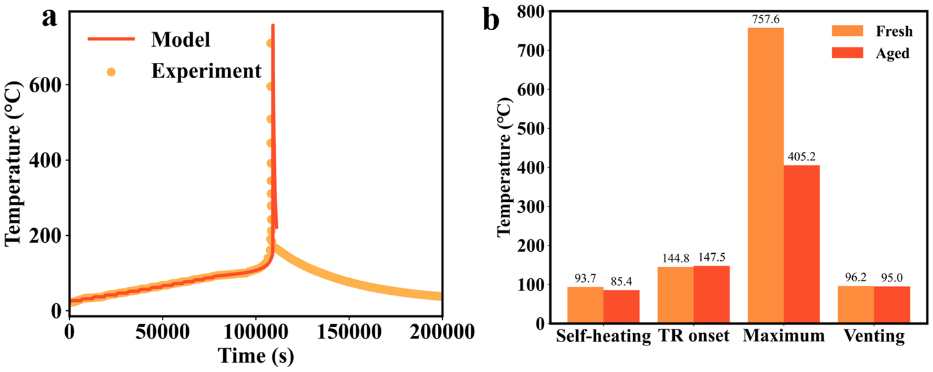


Figure 1: (a) Comparison between the model results and the ARC experimental data for a fresh cell. (b) Predicted failure characteristics of the fresh cell and the aged cell at EoL after 1170 cycles of 0.3C charge / 1C discharge under 25 °C.

References:

1. N. Kirkaldy, M. A. Samieian, G. J. Offer, M. Marinescu, Y. Patel, *ACS Appl. Energy Mater.* **5** (2022), 11, 13367-13376.

# Lithium-Ion Battery Degradation: the Missing Piece in Model Validation

Ruihe Li, Niall D. Kirkaldy, Fabian Oehler, Monica Marinescu, Gregory J. Offer, Simon E. J. O'Kane
*Department of Mechanical Engineering, Imperial College London*
*Exhibition Road, London, UK SW7 2AZ*
*s.okane@imperial.ac.uk*

Lifetime modelling is essential for the further advancement of lithium-ion batteries (LIBs), especially in transportation and energy storage. Recent years have witnessed a surge in lifetime prediction papers using physics-based, empirical, or data-driven models, most of which have been validated against the remaining capacity, sometimes with resistance or temperature. However, there are so many degradation mechanisms in LIBs that any truly comprehensive model will have at least four fitting parameters, casting doubts on models validated against only one or two metrics. Here we highlight the importance of considering degradation modes, which breaks down the degradation into loss of lithium inventory, loss of active material (one in each electrode) and impedance change, as the extra metrics. We show that three models with different levels of complexity can all fit well the remaining capacity and resistance of cells cycled at 70%~85% state of charge at three different temperatures, but only the two models with mechanisms to induce loss of active material (LAM) can fit LAM of both electrodes. Only the model with five fully coupled degradation mechanisms can fit all metrics at all temperatures. This work promotes a greater degree of consistency and rigour in validating lifetime prediction models and enhances understanding of degradation mechanisms.

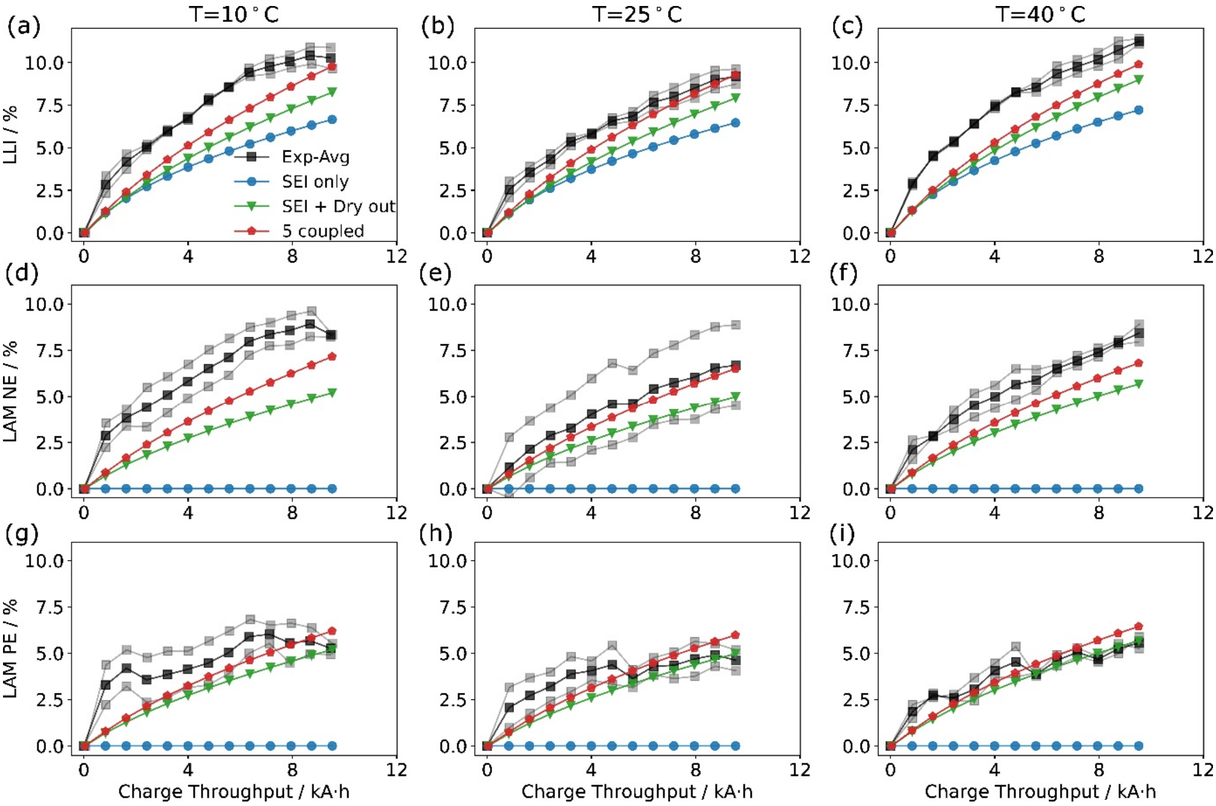


Figure 1: Degradation mode analysis of the 3 models and experiment.

Reference:
1. R. Li, N. D. Kirkaldy, F. Oehler, M. Marinescu, G. J. Offer, S. E. J. O'Kane, *arXiv* **2311** 05482 (2023) https://arxiv.org/abs/2311.05482

# A continuum model for lithium plating and dendrite formation in lithium-ion batteries: formulation and validation against experiment

Smita Sahu[1,2], Jamie M. Foster[1,2]
*[1]School of Mathematics and Physics, University of Portsmouth,*
*Lion Terrace, Portsmouth, PO1 3HF, United Kingdom*
*[2]The Faraday Institution, Quad One, Becquerel Avenue,*
*Harwell Campus, Didcot, OX11 0RA, UK*
*smita.sahu@port.ac.uk*

This work presents a novel physics-based model for lithium plating and dendrite formation in lithium-ion batteries. The formation of Li metal is an undesirable side-effect of fast charging and a primary contributor to cell degradation and failure. The model distinguishes between three types of plated Li metal, namely: (a) Li metal plated within the pores of the solid electrolyte interphase (assumed to be electronically connected to the anode and therefore recoverable); (b) dendrites protruding outside the SEI that remain electronically connected (and are therefore dangerous, potentially leading to a short circuit), and (c) electronically disconnected "dead" Li metal outside the SEI contributing to capacity fade. The model is validated against two independent experiments. First, measurements of: (i) the cell voltage and current during a constant-current-constant-voltage charge and subsequent discharge, and (ii) the Li metal intensities derived from *operando* which directly quantifies the time-resolved quantity of Li metal in the cell during use. Second, against voltage measurements during galvanostatic discharge at a range of C-rates and temperatures. Favourable agreement is demonstrated throughout; particularly in terms of the proportions of reversible and irreversible plating. We also demonstrate that the model reproduces the well-documented trends of being more prevalent at increased C-rate and/or decreased temperature.

References:

1. K. J. Sanders, A. R. Aguilera, J. R. Keffer, B. J. Balcom, I. C. Halalay and G. R. Goward, *Carbon,* (2022), **189**, 377–385.

# Interplay between charging and plating in graphite electrodes via phase-field modelling and operando optical microscopy

M. Lagnoni[1], X. Lu[2], A. Bertei[1]
[1] *Department of Civil and Industrial Engineering, University of Pisa, Largo Lucio Lazzarino 2, 56126 Pisa, Italia*
[2] *School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, GB E1 4NS-London, United Kingdom*
*marco.lagnoni@unipi.it*

Rapid charging of lithium-ion batteries within minutes poses a significant technological challenge, as it leads to notable anode degradation and accelerates battery ageing. This degradation, primarily during fast charging, is closely linked to mesoscopic electrochemical phenomena. A key problem is lithium plating, the deposition of metallic lithium on active material particles, a process promoted by phase-separation dynamics in graphite anodes.

Our study introduces a robust pseudo-2D electrochemical modelling framework [1], based on the phase field approach and non-equilibrium thermodynamics [2]. This model is validated using operando high-resolution optical microscopy to elucidate the rate-dependent spatial dynamics of phase separation, alongside lithium plating and stripping in graphite electrodes during charge and relaxation phases, respectively. Predictions from the mesoscopic model are used to corroborate the parameterisation and validate the phase field framework against both optical and electrical data, particularly under conditions of fast charging at varied current densities (2 and 4 mA cm$^{-2}$). Its application extends to observing multistage phase separation processes, inter/intra-particle lithium exchange, and dynamics of plated lithium back-intercalation. Importantly, the model provides an insight into the material, revealing the distribution of graphite's state of lithiation throughout electrode thickness and particle radius (Figure 1a). Additionally, it enables direct observation of the distribution of intercalation, plating, and stripping reaction currents across the electrode, thereby clarifying the interaction between phase separation and lithium plating-stripping dynamics (Figure 1b).

The modelling framework and its parameterisation are then implemented in 3D microstructure-resolved models, to inform the design of advanced fast charge protocols with rational rest steps to suppress plating.

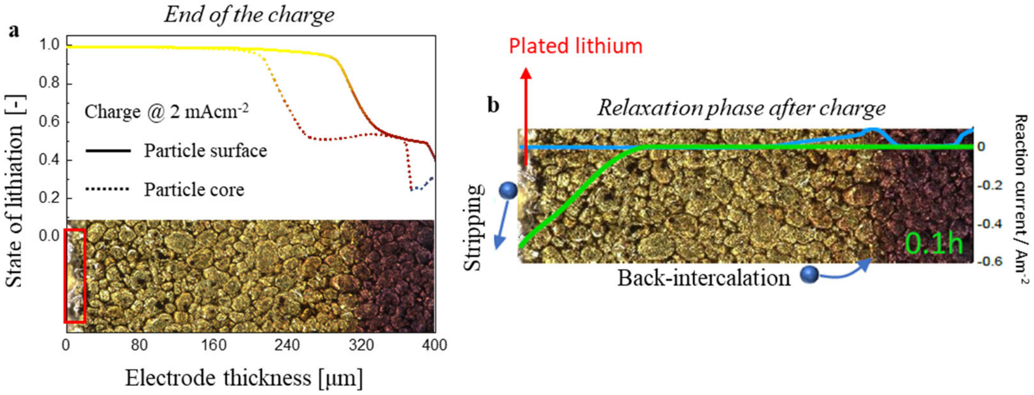


Figure 1: (a) Comparison between phase-field model simulations and operando optical microscopy data of graphite electrode during fast-charge. (b) Predicted reaction current densities during the relaxation phase after fast charging the graphite electrode.

References:
1. X. Lu, M. Lagnoni, A. Bertei et al. Multiscale Dynamics of Charging and Plating in Graphite Electrodes Coupling Operando Microscopy and Phase-field Modelling. *Nat Commun* **14**, 5127 (2023).
2. M. Bazant. Theory of Chemical Kinetics and Charge Transfer based on Nonequilibrium Thermodynamics. *Accounts of Chemical Research* **46** (5), 1144-1160 (2013).

# A complementary model-based approach with electrochemical and operando microscopy experiments to unravel Li plating in Lithium-ion batteries

Niklas Bless, Daniel Schröder
*Institute of Energy and Process Systems Engineering (InES), TU Braunschweig*
*Langer Kamp 19b, 38106 Braunschweig, Germany*
*d.schroeder@tu-braunschweig.de*

Fast charging plays a crucial role in meeting the demands of lithium-ion batteries for automotive applications. The successful implementation of electric vehicles relies on the design and development of appropriate battery cells and charging protocols. However, fast charging presents a significant challenge due to the risk of lithium plating at the anode during charging, which can lead to capacity loss, decreased performance, and safety concerns.

In this work, we propose a physico-chemical modeling approach to analyze lithium plating and fast charging strategies for lithium-ion batteries. Our approach integrates electrochemical and optical operando experiments to complement the model.

The modeling framework builds upon the commonly used Doyle-Fuller-Newman approach and extends it with a surface reaction model specifically designed to describe the nature of lithium plating. This model captures both the plating and stripping reactions as competing processes to intercalation, distinguishing between reversible and irreversible plating [1]. To validate and parameterize the model, we conduct optical operando experiments using an optical test cell and a light microscope. Alongside electrochemical measurements, these experiments provide valuable information on the reversible and irreversible plating behavior. Key aspects include the onset of lithium plating, its reversibility, plating and stripping kinetics, and the quantification of plated and stripped lithium. Furthermore, we investigate various fast charging protocols using the developed model to assess the risk of Li plating under different operating conditions.

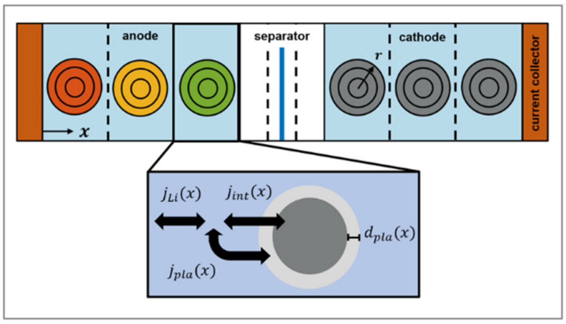


Figure 1: Schematic illustration for the applied physico-chemical model

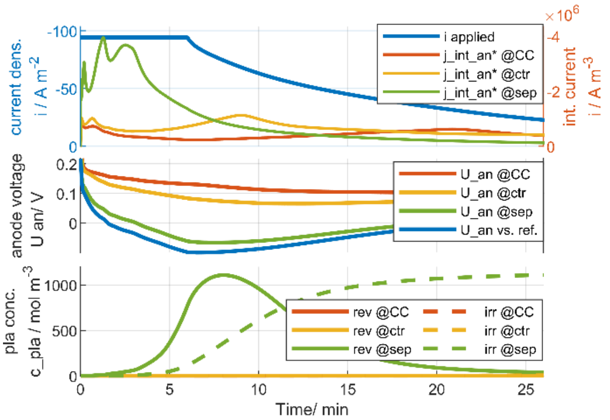


Figure 2: Simulation result for a conventional 3C CCCV charging protocol which exhibits Li plating

References:

1. S. E. J. O'Kane, W. Ai, G. Madabattula, D. Alonso-Alvarez, R. Timms, V. Sulzer, J. S. Edge, B. Wu, G. J. Offer, M. Marinescu, *Physical Chemistry Chemical Physics* 24, 2022, 7909-7922, DOI: 10.1039/D2CP00417H.

# Operando SOC and SOH diagnosis with voltage-controlled models: Application to an LFP battery pack and to smart phone batteries

Wolfgang G. Bessler[1], Jonas A. Braun[1], René Behmann[1], Daniel Chabrol[2], Frederik Fuchs[2]
[1] *Institute of Sustainable Energy Systems (INES), Offenburg University of Applied Sciences, 77652 Offenburg, Germany*
[2] *BENNING CMS Technology GmbH, 79232 March, Germany*
*wolfgang.bessler@hs-offenburg.de*

We have recently introduced a new algorithm for state of charge (SOC) and state of health (SOH) diagnosis of batteries using voltage-controlled models (VCM) [1]. The algorithm uses measured cell voltage as input to an equivalent circuit model, resulting in simulated cell SOC and current as output. By comparing the simulated current with the measured battery current, the SOH is determined. The algorithm is truly operando (working with arbitrary load profiles) and computationally efficient (no observers, filters or neural networks required).

We have applied this algorithm to individual cells in a battery pack of a 24 V class lithium-ion battery with lithium iron phosphate (LFP) chemistry [2]. The battery pack consists of eight serially-connected single cells. Is was operated for 1314 charge/discharge cycles between ca. 20 % SOC and 100 % SOC. Exemplary results are shown in Figure 1. A cell-averaged capacity loss of 9.3 % after five months cycling was observed. While the accuracy of SOC estimation was limited (6.2 SOC-% mean absolute difference compared to a Coulomb counter, probably owed to the flat voltage characteristics of LFP), SOH estimation showed a very high accuracy (1.2 SOH-% mean absolute error compared to laboratory reference tests). To the best of our knowledge, this work is the first time that single-cell SOC and SOH diagnosis was applied to a battery system with LFP cells.

We have also applied the algorithm to smart phone batteries, using real-life data of several Android devices recorded with a specifically-designed app. We present the app and show operando results from > 1 year of operation of several devices, including smart phones and tablets. The combined results underline the accuracy and flexibility of state diagnosis with voltage-controlled models.

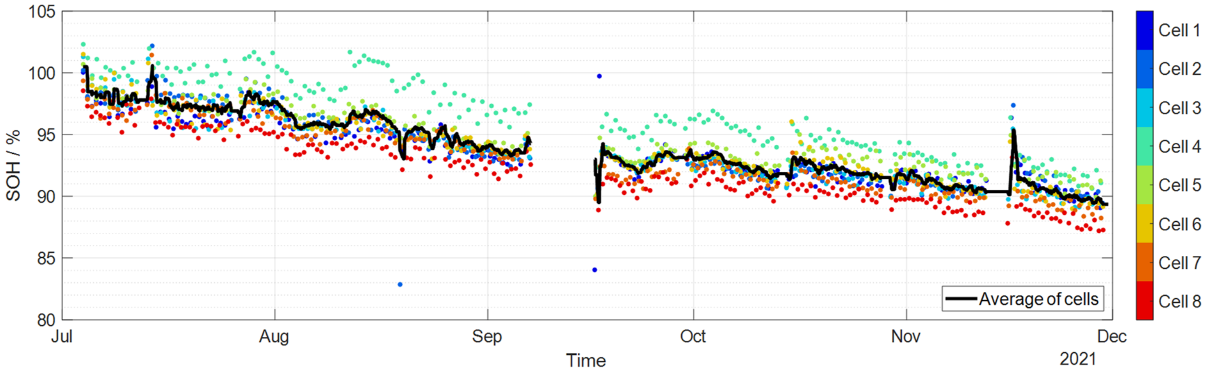


Figure 1: Single-cell operando SOH during operation of a 24 V LFP battery.

References:
1. J. A. Braun, R. Behmann, D. Schmider, W. G. Bessler, *J. Power Sources* **544** (2022), 231828
2. J. A. Braun, R. Behmann, D. Chabrol, F. Fuchs, W. G. Bessler, *J. Energy Sources*, under review (2023)

# Physics Informed Neural Network for solving Single Particle Model without using labeled data

F. J. Méndez-Corbacho, B. Larrarte-Lizarralde, R. Parra, J. Larrain, D. del Olmo, E. Ayerbe
*Materials for Energy Unit, CIDETEC, Spain.*
*Miramón 196, 20014 Donostia-San Sebastián, Spain*
*fmendez@cidetec.es*

Li-ion batteries are gaining escalating attention due to the electrification of strategic sectors. High-fidelity battery cell models have proven to be an efficient manner to study their performance and optimize its design without the expenses of experimentation. The most widely used battery models are the Doyle-Fuller-Newman Model (abbreviated as DFN or P2D), that models the evolution of the lithium concentration in the electrode particles and in the electrolyte, and its simplification, the Single Particle Model (SPM), in which the dynamic inside the electrolyte is ignored. Usually, these models are solved using classical finite element method (FEM) and finite volume method (FVM) solvers. However, the computational cost of classical solvers can be high when a large number of simulations are required. To overcome this problem and show a new approach on battery simulations, we solve the SPM in several ranges applying a novel machine learning technique, referred as Physics Informed Neural Networks (PINN) [1]. The constructed machine learning model can provide nearly instant and accurate solutions to the problem once it is trained by incorporating the electrochemical equations from SPM into the neural network architecture. Moreover, in contrast to classical data-driven machine learning approaches, there is no need to use experimental or previous simulation data in the training process. The potential of this model is shown by comparing its results with in-house and literature data for different lithium-based chemistries and various experimental conditions. The results show no performance variation while decreasing computation time 10 times compared to FEM based model.

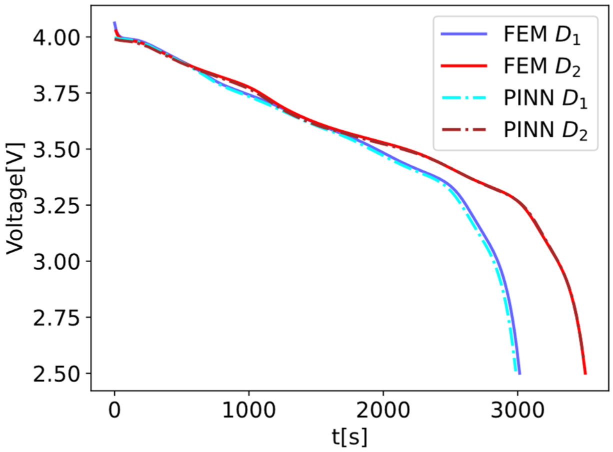


Figure 1: Comparison between two curves using FEM and PINN. The curves, at C-rate 1C, have different diffusion constants ($D_1$ and $D_2$) in the active material of the negative electrode. PINN curves were obtained 10 times faster than FEM curves.

References:
1. M. Raissi, P. Perdikaris, G. E. Karniadakis, Physics-informed neural networks: A deep learning framework for solving forward and inverse problems involving nonlinear partial differential equations. *J. Comput. Phys*. **378**, 686–707 (2019)
2. F. J. Méndez-Corbacho, B. Larrarte-Lizarralde, R. Parra, J. Larrain, D. del Olmo, E. Ayerbe. Physics Informed Neural Network for solving Single Particle Model without using labeled data. *Manuscript in preparation.*

# Modelling Dynamic Limitations of Lithium Transport in Lithium-Sulfur Batteries

M. Cornish, M. Marinescu, D. Sugunan
*Imperial College London*
*London, UK*
*m.cornish14@imperial.ac.uk*

Li-S batteries stand as a promising beyond Li-ion battery technology due to a theoretical specific energy of 2567Wh/kg and lower environmental impact. However, much research is still required to produce commercially viable cells. Within the Li-S modelling community, debate continues regarding which fundamental mechanisms cause some of the limiting behaviour of these cells.

In this talk, a common, yet unmodelled experimental phenomenon is explained first through the experimental data and then through modelling efforts. The phenomenon is a large, temporary loss in voltage during constant current discharge. This effect can be observed in several independent experimental settings, such as during low-temperature operation, under high currents, with low Electrolyte-to-Sulfur (E/S) ratios, as well as in cells with high salt concentrations. The model presented here is the first to prove to capture this effect. Moreover, several other related experimental results are presented, discussed, and predicted by the model. A fundamental explanation for why most Li-S models are unlikely to be able to capture the large voltage loss effect is also given.

The severe loss of voltage observed in experiments is then generalised to what will be referred to as the Current-Temperature Isometry: the observation that the discharge voltage curve under a constant current and constant temperature will be approximately the same as a discharge voltage curve with double the current and held at a temperature 10°C higher. Unpublished experimental evidence is provided for the Current-Temperature Isometry along with modelling results to validate the hypothesis.

The modelling efforts presented here will impact how Lithium is incorporated in the transportation and electrochemical dynamics in future Li-S modelling research. Much experimental research in Li-S is devoted to the control of nucleation and precipitation effects. However, this transport-based phenomenon requires further investigation if Li-S batteries are to be utilised in commercial settings where the E/S ratio is low, and the applied currents are large.

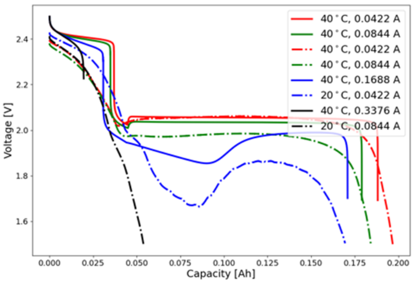


Figure 1: The simple pseudo-spatial 0D Li-S model [3] reproducing the large voltage losses observed at multiple temperatures and currents as found in [1].

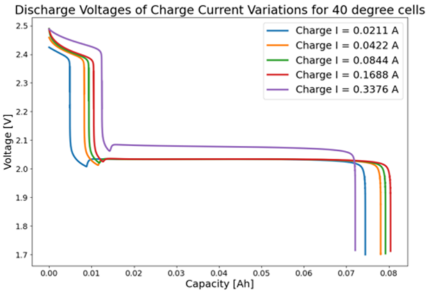


Figure 2: The simple pseudo-spatial 0D Li-S model [3] predicting the discharge capacity changes due to various charging currents as found in [2]

References:
1. Hunt, I., et al. "The effect of current inhomogeneity on the performance and degradation of Li-S batteries" Journal of The Electrochemical Society 165 (2017), 1, A6073.
2. Mikhaylik, Yuriy V., and James R. Akridge. "Polysulfide shuttle study in the Li/S battery system" Journal of The Electrochemical Society 151 (2004), 11, A1969.
3. M. Cornish, M. Marinescu, D. Sugunan, “Modelling Dynamic Limitations of Lithium Transport in Lithium Sulfur Batteries” [Submitted to arXiv]

# Application and customization of Matlab Simscape framework for P2D simulation of batteries

R. Pakuła[1,2], J. Landesfeind[1]
[1] *Department of Engineering Sciences, University of Agder, Grimstad, Norway*
[2] *Morrow Batteries ASA, Grimstad, Norway*
*rafal.pakula@uia.no*

Within the energy transition observed nowadays, batteries play a more and more important role. This proliferating increase in interest has to be met in the research, too. Alongside the laboratory experiments, simulation techniques can help in this research acceleration.

In order to fulfill their function, simulation tools should provide accurate results as well as be simple and easy to use. And although the first condition may be easy to implement in software like COMSOL, Siemens Simcenter, Python, or Matlab [1-4], simulation software is often complicated to use (especially in error handling) or requires detailed programming skills for modifications.

The Simscape library (provided by MathWorks™) offers a drag-and-drop system to represent physical configurations, making the research work much more intuitive (especially for someone without a background e.g. in informatics or modeling). In our team, this framework has been adopted for electrochemical battery simulations by creating new physical domains (e.g. electrode or electrolyte) and implementing PDEs describing the physical and chemical processes occurring in each domain [5].

As a result, the user can analyze the evolution of the parameters like reaction rate, voltages, or concentrations (in both solid electrodes and electrolyte domains). An exemplary outcome of this simulation at a high C-rate is depicted in Figure 1. For this and other charging scenarios, a benchmark with COMSOL™ will be presented to validate Simscape as an alternative and simple-in-use tool in battery research. A live demonstration of example simulations with simple modifications is planned to be shown, as well.

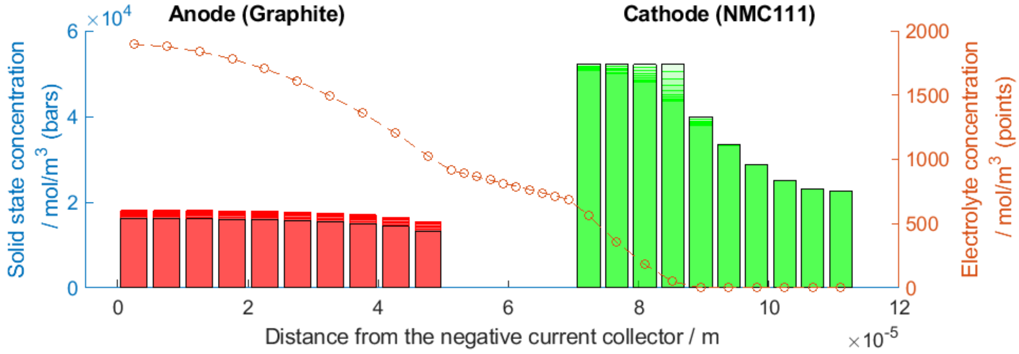


Figure 1: Concentration profiles in the electrode particles (bars) and electrolyte (points) at the end of a 4C CC-discharge (loading: 2.58 mAh/cm², particle radius: 6.3 µm (anode) and 2.13 µm (cathode), thicknesses of layers: 50.2 µm (anode) and 43.0 µm (cathode)). Bars with black frames represent the concentration on the surface of the particles. Particles as well as electrodes themselves are divided into 10 elements by applying discretization.

References:
1. V. Goel and K. Thornton, *MethodsX*, **8**, 101425 (2021).
2. L. Cai and R. E. White, *Journal of Power Sources*, **196**, 5985–5989 (2011).
3. P. X. Mai, T. T. Hai, L. H. P. Pham, and N. C. Hung, *Sustainable Development* (2022).
4. M. D. Berliner, et al., *J. Electrochem. Soc.*, **168**, 090504 (2021).
5. L. Xia et al., IFAC-PapersOnLine, 50, 2169–2174, 2017.

Acknowledgments

We would like to gratefully acknowledge the funding by the Regional Innovation Project in Agder for their financial support and collaboration with Morrow Batteries ASA on the project number ES711295 -RFFAGDER.

# Modeling of Path Dependency in Batteries

Fridolin Röder[1], Srivatsan Ramasubramanian[1], Leonard Jahn[1,2], Patrick Mößle[1,2],
Michael A. Danzer[1,2]
[1]*Bavarian Center for Battery Technology (BayBatt), University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany*
[2]*Chair of Electrical Energy Systems, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany*
*fridolin.roeder@uni-bayreuth.de*

The reliability of battery models is essential for state estimation and lifetime prediction. This can be challenging under realistic conditions when complex phenomena such as path dependency of open circuit voltage (OCV), power and rate capability, or aging are significant. The underlying mechanisms of these phenomena are different, but there are also significant similarities that are relevant for model development, parameterization, and model validation [1]. Here, we present novel modeling and simulation techniques for modeling various short-term and long-term path dependency phenomena in batteries.

In the first part, we present a novel physically motivated equivalent circuit model that allows to model the path dependency of the OCV, i.e. the voltage hysteresis, and the path dependency of the rate capability, which is shown in Figure 1a. The presented Probability Distributed Equivalent Circuit Model (PD-ECM) consists of a parallel network of resistors connected in series with a non-monotonous charge-controlled voltage source. The model provides detailed insight into the complex interplay in the network and the battery state. The model is validated using a commercial LFP cell and compared with common hysteresis models from the literature [2]. In the second part, we study the path dependency of battery aging with a model-based approach using the PyBaMM library [3]. The results show that the path dependency of aging is significantly influenced by the interaction between different degradation mechanisms, e.g. solid electrolyte interface growth and lithium plating. The effect can be seen in the simulation study as shown in Figure 1b, where cells are aged under different conditions, while the aging history clearly influences the subsequent aging behavior. Finally, we give a perspective for studying the path dependency in model and experiment.

To conclude, the presented work addresses two highly important challenges in battery modeling related to path dependency. Thereby promising novel modeling and characterization techniques are presented, which will enable better understanding and prediction of these complex phenomena.

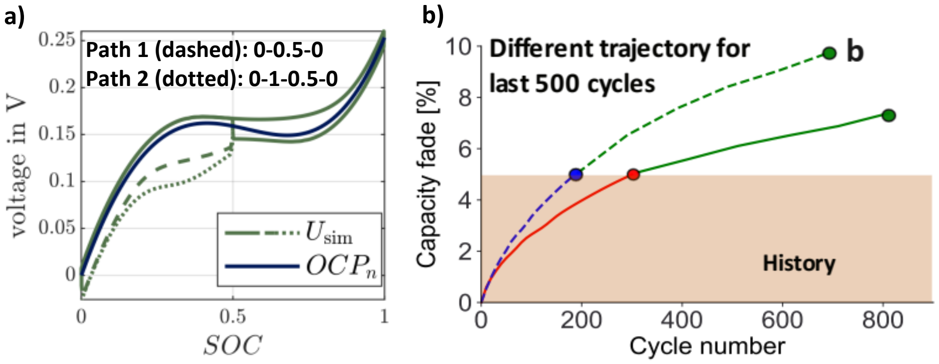


**Figure 1: a) Path dependency of rate capability modeled using the novel PD-ECM, b) simulation of path dependency of aging modeled using interacting degradation processes.**

References:
1. F. Röder, S. Ramasubramanian, Energy Technology 2022, 10, 2200627. DOI: 10.1002/ente.202200627
2. G.L. Plett, Journal of Power Sources 2004, 134, 262-276. DOI: 10.1016/j.jpowsour.2004.02.032
3. S. E. J. O'Kane et al., Physical Chemistry Chemical Physics 2022, 24 (13), 7909-7922. DOI: 10.1039/d2cp00417h.

# Abstracts for Poster Presentations

(abstract withdrawn)

# P2. The NextBMS Project: Improved Battery Models for Enhanced Utilization, Safety and Performance of Batteries

D. Dvorak, H. Kapeller
*AIT Austrian Institute of Technology GmbH*
*Giefinggasse 2, 1210 Vienna, Austria*
*dominik.dvorak@ait.ac.at*

As detailed electro-chemical battery models are usually computationally expensive, current battery management systems (BMS) mostly rely on semi-empirical battery models (e.g., equivalent circuit models) due to limited computational capabilities. However, these models are only valid in the design space where they were characterized and they cannot be used to observe internal processes of the battery. Additionally, State-of-the-Art (SotA) BMS usually use simple measurement of battery voltage, current and temperature to estimate internal battery states. Nevertheless, critical phenomena, like e.g., Li-plating or SEI-growth cannot be detected at early states using this method.

The NextBMS project [1] aims at solving these problems and heading towards optimal battery utilisation by enhancing the overall battery performances, lifetime, reliability, and safety of battery systems. This is achieved by elaborating and implementing solutions at three technical layers: (1) advanced physics-based and adaptable battery models; (2) advanced data acquisition combining sensor-based solutions at battery system/module level and model generated values; and (3) new control algorithms with advanced state estimators and data-based algorithms to increase utilisation while ensuring safety and reliability of the advanced BMS system. NextBMS develops scalable physics-based models for battery management with data transferability between detailed electro-chemical models and computationally efficient equivalent circuit models [2]. The latter features physio-chemical consistency, which means that the parameters and states have a physical meaning, to assure straight-forward utilization of the model while achieving high prediction capabilities in terms of internal battery states and aging phenomena. This approach enables to directly map the electrochemical processes, material properties and geometric parameters of the battery directly into the model topology and the model parameters (Figure 1). A combination of hardware sensors and virtual sensors (coming from the proposed models) is used to increase the amount and quality of information concerning the internal states of the battery. This allows the BMS to estimate internal states of the battery accurately and reliably, and to predict the remaining useful lifetime of batteries more accurately and detect possible failures due to internal processes (e.g., due to battery aging phenomena) earlier than it is possible with SotA solutions. Thus, the proposed solutions lead to an increase in battery utilization, safety and performance at the same time. The entire NextBMS project will be accompanied by a thorough battery testing campaign to prove the validity and performance of the proposed bundle of measures.

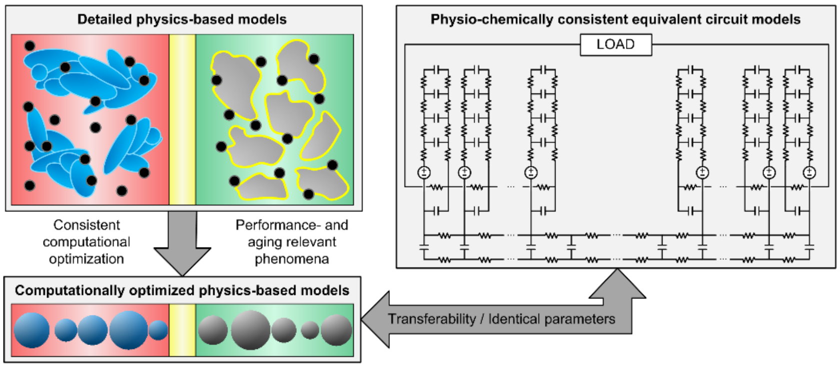


Figure 1: Schematic overview of transferability between different types of battery models [2].

References:
1. NextBMS. (2023). Retrieved from https://nextbms.eu/
2. Katrašnik, T., Mele, I., & Zelič, K. (2021). Multi-scale modelling of Lithium-ion batteries: From transport phenomena to the outbreak of thermal runaway. Energy Conversion and Management, 236(May). https://doi.org/10.1016/j.enconman.2021.114036

# P3. FEM-based Validation of Micro-Indentation to Characterize Mechanical Behaviour of Li-ion Battery Electrodes.

H. Lin[1,2], B. Lewerich[1], E. Knobbe[1], A. Latz[2,3]
*[1]Bayerische Motoren Werke AG, Petuelring 130, 80788 Munich, Germany*
*[2]Helmholtz Institute Ulm, University of Ulm, Helmholtzstraße 11, 89081 Ulm, Germany*
*[3]German Aerospace Center, Wilhelm-Runge-Straße 10, 89081 Ulm, Germany*
*Hung.Lin@bmw.de*

The pronounced swelling nature of silicon particles during battery operation has resulted in an increased interest in the mechanical behaviour of electrodes. Specifically, the homogenized model of the mechanical behaviour has become an area of high interest due to its easy integration into electrochemical-mechanical-coupled full cell simulations. The method of micro-indentation, which uses an indenter with a micrometre-scale flat tip, has gained significant popularity among researchers to assess the mechanical behaviour of electrodes to validate particle-resolved mechanical material models [1][2]. However, the one-dimensionality of this measurement technique, which is required for the development of homogenized models, remains unverified.

This study employs a Finite Element Method (FEM) to investigate geometrical requirements such as the minimum flat tip radius and the minimum distance between indentation points. The challenge in this study is to obtain a material model for the FEM-simulation, which would normally be generated based on the micro-indentation measurements. Therefore, a worst-case-scenario is used to determine the material model: a linear elastic material is employed as model for the mechanical behaviour of the electrode. Low tensional strength is a key mechanical property of electrodes due to the deformability of the particle-binder microstructure [3]. Micro-indentations are expected to exhibit reduced stress concentrations at tip edge due to binder tearing and particle rearrangement. Consequently, the stress concentration in the simulation based on linear elastic material models presents a worst-case-scenario when assessing the one-dimensionality of the measurement.

The strain energy associated with the region beneath the flat tip is compared to an ideal uniaxial-strain scenario. Additionally, the strain energy stored in the area outside the flat tip is compared to the total strain energy of the deformed sample. Based on the simulation results, the authors propose that, for a 60 µm thick electrode, an indenter tip radius of at least 200 µm and a distance between indentation points larger than 1200 µm are recommended to ensure the one-dimensionality of micro-indentation measurements. Experiments with different tip sizes are currently being conducted to validate the findings of this study.

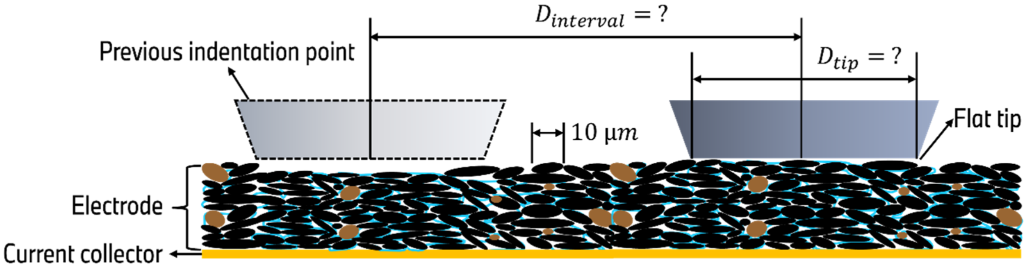


Figure 1: Graphical abstract.

References:
1. D. Schreiner, J. Lindenblatt, R. Daub, G. Reinhart, *Energy Technology*, Wiley-VCH GmbH, Weinheim, 2022
2. C. S. Giménez, B. Finke, C. Nowak, C. Schilde, A. Kwade, *Advanced Powder Technology*, Elsevier B.V., Netherlands, 2018
3. A. H. S. Iyer, P. Gupta, P. Gudmundson, A. Kulachenko, *Materials Science and Engineering: A*, Elsevier B.V., Netherlands, 2023

# P4. Probing the Instable Interface between Solid Electrolytes and High Voltage Cathodes with Operando X-ray Spectroscopy

V. Siller[1], B. Lelotte[1], C. A. F. Vaz[2], C. Jordy[3], V. Pelé[3], M. El Kazzi[1]
[1] *Electrochemistry Laboratory, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*
[2] *Swiss Light Source, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland*
[3] *Saft Groupe SAS, 92300 Levallois-Perret, France*
*valerie.siller@psi.ch*

It is well understood that instabilities at the electrode-electrolyte interface in all-solid-state Li-ion batteries are among the limiting factors for their rate performance and cycle life stability. Such instabilities originate from (i) the limited thermodynamic stability window of the solid electrolyte (SE) and its degradation byproducts and (ii) the cathode surface structural degradation resulting in chemical reactions of the transition metals (TMs). To date, monitoring of the exact surface electrochemical reaction byproducts forming upon battery operation is hindered by the difficulty of accessing the buried electrode-electrolyte interface and the instability of transient species in *post-mortem* analysis.

Motivated by the importance to understand such complex interfaces during battery performance, we have developed a platform that combines surface senisitve non-destructive complementary techniques to perform *operando* X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and X-ray photoemission electron microscopy (XPEEM). Different depth analysis capabilities of XPS and XAS at the electrode-electrolyte interface are explored, employing total electron yield (TEY) and total fluorescence yield (TFY) detection modes [1]. Additional lateral resolution is reached with XPEEM in combining localized microscopy and spectroscopy at the very surface, enabling a differentiated analysis of reaction products at various interfaces [2].

Herein we use this approach to study the interface between the argyrodite SE $Li_6PS_5Cl$ (LPSCl) and the Ni-rich layered oxide cathode $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ ($NCM_{622}$). A composite of $NCM_{622}$ and LPSCl is cycled to high cut-off potentials at 4.6 V while the dynamic changes of chemical bonds together with the corresponding onset potentials are studied in real-time at the electrode-electrolyte interface. Figure 1.a shows colour maps of the *operando* $Ni_{L\text{-}edge}$ XAS spectra in TEY and TFY upon 1st charge, which reveal the surface of the $NCM_{622}$ particles to be rich in reduced $Ni^{2+}$. In order to localize the origin of such reduced species, *operando* XPEEM is performed in Figure 1.b with the possibility to map the interface of $NCM_{622}$ with and without contact to adjacent LPSCl particles at OCP and after 1st charge to 4.6 V. XPEEM confirms increased amounts of $Ni^{2+}$ at the interface with LPSCl, which form an electrochemically inactive layer.

In conclusion, we highlight the unprecedented advantage of combining *operando* XPS, XAS and XPEEM to non-destructively probe the active material degradation mechanisms taking place at the electrified interface of LPSCl-$NCM_{622}$ at multiple depth scales, an approach that is imminently suitable for the study of battery failure more generally.

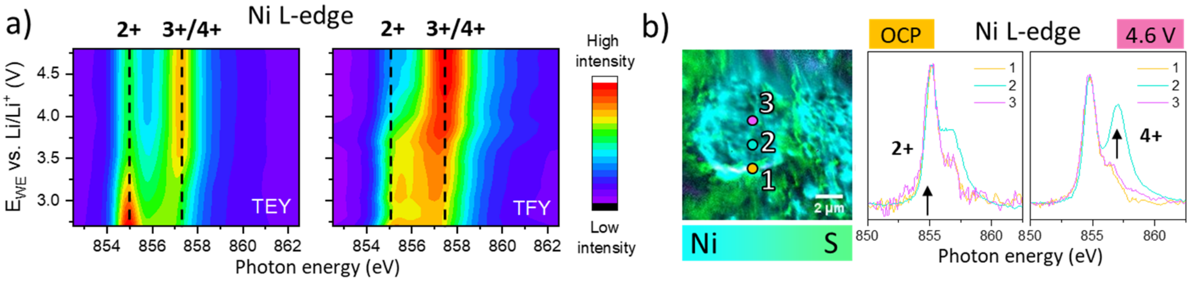


Figure 1. $NCM_{622}$-LPSCl working electrode. (a) *Operando* XAS of $Ni_{L\text{-}edge}$ and (b) *operando* XPEEM with Ni/S colour map and localized $Ni_{L\text{-}edge}$ spectra across the particle at OCP and after 1st charge.

References:
1. M. Mirolo, X. Wu, C. A. F. Vaz, P. Novák, and M. El Kazzi, *ACS Applied Materials & Interfaces* **2021** 13 (2), 2547-2557
2. M. Mirolo, D. Leanza, L. Höltschi, C. Jordy, V. Pelé, P. Novák, M. El Kazzi, and C. A. F. Vaz, *Analytical Chemistry* **2020** 92 (4), 3023-3031

(abstract withdrawn)

# P6. An Effective Model for Sodium Insertion in Hard Carbon

Huy Sy Nguyen[1, 2], Arnulf Latz[1, 2, 3]
[1]*Department of Electrochemistry, University of Ulm, Ulm, Germany*
[2]*Institute of Engineering Thermodynamic, German Aerospace Center (DLR), Ulm, Germany.*
[3]*Helmholtz Institute Ulm (HIU), Ulm, Germany.*
*huy.nguyen@dlr.de*

Sodium ion batteries (NIB) are a potential alternatively for Lithium ion batteries (LIB) because of lower cost and more abundance. As anodes, Hard Carbon (HC) seems to be the most promising candidate for NIB with advantages: stable cycling, large specific capacity, and low-cost precursors. Previous theoretical researches studied general conditions for Na insertion in HC; while experimental studies proved that the properties of Na insertion in HC depend strongly on specific properties material of HC. Our target is building an effective model which can link theoretical researches in general conditions and experimental phenomena for specific materials of HC. In our effective model, HC are treated implicitly; while Na are modelled in the confined space, created by HC. To describe the complexity of Na behaviour in HC, different types of Na with different energy level are introduced, figure 1. The results consist with experimental data; and clarify the contribution of types of Na in open circuit voltage, as well as capacity loss of Na in HC.

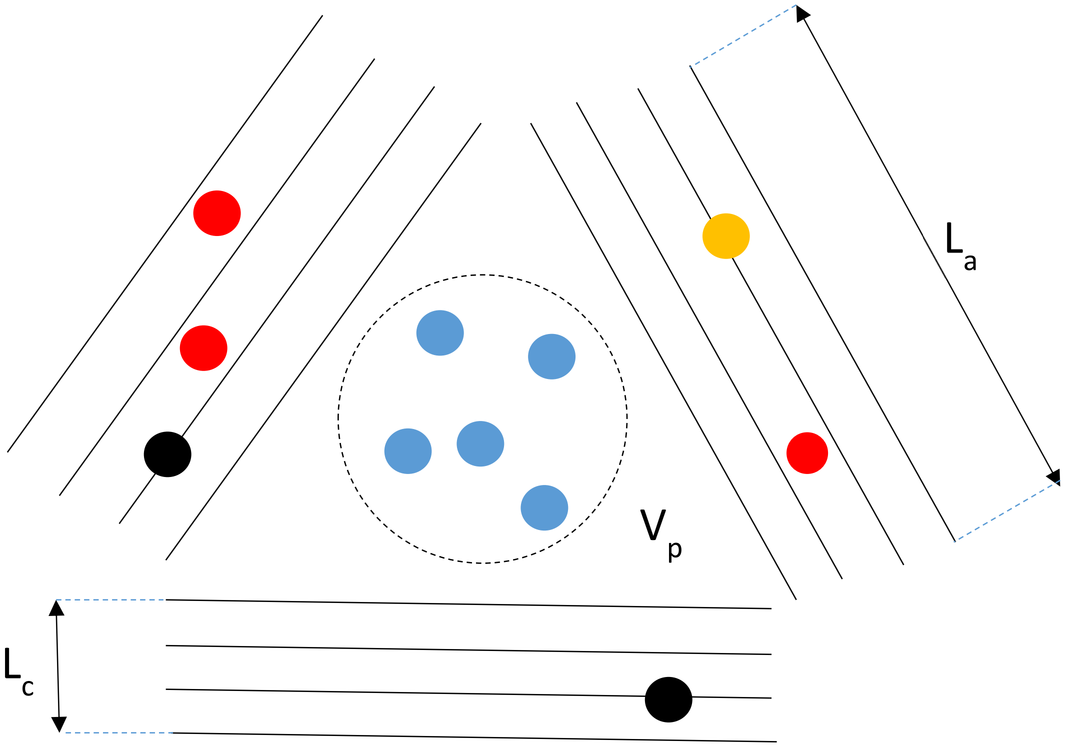


Figure 1: The schematic of effective model of Na insertion in Hard Carbons.

References:
1. H. S. Nguyen and A. Latz, *Phys. Chem. Chem. Phys.* **25** (2023), 41, 28196-28204.

# P7. From Theoretical Prediction to Real Materials: Hurdles and Opportunities

Samuel Franz Gatti[1], Andrea Testino[2], Sigita Trabesinger[1]
[1]*Battery Electrodes and Cells, Electrochemistry Laboratory, PSI, Switzerland*
[2]*Laboratory for Sustainable Energy Carriers and Processes, PSI, Switzerland*
*samuel.gatti@psi.ch*

$Na_3Fe(PO_4)(CO_3)$ was synthesized with high crystallinity employing a hydrothermal method. However, only one out of three equivalents of $Na^+$ per formular unit can be electrochemically extracted, despite the theoretical prediction of two [1]. The reported theoretical predictions were limited on thermodynamic stability of the pristine material and the electrochemical performance. In this study, a combination of GITT, *operando* XRD, Fe K-edge XAS and EIS was used to shed light on limiting factors influencing the performance of such materials.

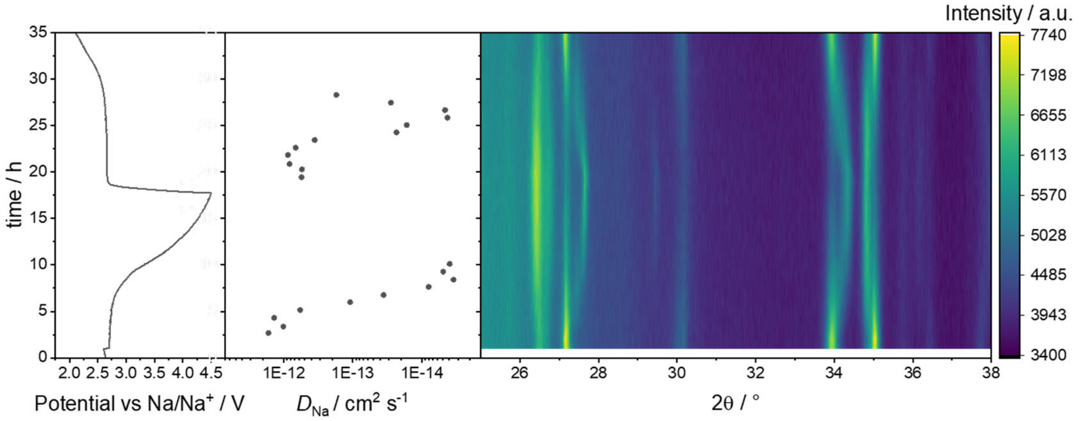


Figure 1: *Operando* XRD correlated to diffusion coefficients obtained by GITT.

EIS shows purely capacitive behavior at the end of charge, indicating blocking conditions for Na+ diffusion are reached, despite the low volume change. The combination of the results indicate a two-phase charge-compensation mechanism, whereas Na-depletion is completed faster for small particles to form desodiated $Na_2Fe(PO_4)(CO_3)$, in which sodium diffusion is blocked. This leads to a continuous drop in diffusion coefficient due to a decreasing number of active particles. Upon discharge or sodiation, the total number of particles is available once again, resulting in a high diffusion coefficient, which drops rapidly as sodiation to $Na_3Fe(PO_4)(CO_3)$ progresses. Therefore, these results give guidance for future development of this class of materials and that theoretical predictions may not just focus on prediction of stable materials, but also investigate the stability of such materials in their desodiated/delithiated states.

Reference:

1. H. Chen, G. Hautier, G. Ceder, *J. Am. Chem. Soc.* **134**(48) (2012) 19619-19627

# P8. Influence of the Testing Protocol on the Chemical Durability of Hydrocarbon Proton Exchange Membranes for Fuel Cells

Z. Han[1], T. Németh[1], M. Yandrasits[2], H. Ren[2], W. Bangay[2], L. Gubler[1]
[1]*Electrochemistry Laboratory, Paul Scherrer Institut, Villigen PSI, Switzerland.*
[2]*Johnson Matthey Technology Centre, Sonning Common, UK*
*zongyi.han@psi.ch*

With an increasing environmental concern on the use of per- and polyfluoroalkyl substances (PFAS) [1], hydrocarbon based proton exchange membranes (PEMs) for fuel cells have drawn people's interest over the past years. The chemical accelerated stressed test (AST) protocol for membranes developed by the US Department of Energy (DOE) has been widely adopted for researchers to assess their newly developed hydrocarbon PEMs. However, the DOE chemical AST protocol for membranes was developed based on the understanding of the degradation mechanism of perfluoroalkylsulfonic acid (PFSA) based PEMs, which degrade faster under lower relative humidity (RH) conditions [2]. Due to the different polymer chemistry and membrane degradation mechanisms, the DOE chemical AST protocol may not be suitable for accelerating the chemical degradation of hydrocarbon PEMs.

To design a more suitable chemical AST protocol for hydrocarbon PEMs, the effects of operating RH and cathode $O_2$ partial pressure ($p_{O2}$) were investigated in this study. A sulfonated poly(ether ether ketone) (SPEEK) membrane was selected as a representative for non-fluorinated hydrocarbon PEMs. Solution-cast membranes of ~22 µm thickness were wet-assembled in a single fuel cell (16 $cm^2$ active area) for fixed-time (4 days) open circuit voltage (OCV) holding tests at different RHs and $p_{O2}$. It was found that under 100% RH, $H_2/O_2$, the membrane failed the most quickly, i.e. within 40 hours. Fuel cell effluent water from anode and cathode exhaust was collected periodically for UV-vis and ion chromatography (IC) analysis. Hydroquinone-like degradation products were detected by UV-vis spectroscopy. Furthermore, under 100% RH, $H_2/O_2$, the degradation products showed the strongest signal in the anode effluent water. IC results of cumulative $SO_4^{2-}$ release (Figure 1, left y-axis) showed that the higher the RH (also $p_{O2}$), the more severe the degradation of the membrane. The average $SO_4^{2-}$ loss is ~100 times higher under 100% RH, $H_2/O_2$ compared to 30% RH, $H_2$/air. Post-test ion exchange capacity (IEC) measurements showed the average IEC loss rate is the highest under 100% RH, $H_2/O_2$ (~0.15 %/h), followed by 100% RH, $H_2$/air (~0.05 %/h) and 60% RH, $H_2$/air (~0.03 %/h), and the lowest under 30% RH, $H_2$/air (~0.01%/h), again indicating that 100% RH, $H_2/O_2$ could be a promising protocol to accelerate the chemical degradation of hydrocarbon PEMs for high sample throughput.

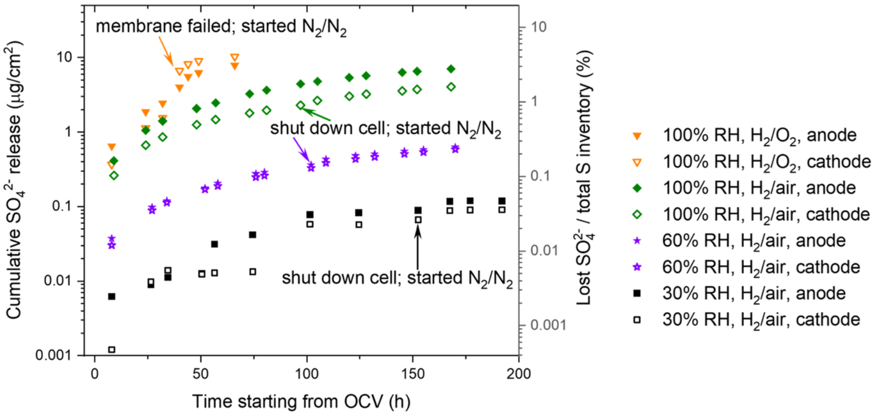


Figure 1: Left y-axis: Cumulative anode and cathode $SO_4^{2-}$ release (µg/$cm^2$) in fuel cell effluent water collected under different operating conditions. Right y-axis: $SO_4^{2-}$ loss (%) as a fraction of the total sulfur inventory.

References:
1. European Commission, Poly- and perfluoroalkyl substances (PFAS), SWD, 2020, accessed Dec. 13, 2023, https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=SWD%3A2020%3A249%3AFIN
2. F. D. Coms, H. Xu, T. McCallum, C. Mittelsteadt, *ECS Trans.* **50** (2013), 2, 907-918

# P9. Water Management in a Zero-gap $CO_2$ Electrolyzer Featuring a Bipolar Membrane in Forward Bias

M. Dessiex[1,2], R. Fischer[1], Ting-Wei Weng[2], F. N. Büchi[1], S. Haussener[2]
*[1] Electrochemistry Laboratory, Paul Scherrer Institute, Villigen PSI, Switzerland*
*[2] Laboratory of Renewable Energy Science and Engineering, EPFL, Lausanne, Switzerland*
*matthieu.dessiex@psi.ch*

The industrial-scale production of synthetic fuels and chemicals is crucial for a carbon-neutral economy. $CO_2$ electrolyzers producing CO is a key step in this effort, but the technology still suffers from durability limitations which hinders them from upscaling.

Bipolar membrane (BPM) in $CO_2$ electrolyzers solves two major issues of the state-of-the-art AEM $CO_2$ electrolyzers. The first is salt deposition in the cathode which induces flooding and leads to poor durability. The second is $CO_2$ crossover which lowers the $CO_2$ utilization.

While BPM $CO_2$ electrolyzers solve these two issues, they also suffer from low durability. It is not clear what causes this low durability. Even in the absence of salt, the cell might still suffer from inadequate water management that might cause flooding or drying of the cell. So far, the water management in BPM $CO_2$ electrolyzers has been poorly understood.

This work carefully analyzes the water management in a $CO_2$ electrolyzer featuring a BPM. The main water transport phenomena are identified and quantified by a combination of ex-situ (conductivity, uptake, diffusion) and in-situ (x-ray tomography) experiments. This set of experiments allows us to conclude the following. First, the BPM $CO_2$ electrolyzer does not suffer from flooding. It is rater under the risk of drying, especially at high current densities (> 400 mA/cm$^2$). Second, wetting the inlet $CO_2$ is insignificant compared to the water consumed in the cathode reaction. This reaction relies on other transport phenomena like diffusion from the anode. Finally, we observe and analyze over-swelling because of water recombination at the BPM junction. This set of conclusions leads to guidelines for designing the next-generation BPM, aiming to reach industrially relevant electrolysis performances.

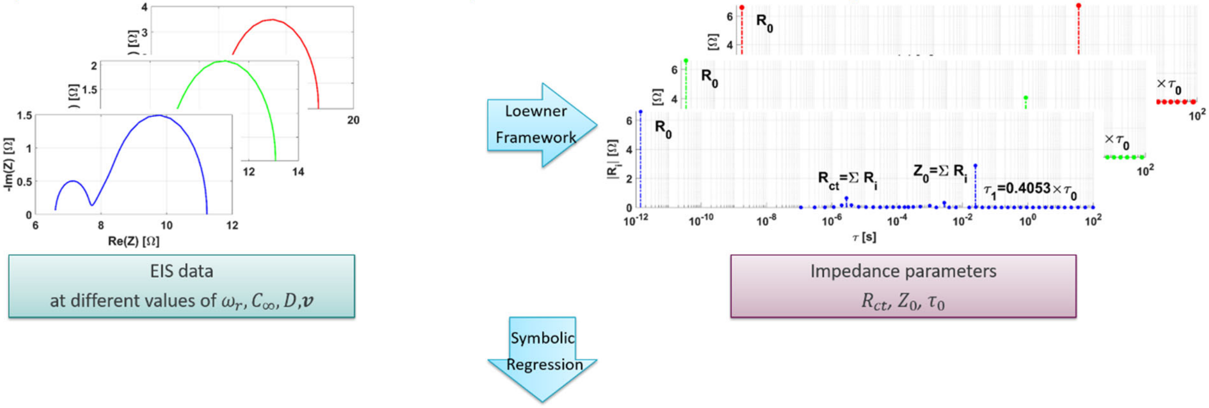
# P10. Data-driven Modeling of Electrochemical Processes through Loewner Framework and Symbolic Regression

B. Patel, A. Sorrentino, T. Vidakovic-Koch
*Max Planck Institute for Dynamics of Complex Technical Systems,*
*Sandtorstraße 1, D-39106 Magdeburg, Germany*
*patel@mpi-magdeburg.mpg.de*

We have recently introduced a data-driven methodology based on the Loewner Framework (LF), which enables the accurate calculation of the distribution of relaxation times (DRT) from electrochemical impedance spectroscopy (EIS) data [1]. Analysis of how DRT vary under different operating conditions provides valuable insight into system behaviour. However, mapping these resistances and time constants to the physics of the underlying system is often challenging.

To address this challenge, we explore the application of a symbolic regression (SR) approach to determine accurate and interpretable mathematical expressions from a DRT generated by LF. As a case study, fast electrochemical reaction in the presence of finite linear diffusion has been considered. Our research shows that the combination of LF and SR proves effective in identifying interpretable mathematical expressions that define a clear relationship between DRT and operating conditions (see Figure 1).

The results highlight the potential of the LF-SR combination to enable a deeper understanding of the dynamic behaviour of electrochemical systems, which can advance interpretation of EIS data.



$$R_{ct} = \frac{0.0023}{C_\infty}\ ; \tau_0 = 2.5921 D^{-1/3} \upsilon^{1/3} \omega_r^{-1}; Z_0 = \frac{8.574\times10^{-7}\times D^{-2/3} \upsilon^{1/6} \omega_r^{-1/2}}{C_\infty}$$

Figure 1: left – EIS spectra; right - distribution of relaxation times.

*Keywords*: Data-driven modeling, Electrochemical impedance spectroscopy (EIS), Distribution of relaxation times (DRT), Loewner framework (LF), Symbolic regression (SR).

Reference:

1. A. Sorrentino, B. Patel, I. V. Gosea, A. C. Antoulas, and T. Vidaković-Koch, "Determination of the distribution of relaxation times through Loewner framework: A direct and versatile approach", *Journal of Power Sources* **585** (2023) 233575

# P11. A Physically Motivated Voltage Hysteresis Model Using a Probability Distributed Equivalent Circuit

Leonard Jahn[1,2], Patrick Mößle[1,2], Fridolin Röder[2], Michael A. Danzer[1,2]
[1]*Chair of Electrical Energy Systems, University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany*
[2]*Bavarian Center for Battery Technology (BayBatt), University of Bayreuth, Universitätsstraße 30, 95447 Bayreuth, Germany*
*leonard.jahn@uni-bayreuth.de*

Modelling of the open-circuit voltage (OCV) is necessary for operando state-of-charge (SOC) estimation of lithium-ion batteries. However, the hysteresis of the OCV, i.e. the dependency on charge discharge history, poses a challenge and is significant for materials such as silicon or lithium iron phosphate (LFP). Numerous phenomenological models that account for the influence of the hysteresis of the OCV have been proposed to be used in a battery management system (BMS), e.g. by Plett [1] or Guenther et al. [2]. These models offer the advantage of low computational cost while maintaining sufficient precision in describing the cell's voltage curve. Unfortunately, their limitation lies in describing the underlying mechanisms of hysteresis and, therefore, they are unable to predict other related phenomena such as the path dependency of power and rate capability [3]. In contrast, mechanistic models can reflect these effects [4], but are generally unsuitable for BMS applications due to their complexity. To address this gap in literature, we propose a probability distributed equivalent circuit model (PD-ECM), that can model the hysteresis of the OCV as well as the path dependency of the power and rate capability, while maintaining computational efficiency.

Motivated by the multi-particle model for the hysteresis in materials undergoing a first order phase transition, as proposed by Dreyer et al. [5], the PD-ECM comprises a parallel network of resistors, each connected in series with a charge-controlled voltage source. The design principal of the network is shown in Figure 1a). The voltage source in each string follows a specific non-monotonous curve shown in blue in Figure 1b), resulting in the distinct hysteresis of the voltage of the overall network shown in yellow. The model shows to be capable of modelling voltage hysteresis with a transition path for partial cycles (Figure 1c)) as well as path dependent rate capability. To validate the PD-ECM, we apply it to a commercial LFP cell and compare it with the results of a hysteresis model from the literature.

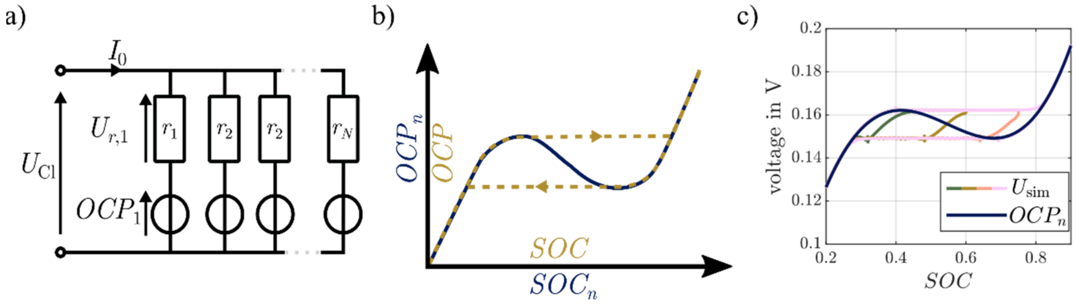


Figure 1: Design principal of the PD-ECM in a) with the underlying non-monotonous voltage curve and resulting OCP hysteresis in b) and simulation of partial cycles in c).

References:
1. G.L. Plett, Journal of Power Sources 134 (2004) 262–276 https://doi.org/10.1016/j.jpowsour.2004.02.032
2. C. Guenther, J. Klee Barillas, S. Stumpp, M.A. Danzer, 3rd IEEE PES Innovative Smart Grid Technologies Europe (ISGT Europe) (2012)
3. M.A. Roscher, J. Vetter, D.U. Sauer, Journal of Power Sources 195 (2010) 3922–3927. https://doi.org/10.1016/j.jpowsour.2009.11.143
4. H. Kondo, T. Sasaki, P. Barai, V. Srinivasan, J. Electrochem. Soc. 165 (2018) A2047-A2057 https://doi.org/10.1149/2.0181810jes
5. W. Dreyer, J. Jamnik, C. Guhlke, R. Huth, J. Moskon, M. Gaberscek, Nature Materials 9 (2010)

(abstract withdrawn)

# P13. Isotope-based Interfacial Characterization Using Operando Neutron Imaging and Online Electrochemical Mass Spectrometry

Leon Skarjan[1], Pierre Boillat[2,3], Thomas J. Schmidt[4,5], Sigita Trabesinger[1]
*[1]Battery Electrodes and Cells, Electrochemistry Laboratory, Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*
*[2]Electrochemistry Laboratory, Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*
*[3]Laboratory for Neutron Scattering and Imaging (LNS), Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*
*[4]Energy and Environment Division, Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland*
*[5]Laboratory for Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland*
*leon.skarjan@psi.ch*

Understanding and controlling interfacial processes, such as chemical and electrochemical reactions, taking place at the interface between the electrodes and the electrolyte is vital to enhancing durability and performance of next-generation batteries [1,2]. Valuable insights can be provided by operando methods, which allow to study the chemical dynamics at different scales, while charging or discharging the cell.

Within the wider framework of the OPINCHARGE project, the different phenomena occurring at the interfaces during operation will be captured by developing and validating multi-scale operando characterization techniques and combining them with computational modelling.

Our group has previously employed operando neutron imaging at SINQ to track the electrolyte-dependent plating and stripping behavior of $^6$Li metal on a copper surface [3]. By developing a novel electrochemical cell, enabling in situ electrolyte exchange, we aim to directly follow the evolution of $^6$Li in lithium metal and silicon SEI, as well as LMFP CEI, with higher spatial and temporal resolution as compared to current capabilities of Neutron imaging in battery field. Furthermore, the effect of isotope labelling specific components of the electrolyte will be investigated in Online Electrochemical Mass Spectrometry (OEMS), potentially enabling to link beneficial changes at the SEI and CEI to specific constituents of the electrolyte.

References:
1. Kristina Edström, E. Ayerbe, I. E. Castelli, I. Cekic-Laskovic, R. Dominko, A. Grimaud, T. Vegge, W. Wentzel, *Adv. Energy Mater.* 2022, 12, 2102678
2. A. Benayad, D. Diddens, A. Heuer, A. Narayanan Krishnamoorthy, M. Maiti, F. Le Cras, M. Legallais, F. Rahmanian, Y. Shin, H. Stein, M. Winter, C. Wölke, P. Yan, I. Cekic-Laskovic, *Adv. Energy Mater.* 2022, 12, 2102687
3. Winter, E., Fundamental Understanding of Critical Parameters Enabling Lithium Metal Batteries, ETH Zürich, 2023. https://doi.org/10.3929/ethz-b-000592384

# P14. Detailed 3D CFD Simulation of PEM Electrolyzers

Clemens Fink, Matija Mlakar
*AVL List GmbH*
*Hans-List-Platz 1, 8020 Graz, Austria*
*clemens.fink@avl.com*

Triggered by the huge demand for green hydrogen in the near future, there will also be a substantial need for the optimization of design and operation for all kinds of water electrolyzers (PEM, solid oxide, alkaline, anion exchange membrane). 3D CFD simulation is the method of choice when it comes to the optimization of geometry features and operating conditions. 3D CFD models for PEM *fuel cells* have been developed extensively in the past 20 years. However, similar models for PEM *electrolyzer cells*, especially regarding the two-phase flow in the porous transport layers (PTLs) and flow channels, are not yet state-of-the-art and only a few publications are available.

In this work, a detailed 3D CFD model for PEM electrolyzers based on the Eulerian multiphase approach is presented [1]. Outstanding features of the model are a 3D resolution of the catalyst layers with detailed modeling of the local two-phase flow (e.g. separate ad-/desorption between fluid and ionomer for gas and liquid) and the inclusion of surface tension effects in the flow channels. The model is tested on a PEM electrolyzer cell with a circular interdigitated anode geometry containing curved channels [2]. Figure 1 shows the distribution of the liquid water in the channels, PTLs and catalyst layers (CLs) as well as the ionic current density in the membrane.

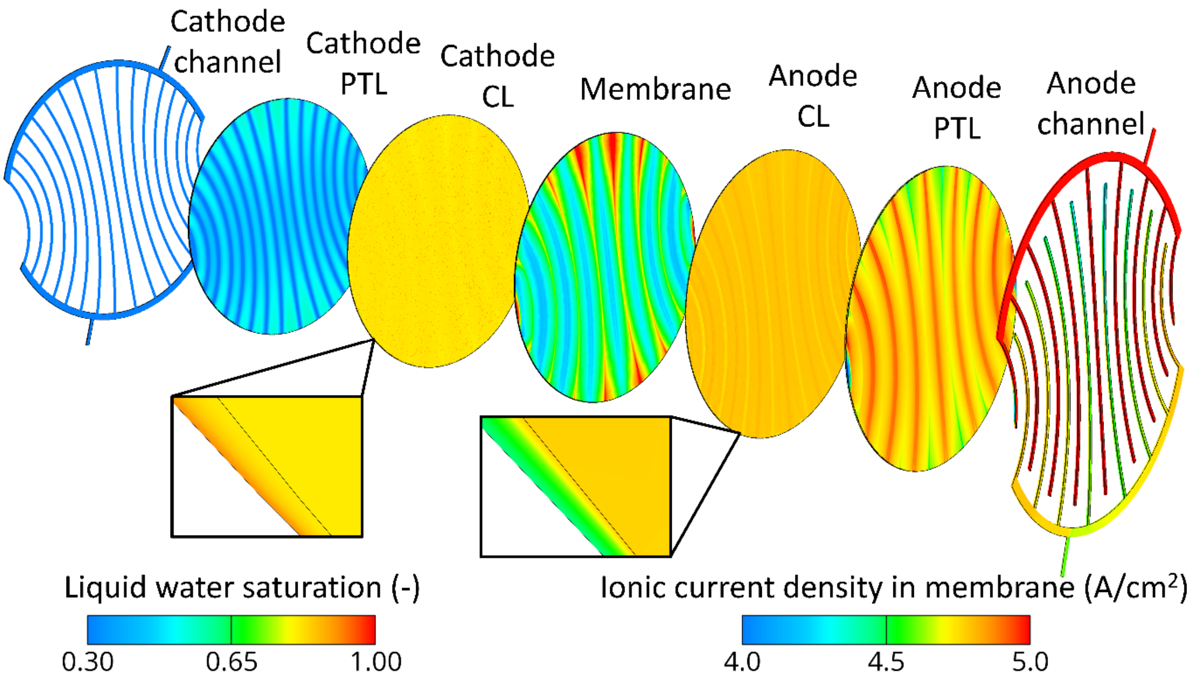


Figure 1: Liquid water saturation (channels, PTLs, CLs) and ionic current density (membrane) @ 2.9 V

References:
1. AVL List GmbH, *FIRE™ M User Manual 2023 R2*, 2023
2. A. C. Olesen, S. H. Frensch, S. K. Kær, *Electrochimica Acta* 293, 2019, 476-495

# P15. Identification of Working Fluids for Indirect Electrochemical Cooling

Lana Liebl, André Bardow, Dennis Roskosch
*Department of Mechanical and Process Engineering,*
*ETH Zurich, Tannenstrasse 3, 8092 Zurich, Switzerland*
*droskosch@ethz.ch*

As global populations and economies continue to expand, the demand for cooling worldwide is projected to triple by 2050 [1]. One promising alternative to state-of-the-art vapor-compression systems is indirect electrochemical cooling [2] (Figure 1). Here, an electrochemical reaction changes the working fluid composition and, as a result, its phase. Thereby, the compression step can be moved from the vapor to the liquid phase, substantially reducing the high compression work of standard vapor-compression cycles and increasing the overall process efficiency.

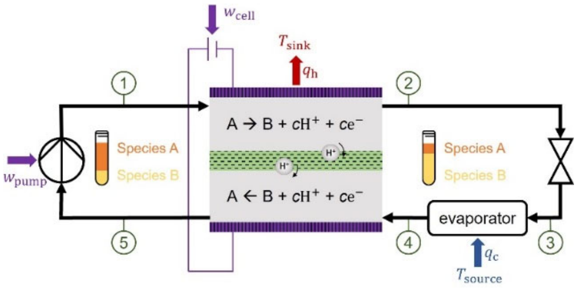


Figure 1: Electrochemical cooling process [3] adapted from James et al. [2]

While the concept of indirect electrochemical cooling is promising, suitable working fluids that undergo the desired transformation at the suitable temperature range have to be identified.

In this work, we follow a combined model-based experimental analysis to identify suitable molecule pairs as working fluids for indirect electrochemical cooling. In the first step, we develop an equilibrium-based thermodynamic process model and evaluate the electrochemical cooling process's performance for various molecule pairs [3]. To that end, we screen an extensive database of potential molecule pairs that could undergo a proton exchange reaction. Employing the 606 feasible molecule pairs found in the screening, we optimize the efficiency of the process. We identify 35 promising molecule pairs that yield up to 100% higher efficiencies than classical vapor-compression systems.

Consequently, electrochemical cooling seems to be a promising alternative to vapor-compression systems. However, the cell model is simplified to enable an extensive screening and does not account for ohmic or kinetic overpotentials in the electrochemical cell. These simplifications strongly impact the process performance. Further, the electrochemical reactions in the two half-cells should be reversible and without side products. Thus, comparing the model results to experimental data is crucial for evaluating the potential of electrochemical cooling and selecting suitable molecule pairs.

Therefore, the second step of our work focuses on experimentally investigating the electrochemical reaction of the selected molecule pairs. Hence, we conduct cyclovoltammetry measurements to examine the relationship between the current and voltage of the electrochemical reactions. These experiments show the electrochemical reaction's selectivity and the cell work needed to achieve a desired reaction rate. Subsequently, we use Raman spectroscopy to identify the products and their concentration after the electrochemical reaction.

The combined model-based experimental analysis thus provides an efficient step-wise approach to identify promising molecule pairs as working fluids for indirect electrochemical cooling.

References:

1. United Nations Environment Programme (UNEP), Kigali Cooling Efficiency Program, Cooling in a Warming World, (2019). https://www.ccacoalition.org/en/resources/cooling-warming-world.
2. N.A. James, J.E. Braun, E.A. Groll, The chemical looping heat pump: Thermodynamic modeling, International Journal of Refrigeration 98 (2019) 302–310.
3. L. Liebl, A. Bardow, D. Roskosch, Indirect Electrochemical Cooling: Model-Based Performance Analysis and Working Fluid Selection, Ind. Eng. Chem. Res. (2024).

# P16. Zero Dimensional Models for SEI Formation in Lithium-ion Battery

Kawa Manmi, Ferran Brosa Planella
*Mathematics Institute, University of Warwick*
*Gibbet Hill Road, Coventry, CV4 7AL, United Kingdom*
*kawa.manmi@warwick.ac.uk*

The solid electrolyte interphase (SEI) is a critical yet poorly understood component in Li-ion batteries. Zero-dimensional models are a common physics-based approach to modelling SEI growth while remaining computationally simple, and various models have been proposed in the literature [1-3]. However, to the best of our knowledge, none of them has been successfully applied and validated to describe SEI growth during the formation cycle, the very first cycle after the battery is assembled, where the capacity fade is much larger than in the subsequent cycles.

In this work, we compare the behaviour of the most common SEI growth models in the literature for the formation cycle and the subsequent ones and we examine the impact of the various parameters and formation conditions. Figure 1 shows the increase in SEI thickness per cycle for a fresh battery and a formed battery, with initial SEI thicknesses of 1e-15 and 5e-9 nm, respectively. We use a C/10 and with the SEI models in [1], [2], [4]. We observe that only a few models show significant contribution to the SEI during formation, as the growth of SEI decreases significantly in the second cycles. Furthermore, these models also exhibit different behaviour in fresh and formed batteries. This is preliminary work towards gaining deeper insight into the complex physicochemical processes governing SEI evolution in the formation cycle.

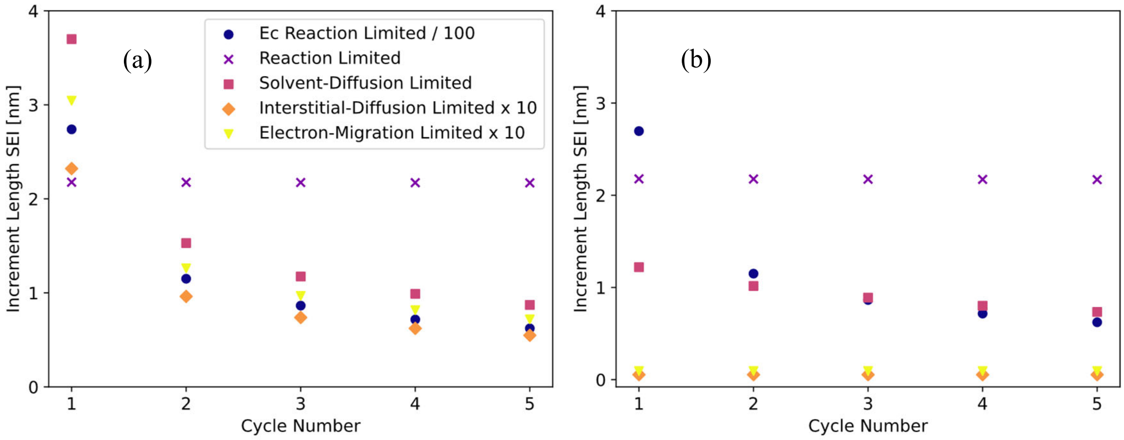


Figure 1: Increase in SEI thickness per cycle for (a) a fresh battery and (b) a formed battery, simulated using the Chen2020 parameter set in PyBaMM [5].

References:

1. X.-G. Yang, Y. Leng, G. Zhang, S. Ge, and W. Chao-Yang, ‘Modeling of lithium plating induced aging of lithium-ion batteries: Transition from linear to nonlinear aging’, *Journal of Power Sources*, vol. 360, pp. 28–40, Aug. 2017, doi: 10.1016/j.jpowsour.2017.05.110.
2. M. Tang, S. Lu, and J. Newman, ‘Experimental and Theoretical Investigation of Solid-Electrolyte-Interphase Formation Mechanisms on Glassy Carbon’, *J. Electrochem. Soc.*, vol. 159, no. 11, pp. A1775–A1785, 2012, doi: 10.1149/2.025211jes.
3. F. Single, A. Latz, and B. Horstmann, ‘Identifying the Mechanism of Continued Growth of the Solid–Electrolyte Interphase’, *ChemSusChem*, vol. 11, no. 12, pp. 1950–1955, Jun. 2018, doi: 10.1002/cssc.201800077.
4. S. G. Marquis, ‘Long-Term Degradation of Lithium-ion Batteries’.
5. V. Sulzer, S. G. Marquis, R. Timms, M. Robinson, and S. J. Chapman, ‘Python Battery Mathematical Modelling (PyBaMM)’, *JORS*, vol. 9, no. 1, p. 14, Jun. 2021, doi: 10.5334/jors.309.

# P17. Analysis of Crucial Effective Transport Parameters of Lithium-ion Batteries within Simulation Studies Based on Impedance Spectroscopy

R. Mühlpfort, L. Pfeifer, A. Heß, Th. Wetzel, P. Seegert
*Karlsruhe Institute of Technology (KIT), Institute of Thermal Process Engineering (TVT), Heat and Mass Transfer, 76131 Karlsruhe, Germany*
*Kaiserstraße 12, 76131 Karlsruhe, Germany*
*raphael.muehlpfort@kit.edu*

The performance and aging behavior of a lithium-ion battery (LIB) are strongly influenced by inner multiphysical processes as well as outer influence factors like the thermal boundary conditions. A valuable and established tool to describe and gain a better understanding of the cell behavior is modeling using equivalent circuit models (ECM). For a deeper understanding and more detailed insights into the processes taking place inside the cell, physically based models, resolving the complex interaction of charge, heat and mass transfer as well as the electrochemical reaction by physical equations (such as Fick's law and Nernst-Einstein-Equation) are needed. An equally well-established characterization method, that can provide experimental data on impedance as a representation of the integral multiphysical behavior of the cell is Electrochemical Impedance Spectroscopy (EIS). At the same time EIS allows to resolve the individual processes taking place inside the cell according to their time constants.

In this work, we combine model-based prediction of impedance spectra with experimentally determined ones to systematically identify the underlying physical parameters and evaluate their importance. The model consists of a combination of an equivalent circuit and a physical pseudo-2D (p2D) model according to Doyle-Fuller-Newman (DFN) and was implemented in COMSOL Multiphysics. This inverse-parameterization approach can be accelerated significantly by adding least square optimization tools, fitting the simulated impedance spectra to an experimental data set by automatically optimizing the values of the physical parameters.

A challenging task by applying a DFN modeling approach combined with an optimization algorithm is to identify the value range of the crucial effective parameters for mass and charge transport, which are influenced by the microstructure of the electrodes. Based on previous work on the sensitivity influence of each model parameter and the usage of an established heterogeneous 3D microstructure model, the range of the effective transport parameters was narrowed down in the following way: a 3D microstructure based on spherical and non-spherical particles is being generated with a drop and roll-algorithm, in which the particle size can be adjusted to replicate the particle distribution of real battery electrodes. The developed microstructure simulation model is then applied on these microstructures to analyze the impedance and voltage behavior as well as to derive crucial effective transport parameters like the tortuosity of the porous electrode. In this contribution the results of variations of the microstructural parameters like particle shape and size distribution are shown and the transfer from a heterogeneous 3D microstructure to a homogenized p2D model are evaluated.

# P18. Investigation of Different Liquid Electrolyte Systems with Lithium Metal Anodes and Their Influence on the Performance and Stability

L. Pfeifer, R. Mühlpfort, A. Heß, Th. Wetzel, P. Seegert
*Karlsruhe Institute of Technology (KIT), Institute of Thermal Process Engineering (TVT), Heat and Mass Transfer, 76131 Karlsruhe, Germany*
*Kaiserstraße 12, 76131 Karlsruhe, Germany*
*leonie.pfeifer@kit.edu*

The use of lithium metal as an anode material offers the potential of a higher energy density compared to standard graphite intercalation anodes and is therefore an interesting option for future batteries. When using lithium metal with standard liquid electrolyte systems from state-of-the-art lithium-ion batteries, a decreased performance and stability is observed, caused by strong SEI formation and dendrite-growth. Both, growth of SEI and of lithium dendrites as well as additional changes of the morphology of the lithium surface have a crucial influence on the voltage and impedance behavior the battery cell. The growth of Li-dendrites may even lead to short circuits and thus to failure of the battery. Accordingly, it is important to investigate and gain understanding of these impact factors to ensure safe and efficient operation of batteries based on lithium metal anodes.

For the characterization of the mentioned effects and influences, electrochemical impedance spectroscopy (EIS) is a reliable and well-established method. It facilitates distinguishing different physical processes within the battery based on their frequency ranges. Through the use of experimental cells, it is possible to extend the detail of the analysis down to the half-cell level. The experimental cells also enable analysis of symmetric cells made up of two lithium metal anodes, excluding distortion of the results by intercalation cathode effects.

In this contribution, we will present the results of an experimental study for lithium metal anodes with different liquid electrolyte systems and different anode materials. A total of six different electrolytes were investigated, following different variations, like for example different solvents or conductive additives. The chosen setup for the voltage and impedance investigations is a symmetrical setup to reduce the influence of the cathode material. In addition to the characteristics of pristine cells, the cycle stability as well as the impact of different current profiles were investigated. The results of the various material configurations are compared over the entire characterization process in order to get a general understanding of the results and the underlying processes.

# P19. Mechanical Stress-field in Pouch Cells due to Lithium-induced Swelling and Gas Formation

A. Giudici [1], C. Please[1], J. Chapman[1],
[1] *Mathematical Institute, University of Oxford, Woodstock Road, Oxford OX2 6GG, UK.*
andrea.giudici@maths.ox.ac.uk

The flow of lithium ions from cathode to anode during a charge-cycle causes swelling in the anode. In general, the amount of swelling depends on the chemistry and the materials used for the electrodes, with strains of the order of 6% being reported for pouch cells [1]. The anode swells in-homogenously, but it is attached to a stiff current collector that constrains its deformation, leading to a complex state of residual stress. This stress-state is believed to couple with the electrochemistry, potentially hindering the efficiency of the battery and contributing to the long-term degradation. Here, we propose a reduced order mechanical model for a pouch cell to capture the complex stress distribution in the electrodes as well as the tension in the current collectors. We compare our 2D model to full 3D Finite Element simulations with good agreement. Finally, we consider the mechanical effects of swelling due to gas formation which can cause bulging of a pouch cell, as observed via X-ray tomography [2]. We propose a simple model to understand the mechanics of the deformation and the associated stress, offering an alternative way to measure the pressure build-up in a pouch cell and its mechanical degradation.

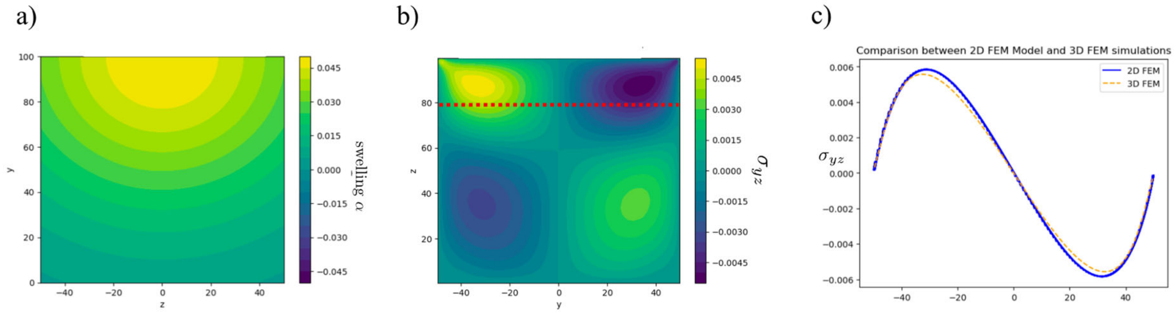


Figure 1: (a) An example of a swelling field and (b) its associated shear stress at the interface between electrode and current collector. (c) Comparison of the shear stress predicted by the reduced 2D model and the full 3D finite element simulations.

References:
1. Leung, P.K., Moreno, C., Masters, I., Hazra, S., Conde, B., Mohamed, M.R., Dashwood, R.J. and Bhagat, R., “Real-time displacement and strain mappings of lithium-ion batteries using three-dimensional digital image correlation”, Journal of Power Sources 271 (2014) 82-86.
2. Du, W., Owen, R.E., Jnawali, A., Neville, T.P., Iacoviello, F., Zhang, Z., Liatard, S., Brett, D.J. and Shearing, P.R., “In-situ X-ray tomographic imaging study of gas and structural evolution in a commercial Li-ion pouch cell”, Journal of Power Sources 520 (2022) 230818.

# P20. Strategic Approach for the Characterization of NCM Cathodes - Determining Kinetics, Transport and Thermodynamics

M. Fath[1,2], C. Drechsler[1], B. Berkes[1], P. Heidebrecht[1], M. Kamlah[2]
*[1]BASF SE, Center of Expertise, Reaction Engineering, Ludwigshafen, Germany*
*[2]Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany*
*maximilian.fath@basf.com*

A variety of parametrization procedures for insertion batteries have been published, with results varying widely between different methods. However, even when utilizing the same method for established materials, both qualitative and quantitative deviations are reported. This is shown by an investigation into the Li-ion diffusion coefficient via the galvanostatic intermittent titration technique [1,2].
Similar variations can be observed for kinetics, ohmic resistances and open circuit voltage. This results in lacking applicability and transferability, and singular parameters cannot be compared due varying boundary conditions. In parts, this is caused by an overlay of multiple effects that are lumped into combined parameters, due to the application of common analytical methods to modern batteries.
This lack of comparability results in a significant challenge for the development of new batteries, as quantifying the effect of battery modifications is crucial for further development.
To improve the reproducibility and applicability of data, a multi-step approach for cell parametrization is proposed. The main component is an optimized GITT-Procedure (exemplarily shown in Figure 1), with current and relaxation phases designed in respect to the distribution of active particle sizes. Furthermore, EIS measurements are used to decouple ohmic and kinetic overpotentials. Lastly, multiple low C-rate tests are utilized to extrapolate the open circuit potential. The measurements are checked against the established Doyle-Fuller-Newman model [3], including an extension for the interaction of particles of different sizes [4]. As each method can provide insights into different cell properties, a combined approach allows to deconvolute lumped parameters and to elucidate the limitations of each method.
Initial results show that this approach significantly reduces the variance of parameter estimates. This allows to properly reflect trends between modified cathodes materials, thus providing a tool for the quantification of CAM or electrode development.

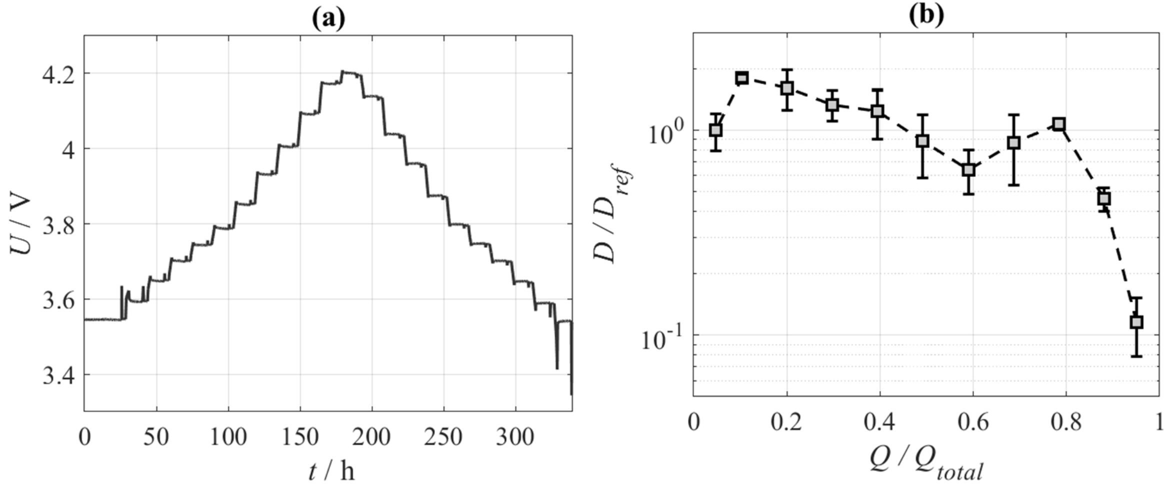


Figure 1: (a) Optimized GITT procedure for charge and discharge. (b) Li-Ion diffusion coefficient in high-Ni NCM over the operational range of the cathode.

References:
1. W. Weppner, R.A. Huggins, *J. Electrochem. Soc.* **124** (1977), 1569
2. S.D. Kang, W.C. Chueh, *J. Electrochem. Soc.* **168** (2021), 120504
3. M. Doyle, T.F. Fuller, J. Newman, *J. Electrochem. Soc.* **140** (1993), 1526
4. M. Ender, *J. Power Sources* **282** (2015), 572-580

# P21. Identification and Parametrization of SEI Growth Models for Various Electrolyte Compositions Using Differential Voltage Analysis

Felix Schomburg, Alexander Schmidt, Fridolin Röder
*Bavarian Center for Battery Technology (BayBatt), University of Bayreuth*
*Weiherstr. 26, 95448 Bayreuth, Germany*
*fridolin.roeder@uni-bayreuth.de*

The cell formation is the final production step in Lithium-ion battery manufacturing. It contributes greatly to the overall cell cost and impacts the cell performance metrics, i.e. safety, ageing behaviour, and fast charging capability [1]. The process step usually comprises multiple charging cycles, during which the majority of the Solid-Electrolyte-Interphase (SEI) is built. The formation process is influenced by the cell design, e.g. electrolyte composition and electrode structure, as well as process parameters, e.g. formation protocol and temperature. These manifold influencing factors make a comprehensive understanding of the formation process difficult [1]. The fragility of the SEI further complicates the generation of a holistic knowledge through purely experimental investigations. It is suggested to utilize mechanistic models combined with novel characterisation methods with low experimental effort to depict key properties of the formation process. Ultimately, this enables a material-tailored design of the process and reduced development cost.

Herein, we first present a method to parametrize continuous SEI growth models. The differential voltage analysis (DVA) based method determines distinct peaks, i.e. feature, in the derivative of the negative electrode potential curves during formation and a reference [2]. Due to the SEI growth, the feature shift during formation in comparison to the reference, which allows the deduction of the loss of lithium inventory $Q_{\mathrm{LLI}}$ as a function of formation time. The method is summarised in Figure 1A. In Figure 1B the $Q_{\mathrm{LLI}}$ curves for three electrolyte compositions are shown. While a qualitatively similar growth curve can be seen, also noticeable electrolyte-specific differences can be observed. The determined points can further be used to parametrise SEI growth models by applying simplifying assumptions. By this also limitations and the validity of the SEI growth models can be tested. The parameterised SEI growth models can further be used to simulate additional influencing factors. In case of the formation protocol, the extrapolation of the $Q_{\mathrm{LLI}}$ showed a good agreement between simulations and experimental data when a "near-shore aggregation" growth mechanism [3] is considered.

In summary, a novel parametrization workflow with low experimental effort for SEI growth models is shown. The use of the method is demonstrated using an electrolyte variation and revealed electrolyte-dependent differences in the growth curves. Lastly, the determined SEI growth models were used to extrapolate the SEI growth for other formation protocols.

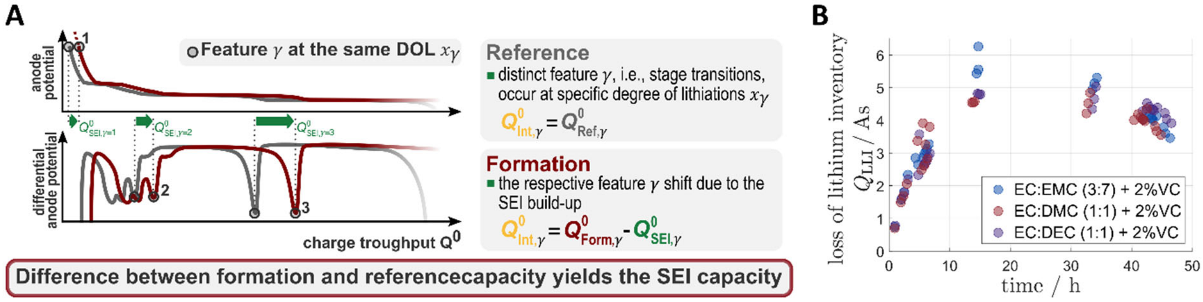


Figure 1: (A) Schematic of the differential voltage analysis method to determine the capacity loss due to lost lithium inventory during formation. (B) $Q_{\mathrm{LLI}}$ as a function of formation time for three electrolytes.

References:
1. S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, D. L. Wood, *Carbon* **105** (2016), 52-76
2. F. Schomburg, R. Drees, M. Kurrat, M. A. Danzer, F. Röder, *Energy Technol.* **11** (2023), 5, 2200688
3. K. Ushirogata, K. Sodeyama, Z. Futera, Tateyama, Yoshitaka; Okuno, Yukihiro, *J. Electrochem. Soc.* **162** (2015), 14, A2670-A2678

# P22. Influence of Intra-particle Concentration Gradients and Lithium Plating on the Thickness Change of a Lithium-ion Pouch Cell

David Schmider, Wolfgang G. Bessler
*Offenburg University of Applied Sciences, Institute of Sustainable Energy Systems*
*77652 Offenburg, Germany*
*david.schmider@hs-offenburg.de*

The behavior of lithium-ion batteries is governed by complex and nonlinear thermal, electrochemical and mechanical interactions. With our recently-published pseudo-three-dimensional (P3D) thermo-electro-mechanical model, we are able to describe these interactions for a commercial small-format (350 mAh) lithium-ion pouch cell with graphite negative electrode and lithium nickel cobalt aluminum oxide / lithium cobalt oxide blend positive electrode [1].

To capture the nonlinear intercalation-induced thickness change of the active materials, we parametrized the model with nonlinear molar volume data as a function of lithium stoichiometry, available from literature. Effective thermal properties of the cell were determined experimentally. Thorough validation of the model shows good performance throughout a broad operating range from 0.05 C to 10 C. Despite the overall good performance, we observed some discrepancies between experimental and simulated data. While a rate-dependent shift to higher displacements towards the end of charge is evident in the experimental data at elevated currents, the model considering only intercalation- and temperature-induced swelling cannot describe this behavior (cf. Figure 1a and 1b).

Here we show that this discrepancy can be attributed to two additional effects. Intra-particle lithium concentration gradients that arise at higher currents, in combination with nonlinear molar volumes, cause an additional nonlinearity in particle expansion. Instead of calculating the molar volume based on a particle-averaged lithium stoichiometry, locally-resolved molar volumes need to be used. Additionally, we have added reversible and irreversible lithium plating reactions, as the deposited lithium layer further contributes to the thickness change (cf. Figure 1c).

The multiphysics model thus allows to decompose the macroscopic thickness changes into individual contributions, resulting in the identification of different regimes. At lower currents the displacement is predominantly governed by intercalation-induced thickness change of the active materials. Already at C-rates above 1C intra-particular concentration gradients contribute to nonlinear swelling. Above 5C there is increased thermal expansion. Lithium plating also sets in above 5C. The improved insight gained by identifying these different regimes can help in preventing detrimental operating conditions.

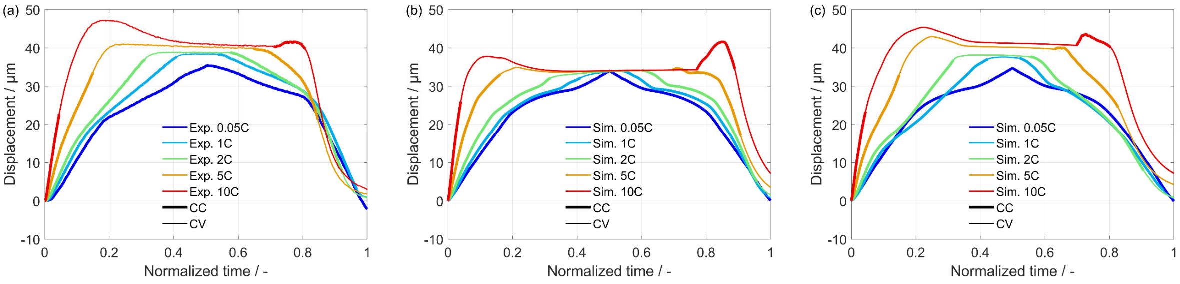


Figure 1: Comparison of experimental thickness change (a), model with intercalation- and temperature-induced swelling [1] (b) and model with additional intra-particle concentration gradients and lithium plating (c).

Reference:

1. D. Schmider, W.G. Bessler, *Batteries* **9** (2023), 7, 354

# P23. The XL-Connect Project: Quantitative Parametric Models for Assessing the Influence of V2X on Battery Degradation in Electric Vehicles

H. Kapeller, D. Dvorak
*AIT Austrian Institute of Technology GmbH*
*Giefinggasse 2, 1210 Vienna, Austria*
*hansjoerg.kapeller@ait.ac.at*

Currently there is no consensus in the literature about the impact of smart charging and V2X strategies on EV battery degradation and common battery models cannot help clarifying the issue since there is a lack of comprehensive battery degradation models that can accurately provide an exact battery ageing assessment under V2X scenarios. A deeper understanding of the degradation mechanisms caused by V2X operations is therefore needed because the lifespan and performance of EV batteries are affected by various factors such as high-power cycles, frequency of charge/discharge cycles, and operating temperatures.

To overcome this lack the XL-Connect [1] project deals with the development and implementation of quantitative parametric models for assessing the influence of V2X on battery degradation in EVs. The investigation of various smart charging and V2X scenarios is made possible by the setup of a comprehensive EV model consisting of several subcomponent models to simulate the EV behaviour and the occurring effects on the EV battery during smart charging. The physics orientated EV model developed in the description language Modelica includes a parametric electro-thermal battery model and considers beside the Heating, Ventilation and Air Conditioning system (as main auxiliary of the EV) all driving resistances of the vehicle. The parametric electro-thermal battery model (Figure 1, left) can be structured in an electric part (V), in a thermal part (T) and in a parameter adaption part (P). The electric model (V) is used to map the dynamic material characteristics from the battery to an electric equivalent circuit. The thermal model (T) is used to consider thermal aspects during operation whereas the parameter adaption block (P) calculates the electric, thermal and aging dependencies based on an Arrhenius equation [2] of the internal battery parameters.

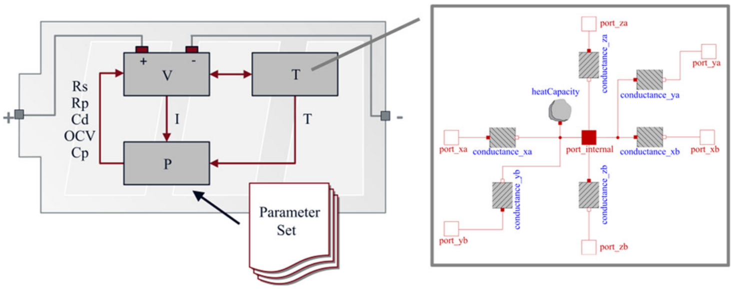


Figure 1: Modular concept of the battery model (left) and thermal model of a prismatic cell (right).

With the implementation of these quantitative parametric models the influence of V2X on the aging rate of a battery system in an EV can be investigated. The battery stack is attached to a cell thermal model (Figure 1, right) fed with variable outside temperatures (e.g., temperature cycle over time). Either the driving current of the EV and the current from a V2X application is withdrawn from the battery or the battery is charged (advanced V2X bidirectional charging). The V2X functionality can be optionally disabled to demonstrate the influence of V2X on the aging rate of the battery. Due to an increased load current withdrawn from the battery the cycling of the battery is higher than without V2X. Hence, studying the influence of V2X on battery degradation in EVs is possible. The cycle-aging has an individual impact on the battery, i.e., the battery capacity decreases, and the internal resistance increases correspondingly.

References:

3. Xl-Connect. (2023). Retrieved from https://xlconnect.eu/
4. D. Dvorak, H. Popp, T. Bäuml, D. Simic, and H. Kapeller, 'Arrhenius-Equation Based Approach for Modelling Lithium-Ion Battery Aging Effects', Oct. 2014. doi: 10.13140/2.1.3382.2405.

# P24. Effect of Aromatic Electron Density on the Durability of Fluorine-free Aromatic Hydrocarbon-based Proton-exchange Membranes

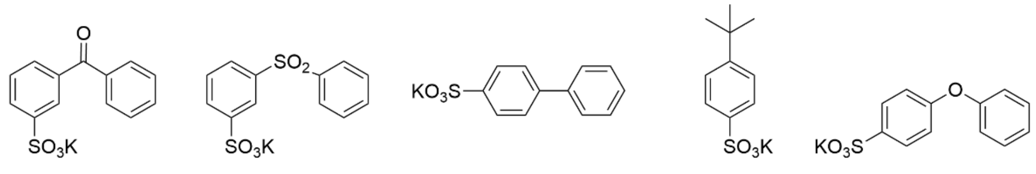
T. Nemeth[1,2], T. Nauser[2], L. Gubler[1]
[1] *Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
[2] *Laboratory of Inorganic Chemistry, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland*
*tamas.nemeth@psi.ch*

Vehicular transportation is a dominant contributing factor to global warming, as it is directly responsible for a third of greenhouse gas emissions in the developed world [1]. The use of hydrogen fuel cells (FC) can mitigate these harmful effects, thus tackling anthropogenic climate change. Research efforts are aimed at replacing the currently used *state-of-the-art* perfluoroalkylsulfonic acid-type (PFSA) proton exchange membranes (PEM) with environmentally friendly fluorine-free alternatives, such as aromatic hydrocarbons.

While the performance of aromatic hydrocarbon-based PEMFCs has been significantly improved over the last decade, factors that influence durability are not yet fully understood. Successful commercialization is presently limited by their increased susceptibility to radical-induced degradation.

We synthesized model compounds, simple aromatic sulfonates, that reflect the structure and electron density of known aromatic hydrocarbon PEMs, Figure 1. We found compelling evidence for the effect of aromatic electron density of PEM constituents on their stability against radical-induced degradation. When we exposed air-saturated aqueous solutions of aromatic sulfonates to radicals, formed *via* a $^{60}$Co γ-source, we observed overstoichiometric degradation of model compounds that contained electron-withdrawing sulfone or carbonyl groups (3BPS, 3SPS), Figure 2. In contrast, the electron rich biphenyl- and diphenyl ether-type model compounds (4PPS, DPS) showed superior stability.

Our findings indicate that ionomers based on electron rich aromatic hydrocarbons are promising constituents for next generation energy conversion devices.



**3BPS** **3SPS** **DPS** **BPS** **4PPS**

Figure 1: Structure of aromatic hydrocarbon-type model compounds, ranked according to increasing electron density (left: electron poor, right: electron rich).

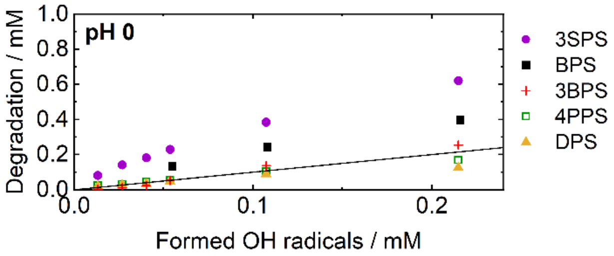


Figure 2: Degree of degradation expressed in mM of air-saturated solutions of 1 mM model compound as a function of cumulatively formed HO$^•$ at pH = 0, established with 1 M $H_2SO_4$. Stoichiometric degradation is indicated with a black line. The data for BPS (black squares) was taken from our previous study [2].

References:
3. Y. Wang, H. Yuan, A. Martinez, P. Hong, H. Xu, F. R. Bockmiller, *Adv. Appl. Energy.* 2 (2021) 100011
4. T. Nemeth, T. de Wild, L. Gubler, T. Nauser, *Phys. Chem. Chem. Phys.* 24 (2022) 895-901

# P25. KMC Simulation Framework to Study SEI Formation in Li Metal Batteries

Aravind Unni[1], Janika Wagner-Henke[1], Ulrike Krewer[1], Perla Balbuena[2]
[1]*Institute for Applied Materials — Electrochemical Technologies, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany*
[2]*Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, USA*
*unni@kit.edu*

Lithium metal batteries exhibit significant potential as the next generation of secondary batteries due to their theoretically high energy density [1], but they face challenges related to poor cyclability and safety hazards arising from the high reactivity of the lithium metal anode. Dendritic deposition of Lithium at the electrode surface poses a primary risk of thermal runaway and explosions due to the short circuits in cells. Additionally, lithium metal's high reactivity with liquid electrolytes leads to the continuous growth of the Solid Electrolyte Interphase (SEI), causing irreversible capacity loss, contributing to poor cyclability. A robust, stable SEI is vital in mitigating these issues; it acts as a protective layer at the lithium anode, helps suppress dendrite growth, and facilitates the quick transfer of lithium ions across the SEI layer.

In this study, we employ 3-D Kinetic Monte Carlo (KMC) simulations with parameters from Density Functional Theory (DFT) simulations to investigate SEI formation. By explicitly modelling each process in the system, and using the DFT parameters to calculate the process rates, we are able to simulate the SEI formation and growth to a much larger timescale. Building on the simulation framework developed by Wagner-Henke et. al for the $LiPF_6$/EC system [2], this presentation extends the work to the LiFSI (salt) in DME (electrolyte) system. The choice of the reaction system is based on studies that have revealed that highly concentrated LiFSI/DME systems have significantly better cycling stability and Coulombic efficiency [3] and hence are promising candidates to stabilize the lithium metal anode in liquid electrolyte. In the poster, I will outline the simulation methodology, present previous results [2] pertaining to Li metal as the anode, illustrating the SEI growth through this model and finally provide insights into the rationale behind moving to a new electrolyte system for this study.

This study aims to gain fundamental insights into the mechanism of SEI formation for the LiFSI/DME system, shedding light on how a stable SEI may be engineered.

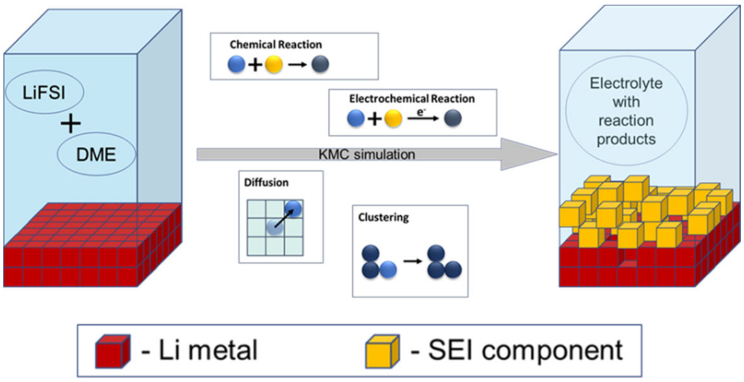


Figure 1: Schematic illustration of SEI formation through KMC simulation

References:
1. Lin, D., Liu, Y. & Cui, Y. "Reviving the lithium metal anode for high-energy batteries" Nat. Nanotechnol. 12, 194–206 (2017).
2. Wagner-Henke et al. "Knowledge-driven design of solid-electrolyte interphases on lithium metal via multiscale modelling" Nat. Commun. 14, 6823 (2023).
3. Zheng, Jing, et al. "Manipulating electrolyte and solid electrolyte interphase to enable safe and efficient Li-S batteries" Nano Energy 50, 431-440 (2018).

# P26. In-Situ Measurement Technique for Data Acquisition in Fuel Cells: Enabling Accurate Energy Balance Modeling

K. Braun, B. Rüppel, L.Weiß, M. Wensing
*Friedrich-Alexander-Universität Erlangen-Nürnberg, Professorship for Fluid Systems Technology,*
*Cauerstraße 4, 91058 Erlangen*
*katharina.braun@fau.de*

Upscaling from single cells to fuel cell stacks and full fuel cell systems is time-consuming and expensive. Modelling and simulations are therefore indispensable. However, models are only as good as the assumptions they are based on. When improving fuel cell systems, all system-relevant dependencies must be modelled correctly. This means that all inputs and outputs of each component, e.g. the fuel cell stack, the humidifier or the compressor, must be known. They are mainly described by thermodynamic state variables, e.g. temperature or pressure, and by process parameters, e.g. heat. These can be used to form mass and energy balances, which are an important basis for understanding the system. System efficiencies can be calculated from this and operating strategies can be developed. There is still a lack of suitable test techniques to obtain all the information required (see Figure 1) to draw up the energy balance, especially of the fuel cell (stack). The ability to accurately and reproducibly set process parameters in the test environment in conjunction with high-resolution measurement technology provides a large amount of useful data for system simulation. Gas diagnostics with Raman scattering is an example of such a measurement technique. By this, the composition, temperature and pressure of a gas mixture can be derived and parameters like relative humidity (RH) and dew point calculated. Raman scattering refers to rare transitions of bonding electrons emitting light at molecule-specific frequencies after laser excitation-, known as the Raman shift [1]. Raman spectroscopy can be used to measure the intensity of the light as a function of the Raman shift. Especially nitrogen, oxygen, hydrogen and water vapor can be detected clearly due to their high signal intensity (see Figure 2). We established a compact in-situ measurement assembly to measure close to the fuel cell stack avoiding condensation problems. Applying this measurement technique to the inlets and outlets of a fuel cell stack promise insightful results. With this type of gas diagnostics, the particularly important parameter of relative humidity can be measured with high temporal resolution of 1s (see Figure 3). Considering the potentials of Raman spectroscopy, it will be of great importance for the analysis of water and energy balances of fuel cells, especially for dynamic tests.

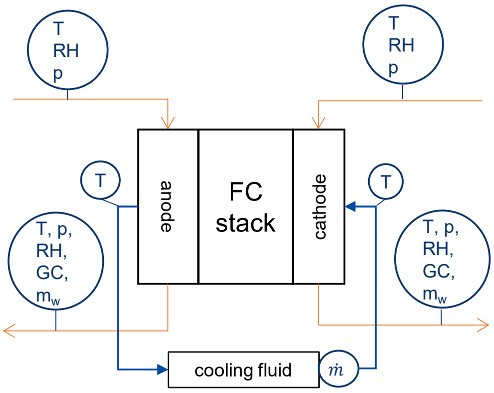


Figure 1: Measuring the energy balance of a fuel cell stack at a test bench – relevant measuring parameters (temperature (T), pressure (p), relative humidity (RH), gas concentration (GC), mass of liquid water ($m_w$))

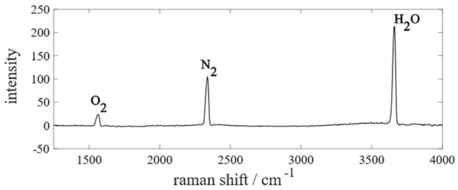


Figure 2: Example of Raman spectrum of humidified air with detected gas signals

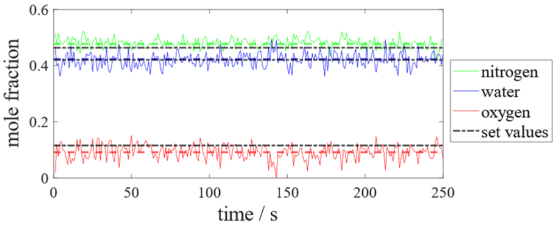


Figure 3: Derived mole fractions from Raman spectra

References:

1. A. Braeuer, *In situ spectroscopic techniques at high pressure*. Amsterdam, Netherlands: Elsevier, 2015. [Online]. https://ebookcentral.proquest.com/lib/kxp/detail.action?docID=4188017

# P27. Modelling Battery Degradation using Neural Ordinary Differential Equations

S. Ramasubramanian[1], C. Lechner[2], J. C. Wurzenberger[2], F. Röder[1]
[1]*University of Bayreuth, Bavarian center for Battery Technology (BayBatt)*
*Weiherstr. 26, 95448 Bayreuth, Germany*
[2]*AVL List GmbH, Hans-List-Platz 1, 8020 Graz, Austria*
*fridolin.roeder@uni-bayreuth.de*

Neural Ordinary Differential Equations (NODE) are a class of machine learning models that use a neural network to learn the dynamics of an unknown process [1]. The method offers a way to integrate known physical information about a process into its framework, which could result in better predictive performance as compared to a purely data-driven model [2]. Our recent work demonstrated that, simple, physics motivated constraints to the growth rate were sufficient to learn a function that describes solid electrolyte interphase (SEI) growth during formation and performs better than a purely data-driven NODE [3]. Therefore, this approach warrants further analysis for different use-cases in batteries.

In this work, we study the use of NODE to model battery aging in a controlled setting. For this purpose, we use the electrochemical simulation tools available in the AVL CRUISE™ M software[4]. We generate synthetic, cyclic aging data under 6 operating conditions at different C rates and temperatures while considering that SEI growth and irreversible lithium plating are triggered during the aging. A part of this data is used for training while the remaining is used for testing. The voltage output for 0.5C cycling at 25℃ is shown in Figure 1a. It consists of a low C rate (C/20) checkup cycle and 0.5C aging cycles. Finally, we perform an OCV fit on the C/20 discharge steps to calculate loss of lithium inventory (LLI) during the tests, which is shown by the black dots in Figure 1b.

We define the NODE model to predict the dynamics of the lithium inventory over time and train it using the calculated LLI from the checkup cycle. The black line in Figure 1b shows the predictions of one variant of a NODE with voltage as the external input for 0.5C cycling at 25℃ during training. Finally, we explore the model space sequentially adding more data or more physical information into the network and analyse their predictive performance on the test set. Our approach shows that neural ODEs are good at learning functions that fit a given training data, but careful consideration is needed while adding physically relevant information to the network for modelling battery degradation. Nevertheless, the presented approach has high potential to model complex battery degradation in which parts of the underlying mechanisms remain unknown.

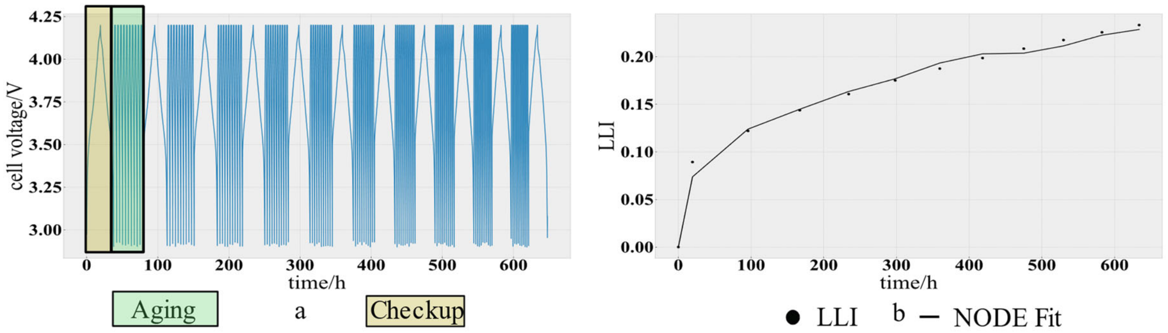


Figure 1: Voltage output from aging study consisting of aging cycles (a) followed by low C rate checkup (b). Calculated LLI from the checkup cycles (black circles) and fitted LLI from the NODE (black line).

References:

1. Chen, R. T., et al., *Advances in Neural Information Processing Systems* 31 (2018)
2. Aykol, M., et al., *Journal of The Electrochemical Society* 168(3) (2021) 030525.
3. Ramasubramanian, S., et al., *Electrochimica Acta* 473 (2024), 143479.
4. Knaus, O., Wurzenberger, J. C., System Simulation in Automotive Industry. In: Hick, H., Küpper, K., Sorger, H. (Eds.): *Systems Engineering for Automotive Powertrain Development*, Springer, 2020.

# P28. Matching Micro- and Mesoscale Parametrization for Electrochemical Battery Simulations

C. Bieneck[1,2], L. von Kolzenberg[1], Arnulf Latz[2,3,4]
*[1]Cellforce Group GmbH, Jopestraße 14, 72072 Tübingen, Germany*
*[2]Ulm University, Albert-Einstein-Allee 47, 89091 Ulm, Germany*
*[3]German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Wilhelm-Runge-Straße 10, 89081 Ulm, Germany*
*[4]Helmholtz Institute for Electrochemical Energy Storage (HIU), 89081 Ulm, Germany*
*conrad.bieneck@cellforce.de*

Electrochemical battery models are useful tools to understand lithium-ion batteries and aid in their continuous improvement. Two main approaches exist depending on the desired depth of analysis. On one hand, the pseudo-two-dimensional (P2D) model [1] offers a good description of the key features of the battery at low computational cost and is thus widely adopted. On the other hand, microstructure simulations resolve the electrochemistry at the microstructure and thus return a deeper insight into critical processes like lithium plating at the cost of longer computation times [2].

Despite their common physical origin, getting consistent results between P2D and microstructural model is challenging. The electrodes geometrical parameters like porosity, tortuosity and electronic conductivity can be determined from microstructure simulations and passed to the P2D model. In contrast, the active material parameters (e.g. diffusion coefficient and exchange current density) are only valid for the P2D model and need a careful adaption to the microstructure.

This talk highlights the relevant steps and the validation workflow to achieve consistent results between P2D and microstructure model. First, we compare geometrical properties e.g. particle size distribution and specific surface area, between P2D and microstructure model and adapt the electrochemical parameters accordingly. Then, we use an adaption of the TauFactor tool [3] to rapidly determine electrode parameters with two different methods.

Figure 1 shows the results of the subsequent validation procedure including an impedance and a constant current simulation. The impedance simulation exhibits only a negligible offset in the low-frequency area. The constant current simulation, in contrast, reveals a significant offset between P2D and microstructure model. The successful model adaption leads to more valid microstructure simulation and hence more validated results, which will aid in optimizing electrode design.

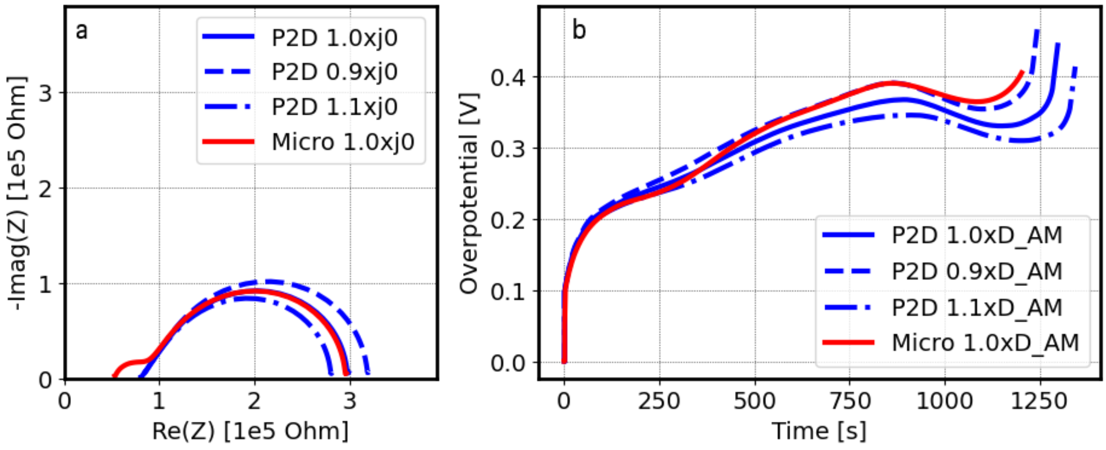


Figure 1: (a) Impedance simulation to validate the exchange current density adaption. (b) 2C constant current simulation for validation of active material diffusion coefficient.

References:
1. M. Doyle, T. Fuller, J. Newman, *J. Electrochem. Soc.* **140**, 1526-1533, 1993
2. A. Latz, J. Zausch, *J. Power Sources* **196**, 3296-330, 2011
3. S. Kench, I. Squires, S. Cooper, *J. Open Source Softw.* **8**, 5358, 2023

# P29. Effective Transport Properties of Granular Cathode Material in Particle and Pore Space Including Intragranular Cracks

A. Pamperin[1], N. Ribic[1], O. Birkholz[1,2], V. Becker[1,3], M. Kamlah[1]
[1]*Karlsruhe Institute of Technology, Institute for Applied Materials, Karlsruhe, Germany*
[2]*APL Automobil-Prüftechnik Landau GmbH, Landau, Germany*
[3] *Daimler Truck AG, Leinfelden-Echterdingen, Germany*
*alexandra.pamperin@kit.edu*

Given the growing need for specialized energy storage systems, it is essential to elucidate the relationship between battery electrode microstructure and physical properties. To this end we focus on the microstructure of porous cathodes and its effect on electronic and ionic transport. These physical properties influence an energy storage cell's electrochemical behaviour and therefore its area of application. While it is possible to use the Finite Element Method to calculate these transport properties spatially resolved, the computational cost is very high. Therefore, a less computationally expensive method, like the resistor network method, is advantageous especially when large arrays of microstructures are examined. The effect of particle shape on the effective transport properties is another area of interest. To this end the resistor network method is extended to mechanically deformed and undeformed ellipsoidal particles. In the case of deformed particles, a Hertzian contact model is used to determine the contact area of two particles while for the undeformed state a geometric approximation is used. Including a Hertzian contact model coupled with a mechanical discrete element method (DEM) enables an investigation of the influence the micromechanical response of ellipsoidal particles to uniaxial compression has on the effective transport properties of the assembly. On the other hand, the geometric approximation of the overlaps of undeformed particles can be used to study the effective transport properties of sintered particle systems.

While the resistor network method approximates the microstructure of the active material using discrete particles, the internal makeup of those particles is also highly salient for the overall transport properties. Therefor first investigations into the influence of intragranular cracks on the transport have been made using two and three dimensional ellipsoids to approximate single cracks. It was possible to construct a predictive analytical function based on the key geometrical crack properties volume, aspect ratio and angle of rotation with respect to the transport direction.

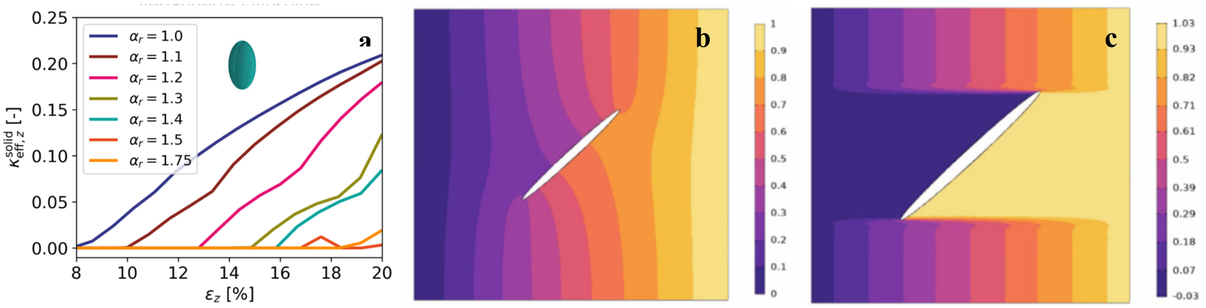


Figure 1: (a) Effective transport through the particle phase of an assembly of 1800 prolate ellipsoids of differing aspect ratio over the uniaxial compression starting from a packing density of 55%. (b) 2D temperature field through domain with elliptical crack and isotropic material properties (b) or anisotropic material properties (c).

References:

1. O. Birkholz, Y. Gan, M. Kamlah, Modeling the effective transport properties of the solid and the pore phase in granular materials using resistor networks, Powder Technology 351, 54-65, 2019.
2. V. Becker, O. Birkholz, Y. Gan, M. Kamlah, Modeling the influence of particle shape on mechanical compression and effective transport properties in granular Lithium-ion battery electrodes, Energy Technology, 9, 2000886, 2021.

# P30. A Physically-informed, Aging-sensitive Equivalent Circuit Model for Predicting the “Knee” in Lithium-ion Battery Aging

Patricia O. Mmeka[1], Matthieu Dubarry[2], Wolfgang G. Bessler[1]
[1]*Institute of Sustainable Energy Systems, University of Applied Sciences, Offenburg, Germany.*
[2]*Hawai'i Natural Energy Institute, SOEST, University of Hawai'i Manoa, Honolulu, USA.*
*patricia.mmeka@hs-offenburg.de*

The increase in lithium-ion battery (LIB) systems in diverse applications such as electric vehicles and stationary energy storage emphasizes the need for the prediction of the lifetime of LIBs for various usage conditions. Aging is path-dependent [1], such that different aging mechanisms (path or causes) are strongly and nonlinearly coupled, leading to nonlinear aging dynamics (“knee” formation) [2], which is challenging to predict. Despite the ability of physiochemical models to describe these aging dynamics, their disadvantages are prolonged computation time and complexity in deriving the parameters.

A physically informed equivalent circuit model (ECM) was newly developed by integrating aging modes (loss of active material LAM, loss of lithium inventory LLI) and describing their rates with physicochemical aging kinetics. A schematic representation is shown in Figure 1a. The model consists of two voltage sources ($V^0_{\mathrm{PE}}(X_{\mathrm{PE}})$ and $V^0_{\mathrm{NE}}(X_{\mathrm{NE}})$), two resistor-capacitor elements ($R_{\mathrm{PE}}$, $C_{\mathrm{DL,PE}}$, $R_{\mathrm{NE}}$, $C_{\mathrm{DL,NE}}$), and a series resistor ($R_{\mathrm{s}}$) representing the half-cell potentials of the two electrodes; the charge-transfer and transport kinetics at the two electrodes; and the electrolyte and current collection system, respectively. The concept of balance equations for charges of the two half-cells ($Q_{\mathrm{NE}}$, $Q_{\mathrm{PE}}$) allows for the incorporation of aging modes into the model. This model is computationally comparatively simple and allows for the simulation of dynamic, complex, realistic load profiles with long simulation times.

The model was parameterized to a 3350 mAh cylindrical cell with graphite anode and NCA cathode, which was studied in detail previously [1]. The rate expressions for each aging mode consist of a calendaric part (dependent on half-cell potential and lithium stoichiometries) and a cyclic part (a function of current and active material relative volume changes). They were parametrized such that the simulated aging modes match previously published experimental data [1]. The model was calibrated with dynamic stress test (DST) operating protocol and was further applied to other, more complex operating protocols, New European Driving Cycle (NEDC) and Federal Urban Driving Schedule (FUDS). Figure 1b shows the performance of the model under a simple operating profile (DST) and more complex operating profiles (FUDS and NEDC). Conclusively, the parameterized ECM qualitatively predicts aging knee for different operating cycles as shown in Figure 1b.

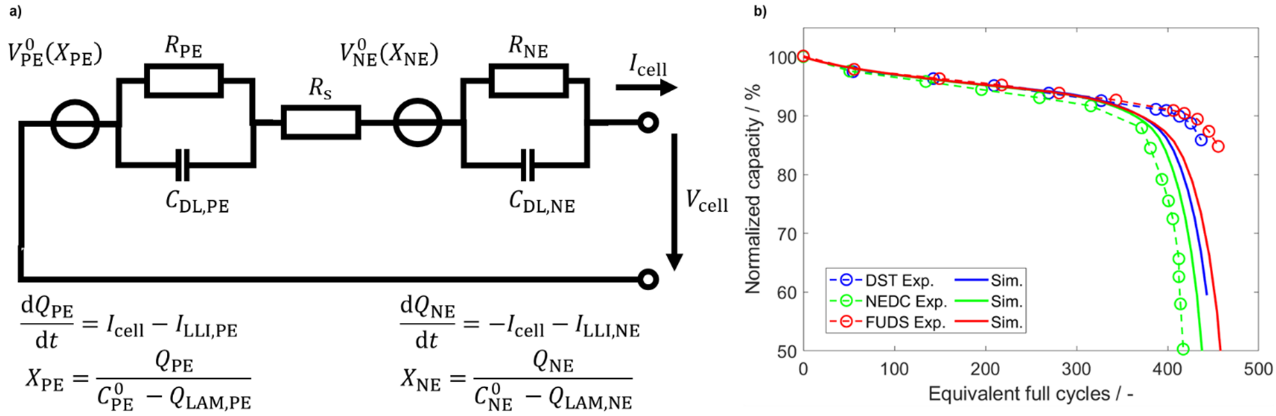


Figure 1. a) Systematic representation of the model and incorporation of aging modes. b) Capacity fading and knee prediction upon cycling with DST, NEDC, and FUDS.

References:
1. G. Baure, M. Dubarry, *Batteries* 5, 2019, 42.
2. P. M. Attia, A. Bills, F. B. Planella, P. Dechent, G. dos Reis, M. Dubarry, P. Gasper, R. Gilchrist, S. Greenbank, D. Howey, O. Liu, E. Khoo, Y. Preger, A. Soni, S. Sripad, A. G. Stefanopoulou, V. Sulzer, *Journal of The Electrochemical Society*, 169, 2022, 060517.

# P31. Investigating Bubble Nucleation and Flow in Membrane-less Water Electrolyzers

Pooria Hadikhani
*Institute of Applied Materials-Electrochemical Technologies, Karlsruhe Institute of Technology*
*Karlsruhe, Germany*
*Pooria.hadikhani@kit.edu*

The transition to a sustainable energy system requires viable technologies for large-scale production, storage, and utilization of green fuels such as renewable hydrogen. Water electrolysis presents a promising approach using renewable energy to generate hydrogen in a carbon-neutral manner. Conventional water electrolyzers that utilize membranes or separators face challenges such as high costs and complexity, which have hindered cost-effective hydrogen production through this technology. Membrane-less electrolyzers (MLEs) provide a distinct opportunity to overcome these barriers through innovative cell architectures that eliminate membranes, which are the main source of degradation [1]. By relying on fluidic flows for product gas separation, MLEs can significantly simplify cell fabrication and reduce balance-of-plant costs. The main objective of this study is to numerically investigate the **effect of bubble flow** on the **efficiency** and **product purity** in MLEs.

An MLE consists of two electrodes and a flowing liquid electrolyte between the electrodes. Products of the water electrolysis reaction are in the form of bubbles. These bubbles nucleate on the surface of an electrode, grow, and then detach from the electrode and flow in the fluidic channels. The nucleation and growth of bubbles on the surface of the electrode reduces the active area for the electrochemical reaction leading to overpotentials. Furthermore, the bubbles flowing between electrodes increase the ohmic resistance between the electrodes. In this research, we quantify the overpotentials due to bubbles nucleating and flowing in MLEs. Figure 1 (a) shows 3D numerical simulations of bubble nucleation and flow in an MLE at the current density of $450\ mA/cm^2$ at different Reynolds numbers (Re) for two different cases: electrolyte without and with surfactant. The bubble coalescence and residence on the surface of the electrode lead to overpotentials. The overpotentials due to bubbles are shown in Figure 1 (b). The overpotential due to bubbles can be decreased by increasing the flow rate of the liquid to accelerate bubble detachment from the surface. Furthermore, bubble coalescence is prevented in an electrolyte with surfactant leading to smaller-sized bubbles flowing between electrodes and lower overpotentials due to bubbles. These simulations are performed using Aphros multiphase flow solver [2].

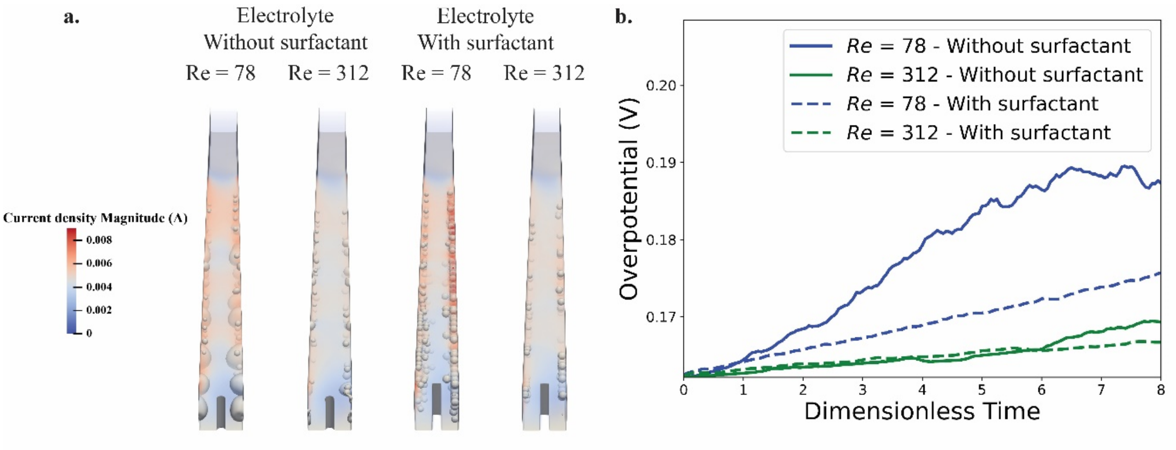


Figure 1: a) Numerical simulation of bubble nucleation and flow in membrane-less electrolyzers at different Reynolds numbers and two electrolytes without and with surfactant, b) ohmic overpotentials and overpotentials due to bubbles.

References:
1. P. Hadikhani, et al., Sustainable Energy & Fuels 5(9) (2021) 2419-2432.
2. P. Karnakov, et al., Science Advances 8(5) (2022) eabm0590.

# P32. Modelling vent gas flow impact on thermal runaway propagation in battery modules/packs with varied void space dimensions

Yang Jiang[1,2], Gregory Offer[1,2], Huizhi Wang[1,2]
[1]*Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, U.K.*
[2]*The Faraday Institution, Harwell Science and Innovation Campus, Didcot OX11 0RA, U.K.*
*yj2519@ic.ac.uk (Y Jiang), gregory.offer@imperial.ac.uk, huizhi.wang@imperial.ac.uk*

The venting of flammable gases can cause fire or explosion and affect thermal runaway propagation in battery modules/packs. Therefore, understanding vent gas mixing behaviours during the initial venting phase is crucial for mitigating safety risks of thermal runaway propagation in battery modules/packs. During the initial venting phase, combustible gases mix with the air inside a module. According to the fire triangle theory [1], if the combustible gas mixture falls below the lower flammable limit (LFL), ignition cannot occur due to insufficient combustible gases. Conversely, when the gas concentration surpasses the upper flammable limit (UFL), ignition is hindered by a scarcity of surrounding oxygen ($O_2$). The configuration of the battery module plays an important role in determining the combustible gases-air mixture behaviours, especially through the influence of the internal void volume. This volume impacts the air/combustible gases ratio within the module, and thus affecting safety.

To investigate the effects of the void space dimension, a multiphase venting model is developed in this study. A concept of combustible area ($v_f$) is introduced and a dimensionless index ($F_{risk}$) is proposed to estimate the flammability risk. Figure 1 shows that the likelihood of gas combustion varies throughout the venting process. As the internal void volume increases, the combustible area during the venting process expands. This is because a larger void volume leads to an increase in oxygen concentration. Consequently, the gas mixture transitions gradually from the oxygen-lean, non-combustible concentration range to the combustible concentration range. Furthermore, this flammability duration $t_f$ increases with increasing void volume in the battery module. Particularly, when the volume fraction of the internal void within the module rises to 39.7%, the gas mixture consistently remains within the combustible concentration range. The findings underscore the significant impact of void space in battery modules/packs on thermal runaway propagation, offering valuable insights for battery module/pack design and safety assessments.

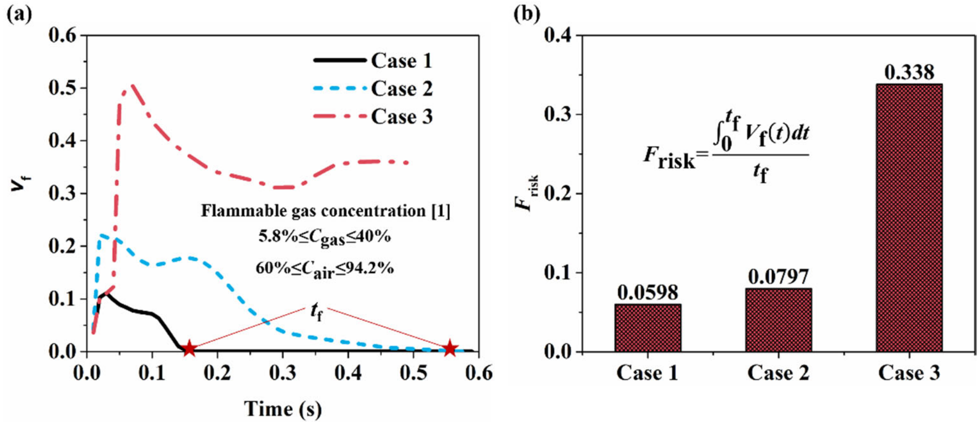


Figure 1: (a) Evolution of the combustible area in battery modules with void volume fractions of 7.9% (Case 1), 18.6% (Case 2) and 39.7% (Case 3). (b) The flammability risk ($F_{risk}$) in battery modules with different void volume fractions.

References:

1. W. Li, S. Rao, Y. Xiao, Z. Gao, Y. Chen, H. Wang, M. Ouyang, *Iscience*, **24** (2021), 5, 2589-0042.

# P33. New Method to Characterize Li Metal and SEI Layer with Atomic Resolution with Inert Gas Transfer and Cryo-FIB

Brandon van Leer, Lin Jiang, Zhao Liu, Letian Li
*Materials and Structural Analysis, Thermo Fisher Scientific, 5350 NE Dawson Creek Drive.*
*Hillsboro, Oregon 97124, United States*

Lithium metal is one of the most promising anode candidates for the next-gen solid state battery. To go through the hurdles for a reliable and cost-effective solid-state battery, it is crucial to build strong fundamental understandings of different parts of a battery at microscopy level. Techniques such as sitespecific DualBeam (FIB-SEM) lamella preparation and subsequent TEM analysis have always been the key steps to unlock atomic resolution for materials science studies. However, due to the air and moisture sensitivity associated with various battery components (Li metal, SEI layer, Solid electrolyte), it used to be a very challenging task to keep sample integrity during the workflow, especially during sample transfer between different instruments.

In the current study, the Thermo Scientific IGST workflow solution was used to enable a DualBeam to TEM workflow by protecting both the bulk sample and the prepared lamella in Ar atmosphere with a CleanConnect transfer module.

Using the CleanConnect module, a bulk Li-metal piece was successfully transferred from glovebox to a Helios 5 Hydra DualBeam without signs of surface oxidation. Due to the low melting point of lithium, the entire TEM lamella preparation process, including bulk milling, lift out, attach to TEM grid and final thinning were carried out at cryogenic temperature (−178°C) with a Thermo Scientific cryo-stage and cryo-EasyLift nano-manipulator. To achieve minimal ion damage to the final lamella, all the ion milling processes were carried out with Ar plasma focused ion beam from a Helios 5 Hydra multi-ion species plasma FIB.

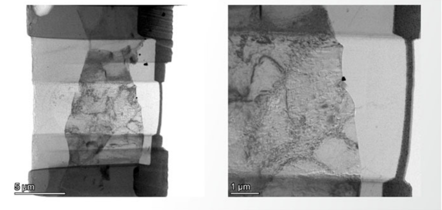


Figure 1: Lithium metal lamella transferred into TEM with ThermoFischer CleanConnect IGST

The prepared lamella was then transferred back to a Thermo Scientific Talos F200X CFEG TEM with IGST workflow and subsequently analyzed in TEM. It is evident that the whole workflow successfully protects the lithium metal lamella from oxidation during transfer between multiple instruments. The lithium metal lamella stays crystalline with minimal signs of surface oxidation. Atomic resolution TEM images from lithium metal were successfully acquired. According to literature survey, this could be the first DualBeam prepared lithium lamella which gives atomic resolution in TEM analysis.

The study successfully shows the capability of the workflow by achieving atomic resolution from Li metal, which is one of the most challenging samples in terms of air, moisture, and temperature sensitivity. The success of the workflow also enables new methods to study other trending topics in the battery world such as characterization of SEI layer evolution, post-mortem analysis in higher resolution whilst keeping the sample in its original state.

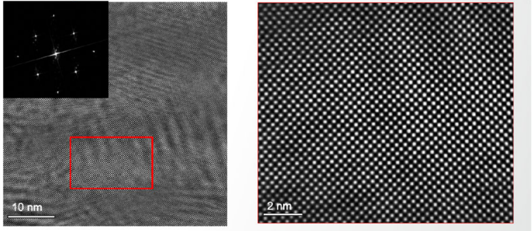


Figure 2: Atomic resolution TEM images from the lithium metal lamella.

# P34. Development and Validation of Physics-based Model for Lithium-Ion Battery Degradation Across Various Aging Conditions

A.K. Jishnu[1], C. Burak[2], Y. Ugur[2], Z.F. Nessa[1], M. Zhuo[1,4], F.B. Planella[3], W.D. Widanage[1,4]
[1] *University of Warwick, WMG, CV4-7AL, Coventry, United Kingdom*
[2] *Eatron Technologies, Warwick Technology Park, 11A Innovation Centre, Warwick CV34 6UW*
[3] *Mathematics Institute, University of Warwick, Coventry, CV4 7AL, United Kingdom*
[4] *The Faraday Institution, Harwell Campus, Didcot, OX11 0RA, United Kingdom*
*jishnu-ak.ayyangatu-kuzhiyil@warwick.ac.uk*

Accurate modelling of electrochemical behaviour and degradation of lithium-ion batteries are critical for developing control algorithms that ensure optimal performance, safety, and longevity. This study aims at developing a physics-based degradation model for a commercial cylindrical cell featuring an NMC 811 cathode and a SiGr anode. The primary objective is to construct a model with high generalisability, capable of accurately depicting degradation behaviour under diverse ageing conditions. The ageing dataset generated for this study features four test conditions at two temperatures (25°C and 45°C), which includes two constant current cycling ("C/3 charge - 1C discharge" and "1C charge - 2C discharge"), and two user profiles (UP1 and UP2) that simulate electric vehicle battery usage. User Profile 1 (UP1) represents light driving patterns like daily commutes, while User Profile 2 (UP2) reflects heavier usage. These profiles are crucial for developing a model relevant to the automotive industry, capturing realistic battery degradation trends under varying driving conditions.

In this study, the Single Particle Model with Electrolyte (SPMe) was employed to describe the short-term electrochemical behaviour of the battery. This model was parameterised using a combination of data from invasive cell teardown experiments and non-invasive cycling tests. For the degradation aspect, two primary mechanisms were identified: SEI (Solid Electrolyte Interphase) growth and stress-induced Anode Loss of Active Material (LAM) [2]. To model these, kinetic and diffusion limited SEI growth model from [1] and an empirical formulation for anode LAM proposed in [2] were coupled with SPMe. The degradation model's long execution time made traditional optimisation-based parameterisation impractical. Alternatively, a systematic trial-and-error approach was employed. The SEI model was initially parameterised exclusively with 7 weeks of user profile ageing dataset, where stress-induced LAM is minimal due to prolonged idle states. LAM model was subsequently parameterised with 250 cycles constant current cycling dataset.

Figure 1 compares the experimental capacity drop with the model's predictions, with additional data used for validation as indicated in the figure. In all cases, the model achieves an RMSE of less than 2%, showcasing its precision and adaptability in various scenarios. This accuracy is beneficial for developing control algorithms for managing battery degradation.

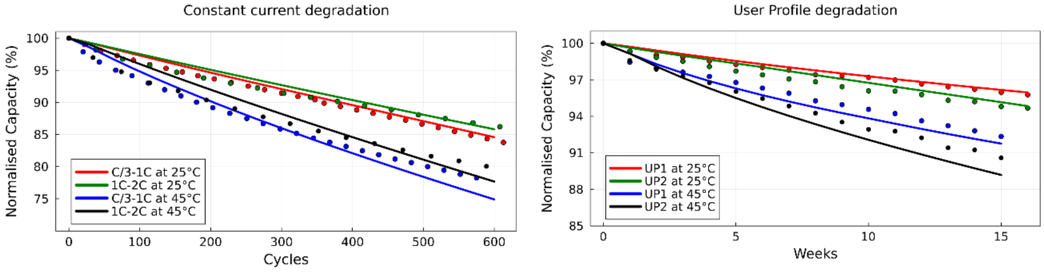


Figure 1: Comparison of experimental capacity drop (circular markers) and model predictions (solid line) for different conditions. (left) Constant current cycling and (right) user profile degradation.

References:
1. Brosa Planella, F.; Widanage, W. D. A Single Particle Model with Electrolyte and Side Reactions for Degradation of Lithium-Ion Batteries. Appl. Math. Model. 2023, 121, 586-610.
2. Reniers, J. M.; Mulder, G.; Howey, D. A. Review and Performance Comparison of Mechanical-Chemical Degradation Models for Lithium-Ion Batteries. J. Electrochem. Soc. 2019, 166 (14), A3189-A3200.

# Model-based optimization of Gas Diffusion Layers material properties by CFD simulation

S. Schneider[1], L. König[1], F. Wilhelm[1], J. Scholta[1]
[1]*Centre for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW)*
*Lise-Meitner-Straße 24, 89081 Ulm, Germany*
*sabina.schneider@zsw-bw.de*

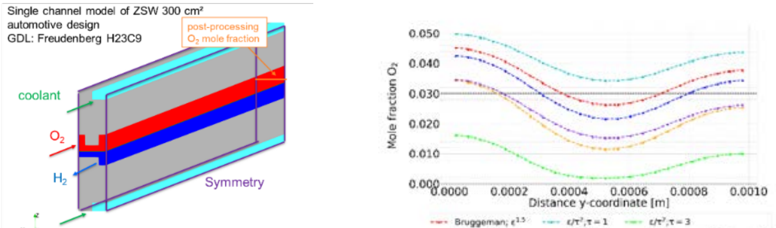
Computational Fluid Dynamic (CFD) software is widely used within the development process of fuel cells. Advanced models that describe the electrochemical and transport processes using formulations such as the Butler-Volmer equation can help to gain a deeper understanding of the processes relevant for fuel cell operation. Some of the most important properties which can be investigated with this type of simulation are the reactant distribution in the reaction layer, the current density distribution and the membrane wetting.

Though these components are not directly involved in the electrochemical processes, the Gas Diffusion Layers (GDL) play a crucial role for the performance and durability of the cells. Their functionality can also be analysed by CFD simulations. The two main mass transport mechanisms, convection and diffusion, are described by conservation equations. Due to the high computational effort, still today only small sections of real fibre structures can be analysed. Thus, to be able to simulate single channels or even the whole cell area, the GDL is usually described as a homogeneous block with anisotropic material parameters. Convection is modelled by an additional source term, known as the Darcy-Forcheimer equation, in the momentum equation. Diffusion processes are described by a diffusion term resp. an effective diffusion coefficient in the species equation. The most relevant parameters for the models are permeability, porosity $\varepsilon$ and tortuosity $\tau$. The tortuosity and the porosity of a specific GDL structure can be determined from imaging data, e.g. by the software GeoDict® [1].

In this work, a parameter study of the GDL properties was carried out using the commercial CFD PEMFC model of ANSYS® Fluent [2]. The focus is on the resulting mass transport properties and finally the locally resolved reactant concentration in the catalyst layer. The aim of the parameter study is to analyse the influence of the GDL properties and to optimize them in order to obtain an improved reactant distribution for a given flowfield design. Specifically, an analysis of the Bruggeman correlation [2] used in Fluent (equation 1) to describe the effective diffusion coefficient $D_{eff}$ in porous media was performed. The results are compared with an alternative, well-documented approach from literature (equation 2) [1]. Figure 1 shows the results of a single channel model of the 300 cm² automotive design developed at ZSW. The study demonstrates that CFD codes are valuable tools to optimise GDL parameters and to support the GDL selection for a specific fuel cell design.

$$D_{eff} = D_{ij} \cdot \varepsilon^{1.5} \qquad (1)$$

$$D_{eff} = \frac{D_{ij} \cdot \varepsilon}{(L_e/L)^2} = \frac{D_{ij} \cdot \varepsilon}{\tau^2} \qquad (2)$$



a) b)

Figure 1: a) single channel simulation model; b) $O_2$ mole fraction in the cathode catalyst for different diffusion coefficient

This work has received financial support by the German Federal Ministry for Digital and Transport within the GALLIA project (NIP II, 03B10114D).

References:

1. GeoDict simulation software Release 2024, by Math2Market GmbH, Germany, doi.org/10.30423/release.geodict2024
2. ANSYS Fluent Theory Guide, 2023R1

# P36. Simulating the Current Split between Active Material Species in Blend Electrodes Using a Transmission Line Model

Maximilian Schamel[1,2], Michael A. Danzer[1,2]
*[1]Chair of Electrical Energy Systems, University of Bayreuth*
*[2]Bavarian Center for Battery Technology (BayBatt), University of Bayreuth*
*Universitätsstraße 30, 95447 Bayreuth, Germany*
*Maximilian.Schamel@uni-bayreuth.de*

One approach to enhance the performance of lithium-ion battery electrodes is the targeted combination of two active storage materials in a blend electrode, e. g. silicon and graphite on the anode side. Nevertheless, the diverging characteristics of two materials in terms of open circuit voltage (OCV) curves and kinetic properties can lead to inhomogeneous degrees of lithiation (DOL) and high local current densities. Therefore, in-depth knowledge of the charge storage process in blend electrodes is necessary, motivating the usage of spatially resolved models.

In this work, a transmission line model (TLM) is applied with spatial resolution in the direction of electrode thickness and on particle level [1]. It is composed of lumped elements and can be parameterized by impedance fitting and OCV measurements. To account for two active storage materials, the standard TLM is adjusted towards a blend electrode model. Therefore, as an initial step, two different OCV curves are assigned, one for each material. Every discrete electrode section is built up by two intercalation paths that are connected in parallel, representing the simultaneous contributions of two materials, as proposed by Costard for simulating impedance spectra of blend electrodes [2]. The lithium storage capacities can be allocated according to the mass-specific material capacities and the materials' weight fractions in the blend electrode. As an example, a silicon/graphite electrode is evaluated. The model structure enables an investigation of local DOLs and reveals which material is mainly active during different periods of electrode lithiation. The silicon fraction is varied virtually to demonstrate its impact on current distribution and useable electrode capacity.

The results show that, at C/20, silicon is preferably lithiated at the beginning, while graphite is dominating at higher electrode DOL (Figure 1). The qualitative findings in terms of current distribution and material DOLs are comparable to the results of more sophisticated physical p2D models or physics-based 3D models [3,4].

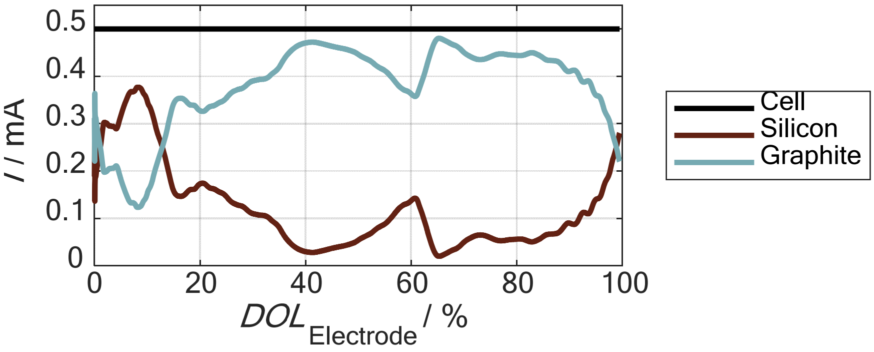


Figure 1: Simulation results: split of applied cell current between silicon and graphite during C/20 lithiation. The predefined capacity of silicon is 25 % of the total electrode capacity.

References:
1. M. Hahn, A. Schiela, P. Mößle, F. Katzer and M. A. Danzer, *Journal of Power Sources,* **477**(2), 228672 (2020).
2. J. Costard, *Einfluss von Mikrostruktur und Materialparametern auf die Leistungsfähigkeit poröser Elektroden für Lithium-Ionen Batterien,* KIT Scientific Publishing (2018).
3. W. Ai, N. Kirkaldy, Y. Jiang, G. Offer, H. Wang and B. Wu, *Journal of Power Sources,* **527**(1), 231142 (2022).
4. C. Liu, O. Arcelus, T. Lombardo, H. Oularbi and A. A. Franco, *Journal of Power Sources,* **512,** 230486 (2021).

(abstract withdrawn)

# P38. Quantifying the O-redox Contribution to the Charge Compensation Mechanism in $Na_{0.67}Mn_{0.62}Fe_{0.19}Al_{0.1}O_2$-cathode Material for Na-ion Batteries

D. Baster[1], T. Schmitt[2], A. H. Clark[2], T. C. Asmara[2], Y. Wei[2], Z. Tao[2], J. B. Falqueto[1], M. El Kazzi[1]
[1]*Electrochemistry Laboratory, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
[2]*Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland*
*dominika.baster@psi.ch*

Manganese-based layered sodium oxides as $Na_{0.67}Mn_{0.62}Fe_{0.19}Al_{0.1}O_2$ (NMFA) attract persistent attention as cathode materials for Na-ion batteries due to the pressing need to reduce the reliance on cobalt and nickel.[1] However, it remains unclear and unquantified the charge compensation mechanism during sodium deintercalation, and whether the process is compensated by the oxidation of Mn, Fe and/or lattice oxygen ($O^{2-}$).

Herein, *operando* X-ray absorption spectroscopy (XAS) acquired at the Mn and Fe K-edges and *ex-situ* high-resolution resonant inelastic X-ray scattering (HR-RIXS) at the O K-edge have been employed to get insight into the charge compensation mechanism in the NMFA cathode. *Operando* XAS spectra have been collected in transmission mode, which by definition is bulk sensitive. While *ex-situ* HR-RIXS exhibits similar probation depth as XAS acquired in fluorescence mode which is near surface/bulk sensitive (100s of nm). The Mn and Fe K-edges XAS spectra demonstrate that upon charge process from 2.73 V to 4.45 V vs. $Na^+/Na$, Mn is unexpectedly oxidized from $Mn^{4+}$ to $Mn^{4.2+}$ (Fig. 1a) with major oxidation at early cycling between 2.73 and 4.0 V, while Fe is oxidized as expected from $Fe^{2.8+}$ to $Fe^{3+}$ with rather major oxidation between 3.5 and 4.45 V (Fig. 1b). These results show no evidence of Mn and Fe redox activity above 4.45 V and therefore no contribution to the charge compensation. Based on the Mn and Fe oxidation evolution together with an accurate compositional analysis by ICP-OES, we quantified that only 46% of the delivered specific capacity has been charge compensated by Mn and Fe oxidation. Thanks to the O K-edge HR-RIXS measurement we proved that the remaining 54% of the specific capacity is charge compensated by the oxidation of lattice oxygen. The O K-edge HR-RIXS spectra (Fig. 1c) show the lattice oxygen ($O^{2-}$) oxidation to molecular oxygen $O_2$ by monitoring both the spectral feature at ~7 eV and the vibrational progression peaks in the range of 0-2 eV. This oxidized oxygen is trapped in the bulk of particles and can be reduced upon the discharge process. These findings can provide a guideline for further designing high-energy cathode materials for Na-ion batteries, which involve cationic and anionic redox processes.

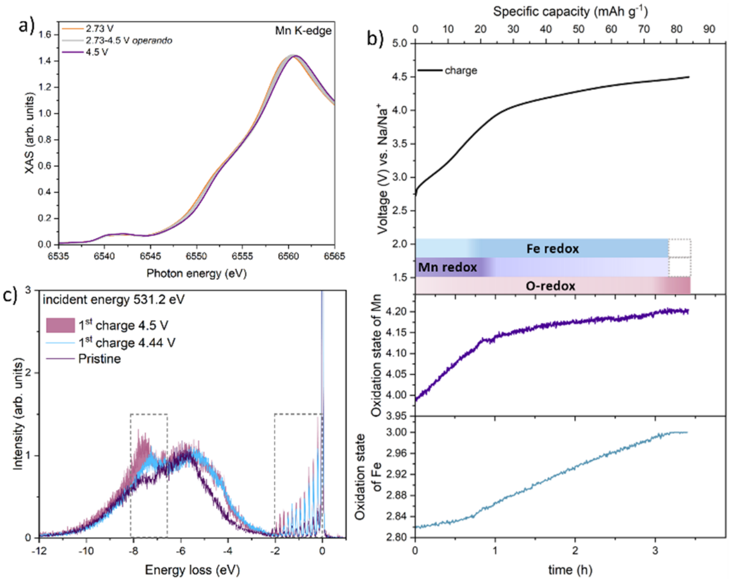


Figure 1 : a) *Operando* XAS spectra acquired at Mn K-edge in Na||NMFA half-cell. b) Redox processes in the bulk of NMFA particles upon charge along with galvanostatic charge curve and evolution of Mn and Fe oxidation state upon the charge process. c) Oxygen K-edge HR-RIXS spectra of the pristine cathode, upon charge state at 4.44 V and at the 1st charge state (4.5 V).

References:
1. E. Marelli, C. Villevieille, S. Park, N. Hérault, C. Marino, *ACS Appl. Energy Mater.* **1** (2018), 11, 5960-5967

# P39. Stereological Multi-scale Modeling of Anisotropic NMC Particles, Combining Methods of Spatial Stochastics and Generative Neural Networks

Lukas Fuchs[1], Orkun Furat[1], Donal P. Finegan[2], Peter Weddle[2],
Jeffery Allen[2], Kandler Smith[2], Volker Schmidt[1]
[1]*Ulm University, Helmholtzstraße 18, 89069 Ulm, Germany*
[2]*National Renewable Energy Laboratory, 15013 Denver W Parkway, Golden, CO 80401, USA*
*lukas.fuchs@uni-ulm.de*

Understanding the nano- and micro-structures of battery materials has become increasingly crucial for studying their structure-property relationships, particularly through numerical simulations of electrochemical or cracking behavior [1]. Lithium-nickel-manganese-cobalt-oxide (NMC811) particles represent an active material in batteries with growing interest. The structure of NMC811 particles is investigated on two length scales: the micro-scale, encompassing particle shape and size (outer shell), and the nano-scale, addressing the inner crystallographic grain architecture. While the outer shell of particles can be measured at reasonable cost by X-ray computed tomography (3D micro-CT) the same is not feasible for the inner grain architecture utilizing e.g. 3D electron backscatter diffraction (EBSD) measurements. Therefore, grain architecture analysis often solely relies on 2D cross-section imagery. However, the results of these 2D measurements strongly vary by their location within the particle, due to the anisotropic grain architecture of NMC811, and thus do not effectively capture their 3D structure. In this presentation, a stereological multi-scale model [2] is proposed that captures both the outer shell and anisotropic inner grain architecture of MC811 particles, see Figure 1. The modeling consists of two parts: first, the coarser scale of particles (outer shell) is modeled by random fields on the sphere, similar to the method presented in [3]. Subsequently, the inner grain architecture is modeled by a novel approach utilizing a generative adversarial network (GAN), which is used to fit a random 3D tessellation stereologically to 2D EBSD cross-sections. This approach overcomes the challenge of acquiring 3D EBSD data. Furthermore, it turned out that this modeling approach is resistant to overfitting, even when just a small amount of EBSD data is used for model calibration. Finally, both models are combined to generate synthetic, but realistic NMC811 particles, providing a valuable data basis for electrochemical and mechanical simulations [1]. By varying model parameters, this allows for the investigation of structure-property relationships for NMC particles that have not yet been measured or even produced [4].

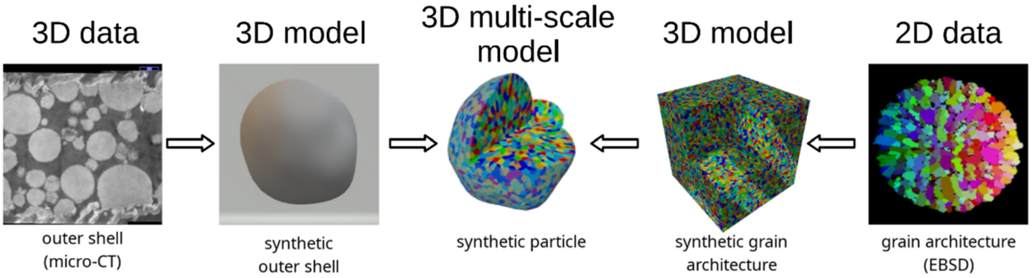


Figure 1: Systematic representation of the modeling approach

References:

1. J. Allen, P.J. Weddle, A. Verma, A. Mallarapu, F. Usseglio-Viretta, D.P. Finegan, A. Colclasure, W. Mai, V. Schmidt, O. Furat, D. Diercks, T. Tanim, K. Smith, *J. Power Sources* **512** (2021), 230415.
2. L. Fuchs, O. Furat, D. P. Finegan, P. Weddle, K. Smith, V. Schmidt, 2024, Multi-scale modeling of anisotropic NMC particles, combining methods of spatial stochastics and generative neural networks, Working paper.
3. O. Furat, L. Petrich, D.P. Finegan, D. Diercks, F. Usseglio-Viretta, K. Smith, V. Schmidt, *npj Comput. Mater.* **7** (2021), 105
4. B. Prifling, M. Röding, P. Townsend, M. Neumann, V. Schmidt, *Front. Mater.* **8** (2021), 786502.

# P40. Kinetic Monte Carlo Simulation Study on the Influence of Solubility on the Initial SEI Growth

S. Zappe, F. Schomburg, F. Röder
*Bavarian Center for Battery Technology (BayBatt), University of Bayreuth*
*Weiherstr. 26, 95448 Bayreuth, Germany*
*fridolin.roeder@uni-bayreuth.de*

To improve lithium-ion batteries in terms of capacity, cycle stability and safety, the properties and growth mechanisms of the solid electrolyte interface (SEI) must be better understood [1]. During the formation multiple reduction reactions appear at the electrolyte|electrode interface and lead to the formation of the SEI. This process depends on many process and material properties, e.g., current, voltage and electrolyte composition. The initial formation occurs in two subsequent steps as recent studies indicate [2, 3]. Upon reduction, the SEI species first diffuse into the electrolyte and form agglomerates. Afterwards the agglomerates deposit on the particle surface and hinder further reduction reactions. The solubility of the agglomerates is a key factor in this process but has barely been investigated. However, it must be considered to determine material-dependent formation protocols.

To study the impact of the solubility a kinetic Monte Carlo (kMC) model is developed. The presented kMC-based multiscale method enables to model chemical processes at the atomistic level while taking macroscopic influencing factors into account. This allows to reduce simulation time, allowing to perform large simulation studies, while maintaining detailed insights. The model is applied in a simulation study and comprises various decomposition reactions leading to multiple inorganic solid components and considers their solubility. In the simulation study, the impact of the SEI species solubilities in the electrolyte on the layer growth and the final interphase structure is investigated. To assess the influence of solubility, the final SEI composition and morphology is evaluated based on criteria, such as its porosity, for a slow and a fast-charging formation protocol. In Figure 1, results for one simulation scenario are shown. The presented simulation results reveal that a faster decrease in anode potential at the beginning of the process leads to much higher reaction rates and saturations. However, upon supersaturation of the electrolyte, a rapid precipitation and layer growth is observed. Furthermore, the results indicate that the solubility of the reaction products in the electrolyte as well as the applied electrochemical protocol influence the layer structure resulting in varying interphase layer properties.

To conclude, a kMC-based multiscale model to study the impact of the SEI solubility on the formation process is presented, which balances molecular details and computational effort. Exemplary results of a simulation study are shown, which illustrate the influence of the solubility and the formation protocol on the resulting SEI composition. The shown model and insights are another step towards a knowledge-based design of material-specific formation protocols.

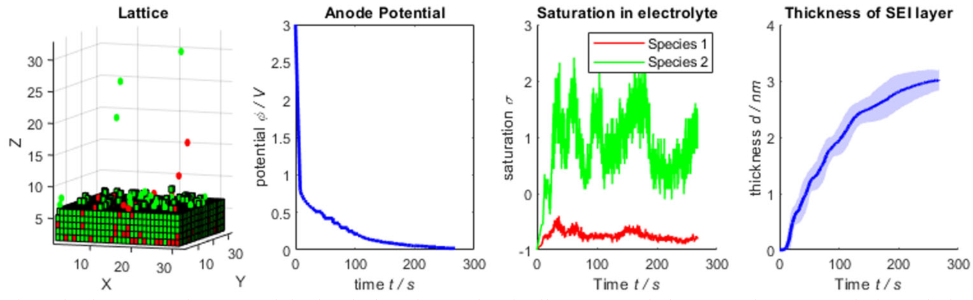


Figure 1: Simulation results provide insights into the influence of the anode potential and the supersaturation in the electrolyte on the SEI growth.

References:
1. S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, and D. L. Wood, *Carbon* 105 (2016), 52-76
2. K. Ushirogata, K. Sodeyama, Z. Futera, Y. Tateyama, and Y. Okuno, *J. Electrochem. Soc.* 14 (2015), A2670-A2678
3. M. Esmaeilpour, S. Jana, H. Li, M. Soleymanibrojeni, and W. Wenzel, *Advanced Energy Materials* 13(14) (2023), 2203966

# P41. Interface Evolution in the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2/Li_6PS_5Cl$ Solid-State Battery Cathodes During Cycling

B. Lelotte[1], V. Pelé[2], C. Jordy[2], C. A. F. Vaz[3], C. N. Borca[3], T. Huthwelker[3], L. Gubler[1], M. El Kazzi[1]
[1]*Electrochemistry laboratory, Paul Scherrer Institut, Switzerland*
[2]*SAFT, Direction de la Recherche, France*
[3]*Swiss Light Source, Paul Scherrer Institut, Switzerland*
*barthelemy.lelotte@psi.ch*

All-solid-state Li-ion batteries (ASSBs) are closer than ever to wide-scale applications. They bring improved safety and increased energy density if the compact solid electrolyte (SE) can mitigate the interface degradation at high operating voltage [1] and prevent the Li metal dendrite growth. Therefore, there is an urgent need to understanding the degradation reaction mechanism taking place at SE/electrodes buried interfaces which is extremely challenging to probe. Such a study requires the use of non-destructive surface sensitive techniques capable to provide chemical analysis with depth profile sensitivity combined with an excellent lateral resolution to discriminate signals originating from the the different particles (active materials, SE and conductive carbon additive) composing the working electrode (WE) [2,3].

In this contribution, we present a detailed study of the interface in the $NCM_{622}$/LPSCl/C WE cycled up to 4.3 V vs. $Li^+/Li$. We observe from the galvanostatic cycling (Figure 1**a**) and impedance spectroscopy (inset) a low coulombic efficiency of 72% during the 1st cycle and a gradual increase of the impedance with the number of cycles, respectively. To explain the electrochemical performance, the chemical evolution of the interface is monitored *ex situ* by soft and tender-X-ray absorption spectroscopy (XAS) at the transition metal (TM) L-edges, and P, S K-edges at the Swiss Light Source. The XAS acquisition is performed by combining measurements with the (i) high lateral resolution and surface sensitivity of X-ray photoemission electron microscopy (XPEEM) and (ii) depth profiling by total electron yield (TEY) and total fluorescence yield (TFY) detection modes. Our results demonstrate that the 1st irreversible charge is mainly associated with LPSCl oxidation but the gradual impedance increase is caused also by the surface degradation on the $NCM_{622}$ leading to the formation of inactive layer rich in reduced TMs species and oxides (Figure 1**b**,**c**).

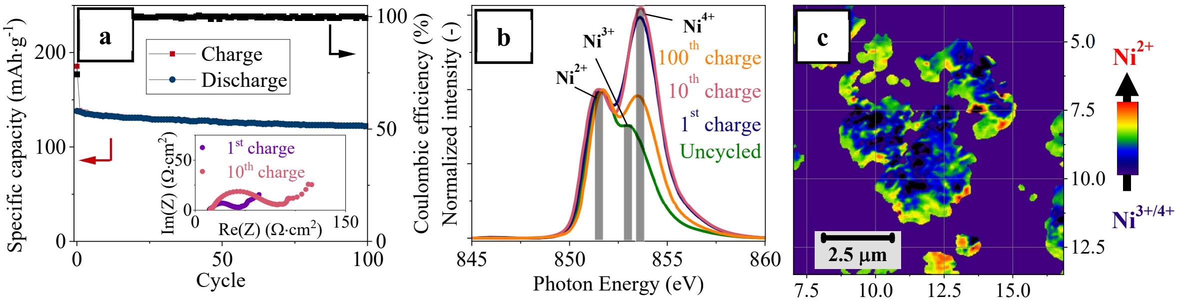


Figure 1: **a** Galvanostatic extended cycling of the $NCM_{622}/LPSCl/InLi_x$ and EIS. **b** XAS spectra of the Ni L-edge in TEY. **c** XPEEM mapping of the Ni oxidation state at the Ni L-edge after 10 cycles.

References:
1. Q. Zhao, S. Stalin, C.-Z. Zhao, L. A. Archer, Designing solid-state electrolytes for safe, energy-dense batteries, Nat. Mater. 2020, 5 229-252
2. D. H. S. Tan, A., Banerjee, Z. Chen, Y. S. Meng, From nanoscale interface characterization to sustainable energy storage using all-solid-state batteries, Nat. Nano. 2020, 15, 170-180
3. X. Wu, M. Mirolo, C. A. F. Vaz, P. Novák, M. El Kazzi., Reactivity and Potential Profile across the Electrochemical $LiCoO_2$–$Li_3PS_4$ Interface Probed by Operando X-ray Photoelectron Spectroscopy, ACS Appl. Mater. Interfaces 2021, 13, 36, 42670-42681

# P42. Grey-box Modelling of Lithium-ion Batteries and Their Slow Voltage Dynamics with Neural Ordinary Differential Equations

Jennifer Brucker, Wolfgang G. Bessler, Rainer Gasper
*Offenburg University of Applied Sciences, Institute of Sustainable Energy Systems*
*77652 Offenburg, Germany*
*jennifer.brucker@hs-offenburg.de*

Lithium-ion batteries exhibit slow voltage dynamics on the minute scale. They show complex behaviour during dynamic profiles such as driving cycles or pulse tests, and slow relaxation times when measuring the true open-circuit voltage. These dynamics are also observable in the low-frequency behaviour of electrochemical impedance spectra. Modelling slow dynamics presents a challenge due to the multiple potential causes involved, including transport processes on the microscale (diffusion inside active material particles), mesoscale (diffusion of lithium ions), and macroscale (thermal gradients). Pure Fickian diffusion results in a differential equation of fractional order in the time domain, which is difficult to handle [1].

We present a grey-box model of a lithium-ion battery cell including the slow voltage dynamics. We combine physical and data-driven modelling techniques using neural networks, specifically neural ordinary differential equations. The model structure is based on an equivalent circuit, where the voltage drop resulting from diffusion is determined by a grey-box model [2]. The grey-box model is inspired by a combination of Fickian diffusion in a spherical particle and the Nernst equation. Fickian diffusion in the active material particles that are assumed spherical is described by a partial differential equation. We used the finite-volume method for discretization along the radius of the sphere. To keep computation time short, we used five discretization volumes. The distribution of these volumes along the radius was treated as a degree of freedom. We used a neural network to represent the diffusion coefficient and its concentration dependency. Additional neural networks are used to represent a series resistance as function of current and state of charge. The grey-box model of the battery is shown in Figure 1.

Model-to-experiment comparisons were performed using experimental full cycle data and data from pulse tests from a 180 Ah large-format lithium-ion battery cell with lithium iron phosphate chemistry as training data. The testing data represents the dynamic load profile of a home storage system. The grey-box model captures the battery voltage dynamics well for medium values of state of charge. However, for nearly empty or full batteries the voltage approximation deviates from the measured values.

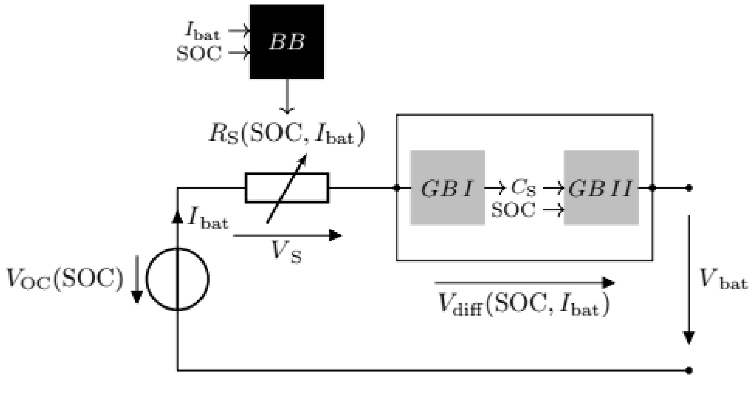


Figure 1: Equivalent circuit model of a battery consisting of a voltage source $V_{\text{OC}}$ dependent on state of charge (SOC), a series resistor $R_{\text{S}}$ dependent on state of charge and current, and a grey-box model for the slow voltage dynamics $V_{\text{diff}}$. The series ohmic resistance is approximated by a black-box model. The grey-box model was taken from Ref. [2].

References:
1. M. Hu, Y. Li, S. Li, C. Fu, D. Qin, Z. Li, Energy 165 (2018) 153-163.
2. J. Brucker, W.G. Bessler, R. Gasper, J. Electrochem. Soc. 170 (2023) 120537.

(abstract withdrawn)

(abstract withdrawn)

# P45. Methods of Machine Learning and Stochastic Modeling for the Structural Characterization of Functional Battery Materials at Various Length Scales

Philipp Rieder[1], Orkun Furat[1], Peter Weddle[2], Jeffery Allen[2], Donal P. Finegan[2], Kandler Smith[2], Volker Schmidt[1]
[1]*Ulm University, Helmholtzstraße 18, 89069 Ulm, Germany*
[2]*National Renewable Energy Laboratory, 15013 Denver W Parkway, Golden, CO 80401, USA*
*philipp.rieder@uni-ulm.de*

Microscopy techniques like scanning electron microscopy (SEM) or X-ray computed tomography (CT) provide detailed image data of the 3D morphology of functional battery materials at various length scales. This allows for the investigation of structure-property relationships, i.e., how the nano-/microstructure influences effective material properties, like electrochemical behavior. However, the structural characterization by means of tomographic image data often entails nontrivial measurement and processing tasks. In this contribution, a workflow is shown for the holistic structural characterization of active material (AM) particles in Li-ion battery electrodes by means of spatial stochastic modeling [1, 2], see Figure 1. For this purpose, image data is acquired at different length scales and with various measurement techniques, namely, CT, SEM and focused ion beam (FIB) - electron backscatter diffraction (EBSD). Then, a stochastic geometry model for AM particles is calibrated to image data, overcoming the limitations of the different imaging techniques (e.g., resolution vs. field of view). Speaking more precisely, the model is fitted using CT data for the outer shell of AM particles, and, in a second step, 3D FIB-EBSD data for the polycrystalline grain architecture as well as 2D SEM data for intergranular cracks. This model can be used to perform virtual scenario analyses, i.e., to generate numerous digital twins of AM particles with statistically similar shape, grain architecture and cracking behavior as observed in measured image data. These digital twins can be utilized as geometry input for numerical (dis)charging simulations to investigate their degradation behavior, e.g., AM particle cracking due to repeated cycling [3].

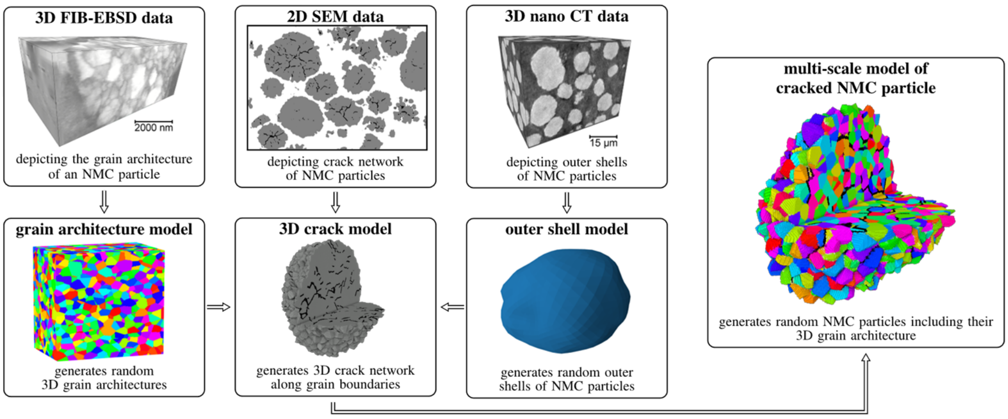


Figure 1: Workflow for the generation of virtual, but realistic cracked NMC particles. 3D FIB-EBSD data and 3D nano-CT data serve as input for the grain architecture model and the outer shell model, respectively [1]. Using 2D SEM data, realizations of these models are further processed to introduce a crack network along the grain boundaries [2].

References:
1. O. Furat, L. Petrich, D.P. Finegan, D. Diercks, F. Usseglio-Viretta, K. Smith, V. Schmidt, *npj Comput. Mater.* **7** (2021), 105
2. P. Rieder, O. Furat, J. Allen, P. Weddle, D. P. Finegan, K. Smith, V. Schmidt, 2024, Stochastic 3D reconstruction of cracked polycrystalline NMC particles using 2D SEM data, Working paper.
3. J. Allen, P.J. Weddle, A. Verma, A. Mallarapu, F. Usseglio-Viretta, D.P. Finegan, A. Colclasure, W. Mai, V. Schmidt, O. Furat, D. Diercks, T. Tanim, K. Smith, *J. Power Sources* **512** (2021), 230415.

(contribution by W.G. Bessler et al. moved to Oral Presentations section)

# P47. Modeling of the Battery Electrode Drying Process

Marcel Weichel[1,2], M. Reder[2,3], S. Daubner[1,2], D. Schneider[2,3], B. Nestler[1,2,3]
*[1]Institute of Nanotechnology - Microstructure Simulations (INT-MSS), Karlsruher Institute of Technology, Straße am Forum 7, 76131 Karlsruhe*
*[2]Institute for Applied Materials - Microstructure Modelling and Simulation (IAM-MMS), Karlsruher Institute of Technology, Straße am Forum 7, 76131 Karlsruhe*
*[3]Instiute of Digital Material Science (IDM), Karlsruhe University of Applied Sciences, Moltkestrasse 30, 76133 Karlsruhe, Germany*
*marcel.weichel@kit.edu*

The performance and degradation behaviour of battery systems are significantly affected by the electrode microstructure [1]. Therefore, actively designing the microstructure properties of such electrodes is a key point to solve future challenges concerning capacity and rate capability in Li and post-Li battery systems. This talk addresses simulations of the drying process for battery electrode manufacturing, which can support the active microstructure design, since the digital representations yield insights of the process. In particular, spatially resolved fields regarding information about the binder distribution, liquid-gas surface and its velocity are obtained, which contains information hardly accessible via experiments. Therefore, the impact of different morphologies on the drying process as well as predictions about the resulting microstructure are attainable through simulations.
During the drying process, numerous physical effects and their coupling need to be covered. This poses challenges for modeling involving multi-phase flow in complex geometries, tracking of moving surfaces, capillary flow and binder transport. In order to address these challenges, the multi-phase field method [2] is employed and enhanced by modeling of the multiphase flow and the wetting behaviour according to [3]. The research data management software, Kadi4Mat [4], is utilized for efficient data handling. To automate the analysis of diverse microstructures and properties during the drying process, a workflow is integrated within the KadiStudio software [5]. This comprehensive workflow facilitates the direct import of SEM images, followed by the simulation of the drying process and subsequent analysis. The primary objective is to demonstrate the exemplary functionality of this procedure. Figure 1 shows preliminary results of the drying process of a nickel manganese cobalt cathode.

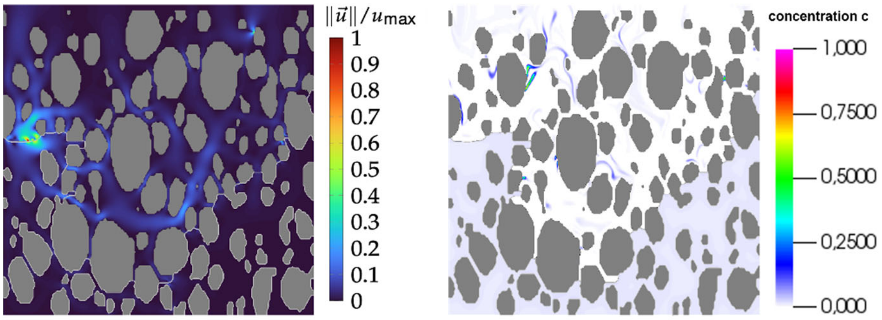


Figure 1: Preliminary results of drying process. (left) velocity and (right) binder concentration.

References:
1. Z. Liu and P. P. Mukherjee, J. Electrochem. Soc. 161(8) (2014) E3248-E3258.
2. B. Nestler, H. Garcke, B. Stinner, Phys. Rev. E 71 (2005) 041609.
3. M. Reder, P.W. Hoffrogge, D. Schneider, B. Nestler, Int. J. Numer. Methods Eng. 123 (2022) 3757-3780.
4. N. Brandt, L. Griem., C Herrmann, E. Schoof, G. Tosato, Y. Zhao, P. Zschumme, and M. Selzer, Data Sci. J. 20 (2021) 8
5. L. Griem, P. Zschumme, M. Laqua, N. Brandt, E. Schoof, P. Altschuh, M. Selzer, Data Sci. J. 21 (2022) 16

# P48. Replacing Microstructure Simulation with a Data-Driven Approach to Model Mechanical Degradation in Electrodes

N. Erhardt, H. Nirschl
*Institute of Mechanical Process Engineering and Mechanics,*
*Karlsruher Institute of Technology, Germany.*
*Nikolai.Erhardt@kit.edu*

A key element in the aging of batteries involves the mechanical deterioration of the battery electrodes. As ions intercalate into the active material particles of a lithium-ion battery, a concentration profile develops along the radial direction, influenced by transport properties and kinetics. The spatial constraints of intercalated ions give rise to mechanical stresses, leading to the degradation of the electrode.

Common cathode materials like Lithium Nickel Manganese Cobalt Oxide (NMC) or Lithium Iron Phosphate (LFP) undergo a shift from a lithium-poor phase to a lithium-rich phase during intercalation. Along this phase boundary, substantial mechanical stresses occur due to the irregularity of the concentration profile, resulting in particle fractures. This can cause electrical isolation and, consequently, the electrochemical inertization of the active particle material, resulting in diminished battery capacity on a macroscopic scale.

Simulating these processes poses computational challenges. Given the current computing capabilities, accurately simulating a sufficient number of cycles for a microstructure simulation describing transport processes within a battery is computationally impractical. Consequently, this study employs data-driven models. To predict radial concentration profiles within the particle, a physics-informed neural network (PINN) is beneficial, incorporating the transport equation into the extended cost function. Classical neural networks (ANN) are utilized to compute the electrical voltage of active material particles. These models are trained using results from microstructure simulations to develop a grey-box model, facilitating the integration of mechanical degradation into the electrode simulation.

Mechanical stresses and deteriorations are thus explored under various galvanostatic discharge rates to delineate an operationally robust window for the aging-resistant battery.

# P49. Pt-Doped Ceria-Zirconia as a Bi-Functional Catalyst for Gas Recombination and Radical Scavenging in PEM Water Electrolysis Cells

Zheyu Zhang[1], Andreas Mühlmann[2,3], Andrea Testino[2,4], Lorenz Gubler[1]
*[1] Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
*[2] Laboratory for Sustainable Energy Carriers and Processes, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
*[3] Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland*
*[4] STI SMX-GE, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*
*lorenz.gubler@psi.ch*

Proton exchange membrane (PEM) water electrolysis cells, when integrated with renewable electricity sources, offer promising potential for green hydrogen production. Challenges such as a pronounced level of hydrogen crossover in thin membranes and ionomer degradation due to radical attack pose concerns in the current technological development. The literature suggests that the use of ceria-zirconia and Pt individually can be beneficial, with the ceria-zirconia known to scavenge radicals and Pt to effectively recombine the crossover hydrogen gas [1,2]. Moreover, the concurrent addition of these two compounds in the membrane has been demonstrated to yield combined benefits, addressing both issues [3].

In this study, we report the successful synthesis and application of a bi-functional catalyst, Pt-doped $Ce_{0.5}Zr_{0.5}O_2$, exhibiting dual functionalities derived from its constituent components – ceria-zirconia and Pt. Two levels of Pt content, 0.5 and 5 wt.%, were selected relative to the ceria-zirconia amount. The corresponding nominal Pt loadings are 4 and 40 $\mu g_{Pt}/cm^2$, respectively, upon the incorporation of the catalyst into the membrane. At a differential pressure with 11 bar at the cathode and ambient pressure at the anode, the hydrogen in oxygen content in the anode gas stream was analysed for Pt (0.5 wt.%) – $Ce_{0.5}Zr_{0.5}O_2$ and Pt (5 wt.%) – $Ce_{0.5}Zr_{0.5}O_2$, with the latter demonstrating a more significant reduction when compared to the results obtained with a reference Nafion NR212 membrane. Constant current tests conducted for 100 hours at 2 A/cm$^2$ indicate that the fluoride release rates (FRRs) of both samples were lower than that of the solution-cast Nafion reference. Specifically, with the same nominal $Ce_{0.5}Zr_{0.5}O_2$ loading, the membrane with a higher Pt loading exhibits a higher FRR. This could be attributed to the enhanced rate of radical formation on Pt, which partially counterbalances the radical scavenging capacity of $Ce_{0.5}Zr_{0.5}O_2$. In summary, Pt (5 wt.%) – $Ce_{0.5}Zr_{0.5}O_2$ has been shown as a promising bi-functional catalyst, which leads to a reduced hydrogen crossover and ionomer degradation rate when incorporated in the Nafion membrane.

References:

1. P. Trogadas, J. Parrondo, V. Ramani, *ACS Appl. Mater. Interfaces.* **4** (2012) 5098-5102.
2. S. Garbe, U. Babic, E. Nilsson, T.J. Schmidt, L. Gubler, *J. Electrochem. Soc.* **166** (2019) F873-F875.
3. Z. Zhang, Z. Han, A. Testino, L. Gubler, *J. Electrochem. Soc.* **169** (2022) 104501.

(contribution by Y. Fischer et al. moved to Oral Presentations section)

# P51. Multi-Level Model-Approach: Future Powertrain Topologies for Fuel Cell-based Commercial Vehicles

Maximilian Röhe, René Berndt, Christian Bessai, Gunnar Prietzsch, Hubertus Ulmer, Ralf Wascheck
*IAV GmbH*
*Rockwellstraße 16, 38518 Gifhorn (GERMANY)*
*maximilian.roehe@iav.de*

Fuel cell (FC)-based drive systems represent a possible $CO_2$-free technology path, especially for commercial vehicles. Drive powers in the range of 200 to 400 kW are required depending on the application. To be able to provide these powers, a modularization strategy of individual FC systems into a powerful overall unit is one solution. Herein, a model-based study of possible variants of FC powertrains for heavy on-road commercial vehicles is shown including their optimization and evaluation using model-based tools regarding performance, efficiency, degradation, and costs.

The FC systems optimization and evaluation are based on the representative "VECTO Long Haul" cycle [1]. For simulation, the cycle serves as input to a longitudinal dynamic vehicle model (LVM), which determines the required electrical power to drive the cycle. Using a genetic algorithm, range and consumption are optimized using a fuel cell system model (fig. 1, left) depending on tank and battery size with the constraints of system mass and volume. Finally, the performance and efficiency behavior of the FC driven powertrain as well as the platinum catalyst degradation behavior are evaluated in a long-term simulation.

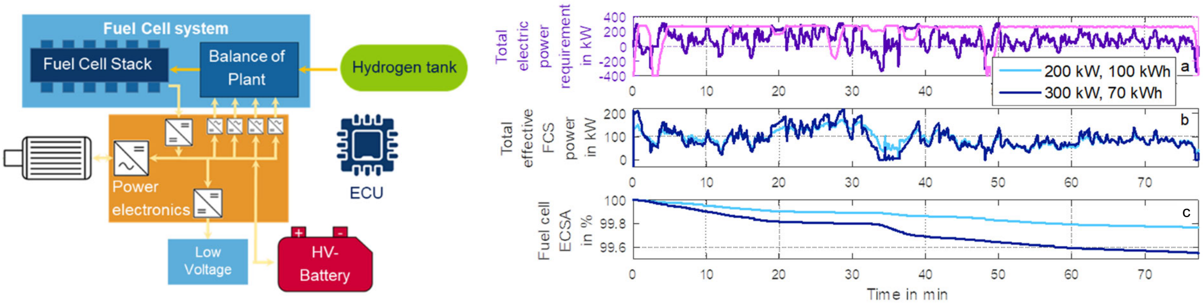


Figure 1: left: IAV simulation environment for the optimization of fuel cell powertrains; right: Simulation of the long-distance cycle, BoL for both system topologies (200 kW fuel cell system with 100 kWh battery and 300 kW fuel cell system with 70 kWh battery) [2].

With aid of the model, two different systems with a 200 kW and a 300 kW fuel cell respectively are compared. Selected time dependent simulation results of the begin-of-life (BoL) driving cycle for both system configurations are shown in fig. 1, right: As can be seen from (a), the driving profile results in a highly dynamic electrical power demand that includes acceleration and braking phases. The control unit distributes the total power demand to the FC system (b) and battery, reducing the dynamics of FC operation. A higher degradation of FC catalyst (c) is evident for the 300 kW FC variant, resulting from the overall higher cell voltage and the FC dynamics.

The long-term simulation of 10,000 hours reveals that the platinum catalyst surface decreases by 33 % for the 200 kW FC system and by 44 % for the 300 kW system. However, due to the lower overvoltage, the 300 kW FC system remains more efficient over the life cycle and more favorable in consideration of the purchase cost of the fuel cell system and hydrogen costs over the life cycle.

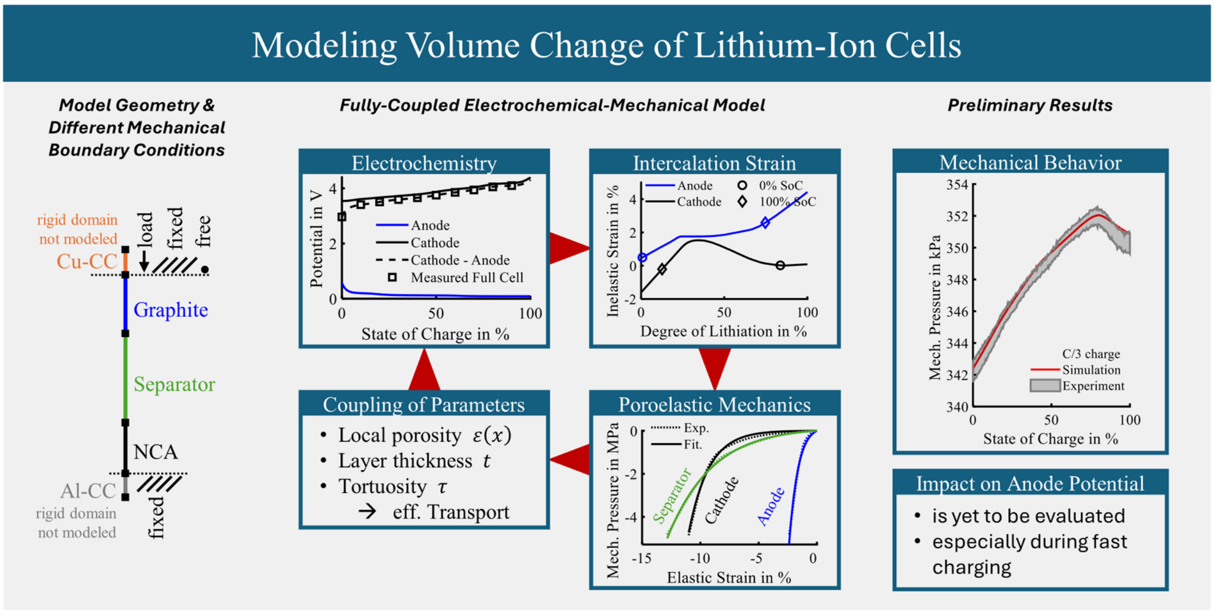
References:

1. Rexeis et. al, *VECTO tool development: Completion of methodology to simulate Heavy Duty Vehicles' fuel consumption and CO2 emissions*, Report No. I 15/17/Rex EM-I 2013/08 1670, 2017.
2. Bessai et al., *MTZ*, 02-03|2024, 2024, 16-23, accepted manuscript.

# P52. Modeling the Volume Change of Lithium-Ion Battery Cells due to Lithium Intercalation and External Pressure with Subsequent Porosity Changes

A. Durdel[1], J. Brehm[1,2], V. Elender[2], A. Aufschläger[1], M. Altmann[2], P. Kotter[2], A. Jossen[1]
[1] *Technical University of Munich, School of Engineering and Design, Department of Energy and Process Engineering, Chair of Electrical Energy Storage Technology; Arcisstraße 21, 80333 Munich, Germany*
[2] *Bayerische Motorenwerke AG, Petuelring 130, 80788, Munich, Germany*
*axel.durdel@tum.de*

Active materials in lithium-ion batteries experience (de-)intercalation-induced volumetric work during cycling [1]. This volumetric work might cause a change in coating thickness, porosity, or both [2], posing a major challenge developing high-performance and long-lasting batteries. Here, we present a novel p2D-mechanical modeling approach to predict the electrochemically induced volume change and subsequent local porosity change of lithium-ion battery cells. The model combines the physics-based electrochemical reaction using the Doyle-Fuller-Newman model [3] with poroelastic mechanical deformation. The model is parametrized, fitted, and validated using experimental data obtained from different types of lithium-ion battery cells. Preliminary results are promising and show satisfying overlap with experimental data. The model also reveals the underlying electrochemical and mechanical mechanisms that lead to the volume change, which can help design better electrode materials and cell structures. Our study demonstrates the potential of the p2D modeling approach in predicting the complex electrochemical-mechanical behavior of lithium-ion battery cells, which can significantly accelerate the development of high-performance and long-lasting batteries for various applications.



- Local porosity $\varepsilon(x)$
- Layer thickness $t$
- Tortuosity $\tau$
  → eff. Transport

- is yet to be evaluated
- especially during fast charging

Figure 1: (left) Schematic of the one-dimensional model geometry including mechanical boundary conditions. (center) Schematic showing the coupling of the electrochemical model and poroelastic mechanical model. (right) Preliminary results and outlook.

References:
1. Franz B. Spingler *et al.* 2021 *J. Electrochem. Soc.* **168** 040515
2. Parthasarathy M. Gomadam and John W. Weidner 2006 *J. Electrochem. Soc.* **153** A179
3. Marc Doyle *et al.* 1993 *J. Electrochem. Soc.* **140** 1526

# P53. Phase-field Study of Intercalation Processes in LFP-platelets

P. Lorson[1], S. Daubner[1], J. Naumann[1], R. Schoof[2], M. Kamlah[1]
[1] *Institute for Applied Materials, KIT, Karlsruhe, Germany*
[2] *Institute for Applied and Numerical Mathematics, KIT, Karlsruhe, Germany*
*paula.lorson@kit.edu*

Lithium iron phosphate (LFP) has found widespread application in commercial batteries and is a material that undergoes phase separation during cycling. Computational studies rely strongly on the underlying assumptions. Most battery models assume Fickian diffusion, but this does not reflect the phase separation behaviour of LFP. Therefore, it is necessary to develop models which capture the essential effects while being computationally efficient.

In this work, a one particle model of a LFP-platelet with a large ac-facet is presented, which can be seen in Figure 1a). Lithium can only intercalate via the ac-facets. A step-wise dimensional reduction to a one-dimensional system is possible due to the assumption of an infinitively fast diffusion within the diffusion tunnels that are perpendicular to the ac-facets, as well as the assumption of symmetry with respect to the width of the platelet [1] which is shown in Figure 1b) and c). The phase separation can be described by a model based on the works of Cahn and Hilliard [2].

The model was implemented with a constant intercalation reaction in Comsol Multiphysics and in deal.ii [3]. Figure 2 shows an exemplary normalized concentration profile within the particle at different times during discharge. Spontaneous phase separation takes place which is followed by a coarsening process. The intercalation reaction predominantly takes place at the phase boundaries filling the particle. A parameter study was performed to understand the influence of various model parameters. This study suggests that a fast diffusion within the ac plane promotes phase separation while a faster insertion reaction and higher surface energy can lead to a suppression of phase separation. The goal of this work is the integration of the particle model into cell scale simulations e.g. via the Doyle-Newman-Fuller-model [4].

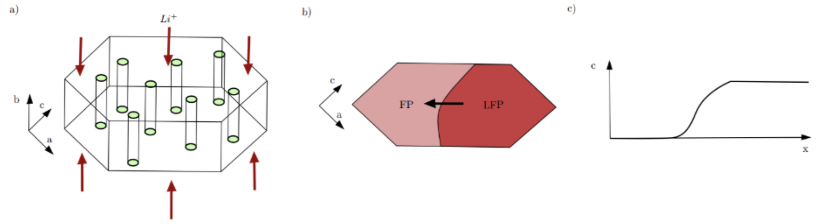


Figure 1: a) 3D Platelet b) 2D concentration profile c) 1D concentration profile.

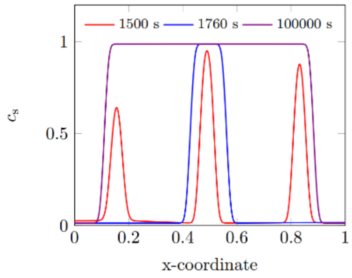


Figure 2: Normalized concentration profile for a very slow intercalation reaction for different times.

References:

1. P. Bai, D. A. Cogswell, and M. Z. Bazant, *Suppression of phase separation in $LiFePO_4$ nanoparticles during battery discharge*, Nano Letters, 11(11) (2011) 4890-4896
2. J.W. Cahn, *On spinodal decomposititon*, Acta Metallurgica, 9(9) (1961) 795-801
3. D. Arndt, W. Bangerth, M. Bergbauer, M. Feder, M. Fehling, J. Heinz, T. Heister, L. Heltai, M. Kronbichler, M. Maier, P. Munch, J.-P. Pelteret, B. Trucksin, D. Wells, S. Zampini, *The deal.II Library, Version 9.5*, Journal of Numerical Mathematics, 31(3) (2023) 231-246
4. M. Doyle, T. F. Fuller, and J. Newman, *Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell*, Journal of The Electrochem. Soc., 140(6) (1993) 1526-1533

# P54. Impact of Polymers on Hybrid Solid-State Battery Performance: Modeling and Simulation

M. Scheller[1,2], A. Durdel[1], A. Frank[1], A. Jossen[1]
*[1]Technical University of Munich (TUM), TUM School of Engineering and Design, Department of Energy and Process Engineering, Chair of Electrical Energy Storage Technology, Munich, Germany*
*[2]TUMint Energy Research GmbH, Garching b. München, Germany*
*maximilian.scheller@tum.de*

Recent literature highlights the advantages of incorporating solid-polymer-electrolytes (SPEs) in solid-state batteries (SSB). SPEs might improve the mechanical contact between the solid electrolyte (SE) and the active material (AM), compensate volume changes of the AM, or prevent electrochemical instabilities [1, 2]. Still, drawbacks regarding cell performance are expected due to additional polymer-related polarization. In this work, the pseudo-two-dimensional (p2D) physicochemical model is extended to account for Li-ion transport in the SPE and in a ceramic SE, as well as for the charge transfer at the SPE|ceramic interface using Butler-Volmer-type kinetics [3, 4]. A cell design using the SPE as a thin coating on the anode and cathode AM is considered. In Fig. 1 the model approach and the desired cell design are depicted. Polarization analysis discloses a dominant polarization contribution from the SPE|ceramic charge transfer and facilitation of charge transfer with increasing discharge C-rate. Variance-based global sensitivity analyses demonstrate that as the exchange current density between SPE and ceramic SE increases, polarization losses exhibit an exponential-like reduction. Additionally, the radius of the active material particles within the composite cathode exerts a significant and dominant influence on cell performance. Based on these findings, different performance-optimized cell designs are simulated to give a perspective for future work.

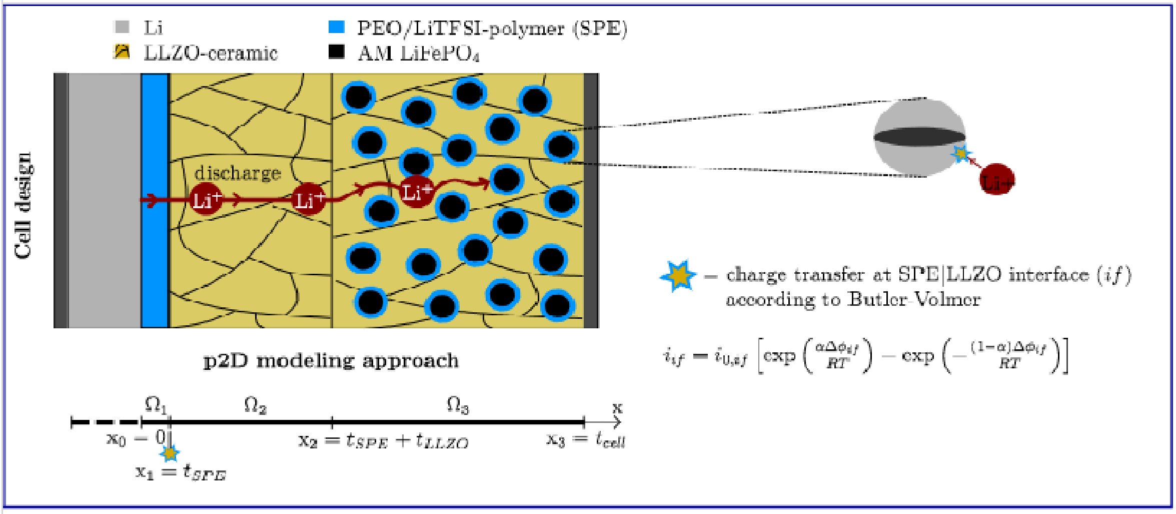


Figure 1: Schematic of the cell design consisting of a Li-metal anode, a ceramic SE separator (domain $\Omega_2$), and an LLZO/LFP composite cathode (domain $\Omega_3$). As highlighted in blue, an interlayer of SPE (domain: $\Omega_1$) is incorporated on the Li-metal anode and as a coating on LFP particles.

References:

1. S. Sen, E. Trevisanello, E. Niemöller, B.-X. Shi, F. J. Simon and F. H. Richter, *J. Mater. Chem. A*, 9(35), 1870-8732 (2021).
2. M. Ihrig, R. Ye, A. M. Laptev, D. Grüner, R. Guerdelli, W. S. Scheld, M. Finsterbusch, H.-D. Wiemhöfer, D. Fattakhova-Rohlfing and O. Guillon, *ACS Appl. Energy Mater.*, 4(10), 10428-10432 (2021).
3. M. Schleutker, J. Bahner, C.-L. Tsai, D. Stolten and C. Korte, *Physical Chemistry Chemical Physics: PCCP,* 19(39), 26596-26605 (2017).
4. D. Brogioli, F. Langer, R. Kun and F. La Mantia, *ACS Applied Materials & Interfaces,* 11(12), 11999-12007 (2019).

# P55. Multiscale Reaction Modeling via a Subgrid Approach for the Lattice Boltzmann Method

Julius Weinmiller, Benjamin Kellers, Timo Danner, Arnulf Latz
*German Aerospace Center (DLR) at the Helmholtz Institute Ulm (HIU)*
*Wilhelm-Runge-Str. 10, 89081 Ulm, GERMANY*
*julius.weinmiller@dlr.de*

Many electrochemical effects impact processes of interest over multiple length scales. Examples in the field of batteries and fuel cells are for instance nucleation and growth, occurring in lithium-sulfur batteries [1], or (electro)-chemical reactions at platinum nano-particles in fuel cells [2]. Understanding the impacts across length scales is vital to understanding a system at a whole. For that, computational simulations can provide detailed insight. For mesoscopic problems, lattice Boltzmann methods (LBM) have seen increasing usage due to their sound physical basis and efficient computational parallelization [2,3].

However, accurate simulation of multiple length scales requires spatial resolution at the smallest scale, which quickly becomes too expensive to compute the relevant meso- or macroscopic processes. A solution is to develop subgrid models for the smallest scales, while fully resolving the larger scales. Despite the relevance for multiple applications, this approach has been implemented in only a simplified manner to reactive boundaries in LBM [3,4].

In this contribution, we present a novel composite dynamics framework developed within the lattice Boltzmann method. This enables the simulation of multiple scales, making LBM more versatile in simulating mesoscopic phenomena while including nanoscopic effects.

Our model has been applied to simulate and study nucleation and growth in porous cathodes of lithium-sulfur batteries, see Fig. 1. The simulation results successfully capture the nucleation phenomena, simulating subgrid nucleation and growth, and subsequent grid scale growth. This study elucidates effects such as surface passivation, and thus aids in developing better battery systems in the future.

**Acknowledgements:** Funded by the Federal Ministry of Education and Research with the SulForFlight project 03XP0491

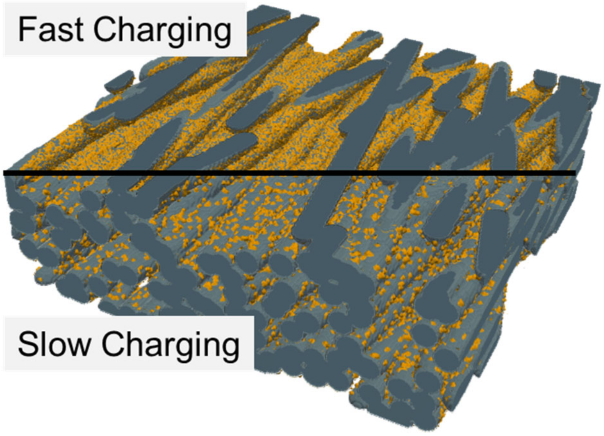


Figure 1: Sulfur growth (yellow) on carbon fiber cathode (grey) for fast and slow charging rates of lithium-sulfur batteries at the same charge transfer.

References:
1. Danner, T.; Latz, A., *Electrochim. Acta* **2019**, 322, 134719. DOI: 10.1016/j.electacta.2019.134719
2. Jahnke, T.; Futter, G.; Latz, A.; et al., *J. Power Sources.* **2016**, 304, 207-233. DOI: 10.1016/j.jpowsour.2015.11.041
3. Fang, W.; Qiao, R.; Kang, Q.; Tao, Q., Int. Commun. Heat Mass Transf. **2021**, 129, 105740 DOI: 10.1016/j.icheatmasstransfer.2021.105740
4. Fazeli, H.; Masoudi, M.; Patel, R.; et al., *ACS Earth Space Chem.* **2020,** 4(2), 249-260. DOI: 10.1021/acsearthspacechem.9b00290

# P56. Influence of Partially Constricted Flow Channels (*Bottlenecks*) on Polymer Electrolyte Fuel Cell Performance

P. Balestriere, A. Menard, D. Belin
*Symbio, 10 rue Specia 69190 Saint-Fons, France*
*pierrick.balestriere@symbio.one*

The effectiveness of polymer electrolyte fuel cells (PEFCs) greatly relies on the design of the flow field, significantly impacting the distribution of reactant concentration, pressure drops, local current density, among other factors. Improving this aspect is crucial for PEFCs to be commercially viable. Within a cell, the gas diffusion layer (GDL) serves to establish a uniform distribution of reactant concentration over the active area and facilitates the collection of electronic current. However, the oxygen concentration could be relatively small under the rib, adversely impacting the cell's performance.

Comprehensive studies have been conducted to achieve sufficient reactant supply, efficient water removal, and uniform distribution of physical variables of interest, thereby enhancing overall cell performance [1], [2], [3].

In order to enhance cathode gas transfer in both the in-plane and through-plane directions, a flow field with a partially constricted design - named in the following *bottleneck* - was evaluated, as Toyota's recently introduced flow field for the second-generation Mirai vehicle. This study directly analysed through simulation how different narrowed structure shapes in flow fields affect cell performance, potentially aiding cell design.

The software COMSOL was used to solve the equations in 3D. Solving the fluid dynamics and electrochemical equations, gas concentrations and current density were established for a given cell voltage. It is showed that gas channels featuring bottlenecks demonstrate improved performance as they facilitate a portion of the reactant gas to enter the GDL, thereby enhancing mass transfer. Bottleneck geometries influence on performance will be further discussed.

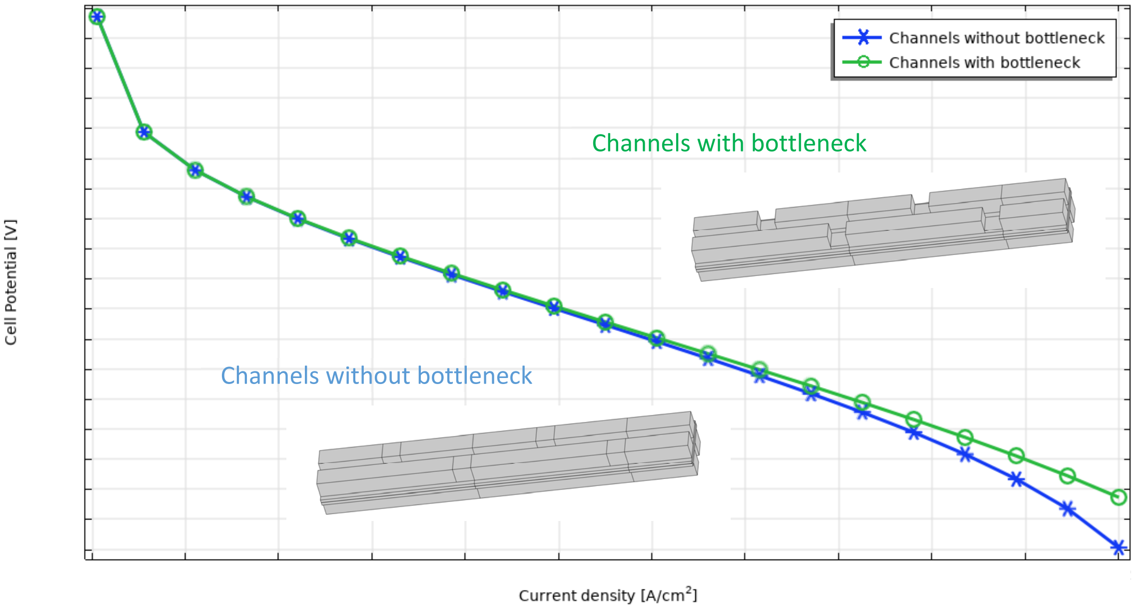


Figure 1: Polarization curves for 2 different geometries

References:

1. Yoshizumi TKHA et al, Development of high-performance FC stack for the new MIRAI, *SAE Technical Paper*, 2021
2. Wang Y et al, Numerical investigation of tapered flow field configurations for enhanced polymer electrolyte membrane fuel cell performance. *Appl Energy*, 2022; 306:118021
3. Yulei Ma et al 2022 *Meet. Abstr.* MA2022-02 1454

# P57. Lattice Boltzmann Simulation of PEMFC Catalyst Degradation through Electrochemical Ostwald Ripening

Alina T. Anzaldo G.[1], Arnulf Latz[1, 2], Thomas Jahnke[1]
[1] *German Aerospace Center (DLR), Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany*
[2] *Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Albert-Einstein-Allee 11, 89081 Ulm, Germany*
*alinatlaneci.anzaldogrundler@dlr.de*

Among other factors, achieving CO2 savings targets relies on addressing high-power vehicles, wherein Polymer Electrolyte Membrane Fuel Cells (PEMFCs) emerge as a promising alternative for emission reduction. However, their implementation demands substantial research efforts. PEMFCs must endure higher temperatures and exhibit extended life time, necessitating thorough degradation analyses. Experimental studies face time constraints, making simulations a valuable tool to complement investigations, significantly reducing development time and costs. Furthermore, these validated models open pathways to optimize technology advancements.

This project focuses on simulating the degradation of PEMFC catalysts, employing the Lattice Boltzmann Method (LBM) and grounded in the PALABOS library [1]. The LBM approach allows for microstructure resolved simulations of the degradation processes and therefore for investigating the influence of catalyst layer material properties. Specifically, the study centers on modeling Electrochemical Ostwald Ripening—a phenomenon wherein smaller nanoparticles of Pt dissolve and platinum ions precipitate on larger Pt nanoparticles (see Figure 1). As this process unfolds, the catalyst's active surface area diminishes, marking its degradation. The dissolution and precipitation are described using local reactive boundary conditions [2] coupled to the diffusion of platinum ions between the particles.

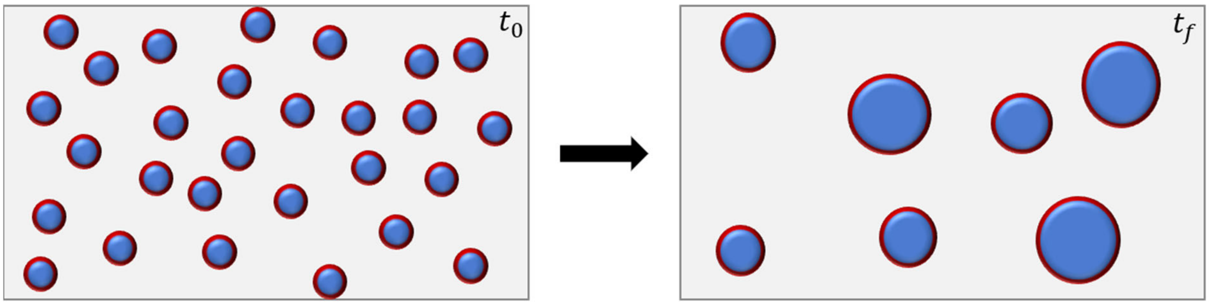


Figure 1: Schematic representation of Electrochemical Ostwald Ripening: The blue spheres in the illustration depict Pt nanoparticles, while the red contour represents the active surface of the catalyst. The diagram illustrates the process wherein larger nanoparticles grow and smaller ones dissolve, resulting in a reduction of the active surface.

*The project PEMTASTIC is supported by the Clean Hydrogen Partnership and its members Hydrogen Europe and Hydrogen Europe Research under the Grant Agreement 101101433.*

References:

1. J. Latt, O. Malaspinas, D. Kontaxakis, A. Parmigiani, D. Lagrava, F. Brogi, M. B. Belgacem, Y. Thorimbert, S. Leclaire, S. Li, F. Marson, J. Lemus, C. Kotsalos, R. Conradin, C. Coreixas, R. Petkantchin, F. Raynaud, J. Beny, B. Chopard, Palabos: Parallel Lattice Boltzmann Solver, *Computers & Mathematics with Applications,* **81** (2021), 0898-1221
2. J. Weinmiller, M. P. Lautenschlaeger, B. Kellers, R. Danner, A. Latz, *General Local Reactive Boundary Condition for Dissolution and Precipitation using the Lattice Boltzmann Method*, arXiv:2306.10794, (2023)

# P58. PEM FCEV Cold Start Control Strategy Investigation of Digital Twin Based on Multi-Physics System Simulation

Christian Altenhofen[1], Navin Fogla[2], Jake How[2]
[1] *Gamma Technologies GmbH, Stuttgart, Germany*
[2] *Gamma Technologies LLC, Westmont, USA*
*altenhofen@gtisoft.com*

The ability for a fuel cell vehicle (FCEV) to start under sub-zero ambient temperatures is critical for the adoption of the technology in the mobility industry.

Challenges associated with such startups include reduced reactant diffusion and kinetics, and the buildup of ice which can further limit species transport and lead to degradation. Many different cold start strategies can be enabled, and physical testing of this large design space is expensive and time consuming, particularly under these extreme conditions which are prone to damaging equipment. This presentation demonstrates how the multi-physics simulation software GT-SUITE is used to analyze and optimize various warm up procedures.

The PEM fuel cell model in GT-SUITE combines fluid, thermal, and electrochemical physics within a transient, vehicle simulation. The phase change of water between vapor, liquid and ice is captured allowing detailed investigations of transport limitations within the MEA. [1] This study evaluates a 100 kW fuel cell stack in a sedan-type vehicle and evaluates the effect of various parameters, including current and voltage ramp rates, reactant stoichiometry, and external heating. Additionally different starting conditions based on shut-down strategies will be evaluated. Successful control strategies bring the fuel cell up to 50% of rated power without failing due to excessive ice formation. Out of these successful strategies, minimum warm-up time and energy are evaluated to determine the optimal approaches that also satisfy US DOE performance targets. [2].

Running these simulated cold starts reveals plenty of insights into temperature distribution, water management and species concentrations during complex transient events difficult to probe through real-world testing. In summary, GT-SUITE is a powerful tool for accelerating cold start prototype development before committing to hardware.

References:

1. Huo, S., Jiao, K., & Wan, J.. *On the water transport behavior and phase transition mechanisms in cold start operation of PEM fuel cell.* Applied Energy, 233-234(April 2018), 776-788.
2. Hydrogen and Fuel Cell Technologies Office, *DOE Technical Targets for Fuel Cell Systems and Stacks for Transportation Applications* (2023), https://www.energy.gov/eere/fuelcells/doe-technical-targets-fuel-cell-systems-and-stacks-transportation-applications

# P59. Improving Heavy-duty FCEV Efficiency by Air System Modeling

B. Dursun, Ö. Andersson
*Deparment of Energy Sciences, Combustion Engines Division, Faculty of Engineering (LTH), Sweden*
*beyza.dursun @energy.lth.se*

The surging demand for truck transport has heightened interest in alternative powertrain technologies for heavy-duty vehicles (HDVs) to address rising greenhouse gas emissions. Globally, targets aim to reduce $CO_2$, $NO_x$, and PM emissions from conventional HDVs, which contribute over 25% of road transport greenhouse gas emissions. Current legislation mandates a 15% reduction in new truck emissions by 2025 and a more substantial 30% reduction by 2030 [1]. Conventional HDVs, mainly diesel-powered, emit pollutants, driving initiatives to enhance operational efficiency and adopt alternative fuels for lower emissions. Achieving zero-emission status requires deploying distinct technologies. This paper addresses the imperative need for enhancing energy efficiency and long-term durability in hydrogen-powered fuel cell electric vehicles (FCEVs). While fuel cell (FC) electrical efficiency is high under ideal conditions, inefficiencies within balance of plant (BoP) components can impact overall performance, especially in heavy-duty vehicles. Efficiency reductions at high loads highlight the necessity for precise matching of FC system components to specific vehicle applications. The key focus is on optimizing the air supply system, particularly the compressor, which consumes a significant portion of the total fuel cell electric output at high loads. Effective control of humidity levels in the intake air is crucial to prevent performance losses and fuel cell degradation [2]. This study aims to develop physics-based models for critical air supply system components in FCEVs and integrate them into an open-platform vehicle simulation software. The goal is to facilitate the evaluation and optimization of concepts tailored for heavy-duty vehicles, contributing to a competitive total cost of ownership for FCEVs and positioning them as viable alternatives in the transition to zero-emission transportation.

References:

1. ACEA. Factsheet $CO_2$ Standards for Heavy-Duty Vehicles. https://WwwAceaAuto/Files/Fact-Sheet-CO2_standards_for_heavy_duty_vehiclesPdf 2023:1-6.
2. Pischinger S, Schönfelder C, Bornscheuer W, Kindl H, Wiartalla A. Integrated air supply and humidification concepts for fuel cell systems. SAE Tech Pap 2001;2001. https://doi.org/10.4271/2001-01-0233.

# P60. Characterization and Optimization of Lithium-Ion Battery Materials via Particle-Scale Measurements and Simulations

Johannes Hörmann[1,2], Ashutosh Agrawal[1], Simon Hein[1,2], Dennis Kopljar[1], K. Andreas Friedrich[1,4],
Timo Danner[1,2], Arnulf Latz[1,2,3]
*[1] German Aerospace Center (DLR), Institute of Engineering Thermodynamics, 70569 Stuttgart, Germany*
*[2] Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), 89081 Ulm, Germany*
*[3] Ulm University, Faculty of Natural Sciences, Institute of Electrochemistry, 89081 Ulm, Germany*
*[4] University of Stuttgart, Institute of Building Energetics, Thermotechnology and Energy Storage, 70569 Stuttgart, Germany*
*johannes.hoermann@dlr.de*

A precise characterization and optimization of electrochemically active materials (AM) plays an important role in further advancing lithium-ion battery technology. These active materials are typically polycrystalline particles with a diameter of several microns. The properties of AM particles are a major factor in the resulting energy density, rate capability and cycling stability of a battery cell. Therefore, quantification and prediction of material properties is imperative for battery development. However, on electrode scale AMs are mixed with conductive additives and binders forming a complex porous electrode microstructure filled with a liquid electrolyte. This poses several challenges for material characterization. On the one hand, most conventional methods rely on measurements of composite electrodes with many design variables. This introduces uncertainties in the characterization process. For example, the intrinsic AM conductivity is masked by the conductive network that is formed together with the conductive additives. On the other hand, polycrystalline AM particles also inherit a complex inner microstructure themselves, which has a direct influence on its electrochemical performance. A better understanding of the inner particle structure and its related transport processes is required to identify and eliminate bottlenecks for mass and charge transport. These aspects motivate the development of characterization and simulation techniques on the particle scale.

For our investigation, we apply a complementary approach by combining simulations and experiments on the particle scale. We developed an optimized single-particle measurement (SPM) setup allowing electrochemical measurements on single AM particles. This includes rate tests, electrochemical impedance spectroscopy (EIS), and galvanostatic intermittent titration technique (GITT). Thereby, information on electrochemical properties of AMs can be acquired without any influence of an electrode microstructure. To complement these measurements, we extended a previously developed transport model, cf. [1,2]. The derivation of the model relies on a physics-based continuum modelling approach, which only uses physically interpretable parameters as input. By combining experiments and simulations, we investigate and quantify how different particle structures as well as surrounding conditions of the experiment influence the accuracy of the SPM measurement setup. Furthermore, different particle properties can be linked to interior dynamics and, consequently, to particle performance via simulations with varying 3D particle microstructures.

References:
1. A. Latz, J. Zausch, Journal of Power Sources, **2011**, 196 (6), 3296-3302.
2. BEST - Battery and Electrochemistry Simulation Tool, ITWM, https://itwm.fraunhofer.de/best, accessed: 2024-01-11.

# P61. Bipolar Membranes for $CO_2$ Co-Electrolysis: Optimization and Characterization by X-ray Tomography

R. Fischer[1], M. Dessiex[1,2], F. Marone[3], F. N. Büchi[1]
*[1] Electrochemistry Laboratory, Paul Scherrer Institute, Villigen PSI, Switzerland.*
*[2] Laboratory of Renewable Energy Science and Engineering, Ecole Polytechnique Fédérale de Lausanne, Switzerland*
*[3] Swiss Light Source, Paul Scherrer Institute, Villigen PSI, Switzerland*
*robert.fischer@psi.ch*

Salt precipitation and $CO_2$ crossover due to the formation of carbonate ions that replace hydroxide as charge carriers are substantial challenges to the durability and practical application of alkaline electrolyte membrane (AEM) $CO_2$ co-electrolysis (CO2ELY) [1]. Bipolar membranes (BPM) employed in forward bias can prevent both issues. The acidic anode suppresses carbonate salt precipitation by eliminating the counter cations present in the alkaline anode electrolyte in AEM CO2ELY. Carbonate ion recombination to $CO_2$ and water at the alkaline-acidic BPM junction greatly reduces $CO_2$ crossover [2]. The current dependent production of neutral species at the BPM junction has a strong influence on mass transport mechanisms and structural dynamics of cell components including membrane swelling, membrane delamination [3,4] or catalyst layer integrity [4]. Time-resolved (1s/scan, 1scan/min, 2.75um voxel size) synchrotron and static (3um voxel size) laboratory X-ray tomographic microscopy (XTM) were used to investigate material and operation dependent structural dynamics on micrometre scale.

We studied CO2ELY employing a commercial BPM (Fumasep, Fumatech). The membrane displays strong volumetric swelling (>25%) under operation. Swelling correlates with the applied current and goes beyond a fully saturated membrane without applied current. We attribute the swelling behaviour to the production of water at the BPM junction. Similarly, the production of $CO_2$ at the junction can lead to delamination of the BPM layers. However, a minimal current density (>50mA/cm$^2$) is required to provoke membrane delamination. Cells operated for the same amount of passed charge, but lower current density, show no or only little membrane damages. XTM also reveals that the composition of the Fumasep BPM is not optimal for forward bias BPM CO2ELY. The cation exchange layer is thinner and more heterogeneous than the anion exchange layer which favours $CO_2$ crossover over more desirable back-diffusion.

Produced water and $CO_2$ do not only accumulate at the junction, but redistribute diffusively within the membrane explaining the $CO_2$ crossover still present in BPM CO2ELY [2]. The transport mechanisms of water and $CO_2$ change from ionic transport and electro-osmotic drag in AEM CO2ELY to a multi-component interplay of several transport mechanisms in BPM CO2ELY.

Modelling efforts considering all pathways of charged and neutral species ($OH^-$, $CO_3^{2-}$, $HCO_3^-$, $H^+$, $H_2O$, $CO_2$) in conjunction with experimental ex-situ and operando tests are needed to better understand BPM and tune material properties to favour forward bias BPM CO2ELY and avoid degradation.

References:
1. Garg, S., Xu, Q., Moss, A. B., Mirolo, M., Deng, W., Chorkendorff, I., Drnec, J., & Seger, B. (2023). *Energy & Environmental Science*, 16(4), 1631-1643
2. Pătru, A., Binninger, T., Pribyl, B., & Schmidt, T. J. (2019). *Journal of the Electrochemical Society*, 166(2), F34-F43
3. Disch, J., Ingenhoven, S., & Vierrath, S. (2023). *Advanced Energy Materials*, 13(38), 2301614
4. Fischer, R., Dessiex, M., Marone, F., & Büchi, F. N. (2024). *under review.*

# P62. Dynamic Model-based Analysis of Mass Transfer Effects on Electroorganic Oxidation Processes

Paul Neugebauer, Philipp Röse, Ulrike Krewer
*Institute for Applied Materials – Electrochemical Technologies, Karlsruhe Institute of Technology,*
*Adenauerring 20b, 76131 Karlsruhe, Germany.*
*Paul.neugebauer2@kit.edu*

Electrifying organic synthesis is vital for the transition to energy- and resource-efficient synthesis processes and net zero-carbon emission. The electrosynthesis of organic chemicals has been a niche technology, but the need for sustainable synthesis processes is growing in the chemical industry.[1] Using (over-)stoichiometric redox agents becomes obsolete, when electrical energy is directly used.[2] Despite ongoing experimental studies of various organic syntheses, only a few have been successfully transferred to a technical scale.[3] There is a lack of methods for knowledge-based process optimization and electrolyser design, in particular tools for model-based analyses and simulations. However, optimizing process conditions in electrolysers with high current efficiency, conversion rates, and selectivity, thereby bolstering their economic viability, necessitates a detailed analysis of reaction parameters. Dynamic macrokinetic modelling stands out as a crucial methodology, offering valuable insights into mass transport and reaction kinetics at electrodes. Once thoroughly validated, it promises to guide experiments to determine optimal operating conditions predictively.[4]

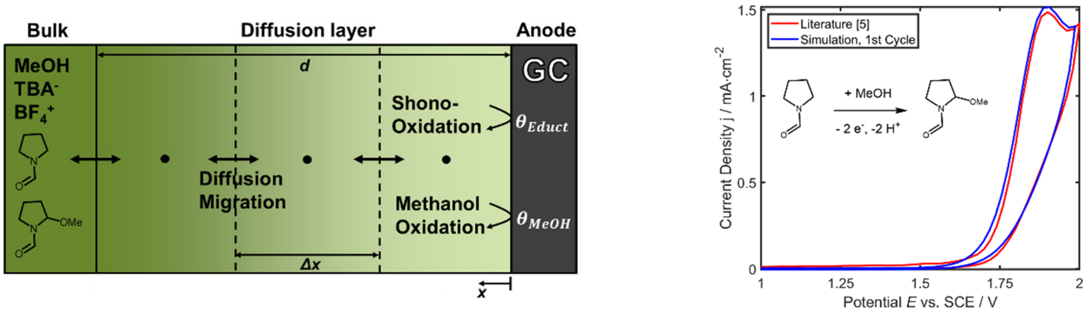


Figure 1: (left) Scheme of model domain; (right) experimental and simulated cyclic voltammogram[5] of the oxidative methoxylation of N-formylpyrrolidine (conditions: 0.1 M TBABF$_4$, 5 mM N-formylpyrrolidine, scan rate of 25 mV s$^{-1}$).

In this work, we present a systematic model-assisted approach to unravel the interactions between mass transport and reaction kinetics of the electrochemical oxidative methoxylation of *N*-formylpyrrolidine to *2*-methoxy-*N*-formylpyrrolidine (Shono-oxidation). An experimentally validated macrokinetic model (fig. 1, left) is developed, which includes a simplified description of the reactions at the electrode's surface and the species fluxes in the diffusion layer. The simulations can accurately reproduce cyclic and square wave voltammograms under various reaction conditions (fig. 1, right). Parameter studies of the applied potential, the diffusion layer thickness, and the ratio between reactant diffusion and reaction rates provide information on dependencies on conversion and Faraday efficiency. The simulations show that a high mass transfer rate is essential to achieve high Faraday efficiency, exposing a mass transfer domination of this system. This is why we propose to reduce the diffusion length in the cell by promoting turbulence or applying high flow rates. This work shows that model-based macrokinetic analysis can describe complex interactions in reaction and transport processes in an organic electrosynthesis in great detail and provide valuable knowledge for process optimization.

1. J. L. Barton, *Science* **2020**, *368*, 1181.
2. J. Seidler, J. Strugatchi, T. Gärtner, S. R. Waldvogel, *MRS Energy Sustain,* **2020**, *7*, E42.
3. R. C. D. Brown, *Chem. Record* **2021**, *21*, 2472-2487
4. B. J. M. Etzold et al., *Chem. Eng. J.* **2021**, *424*, 130501.
5. A. A. Folgueiras-Amador et al., *Electrochem. Commun.* **2019**, *100*, 6.

# P63. Modelling Carbon Loss During Startup and Shutdown Operation of PEM Fuel Cells

M. Bültel[1], A. Thüring[1], B. Ringeisen[2]
*[1] TLK-Thermo GmbH, Braunschweig, Germany*
*[2]Institute of Vehicle Propulsion Systems, University of Kaiserslautern-Landau,*
*Kaiserslautern, Germany*
*m.bueltel@tlk-thermo.com*

Accelerated degradation of fuel cell (FC) catalyst support occurs during startup and shutdown operation, when the cathode potential rises above levels observed during static FC operation. Simulating carbon loss requires local resolution of electrode potentials. Therefore, an existing 1D-along-the-channel stack model from the *TIL_HydrogenEnergySystems* Modelica library [1] was extended with a more detailed membrane electrode assembly model, which includes control volumes for the gas diffusion layer, catalyst layer, and membrane and resolves mass and heat transfer between each layer. An electrochemical model within the catalyst layer takes into account hydrogen oxidation, oxygen reduction, platinum oxidation, and carbon corrosion reactions.

Figure 1 (a) and (b) show the evolution of the electrode potentials during startup at the cathode and the anode, respectively. Initially, the gas channels at both electrodes are filled with 70% humidified air at 80 °C, when at 300 s supply of hydrogen to the anode starts. Subsequently, the electrode potential at the anode drops towards 0 V. The cathode potential rises towards the gas channel outlet, which leads to corrosion of the catalyst support.

Carbon loss depending on the stack temperature and cathode gas channel humidity at the time of startup is shown in Figure 1 (c). We observe an increase in carbon loss at higher humidities, as well as at higher temperatures. These results are in agreement with experimental results from [2, 3].

With this modelling framework, we aim to investigate further points of interest, like FC thermal management, mitigation strategies for catalyst degradation, and critical modes of operation, e.g. anode dead-end operation.

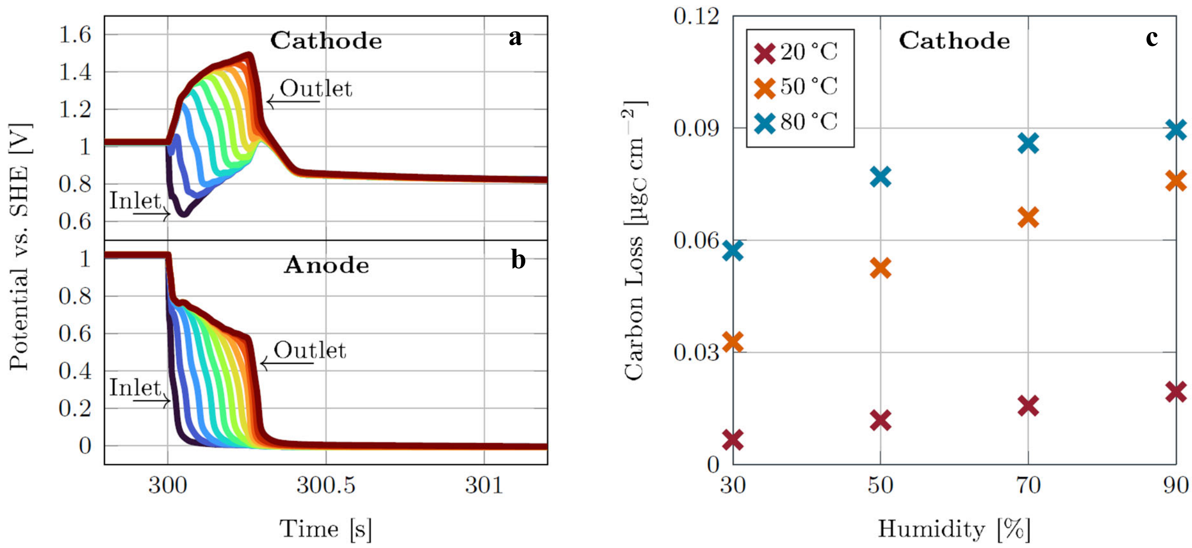


Figure 1: Local evolution of the electrode potentials at cathode (a) and anode (b) for 80 °C and 70% humidity during startup. Carbon loss at cathode due to corrosion during startup for varying stack temperatures and humidities in the cathode gas channel (c).

References:
1. TLK-Thermo GmbH. TIL Suite. 2023. https://www.tlk-thermo.de/software/til-suite.
2. T. Mittermeier, A. Weiß, F. Hasché, G. Hübner, H. Gasteiger. J. Electrochem. Soc. **164,** 2017, F127
3. T. Mittermeier, A. Weiß, F. Hasché, H. Gasteiger., J. Electrochem. Soc. **165,** 2018, F1349

# P64. Monolithic Coupling of a CatMAP Based Microkinetic Model for Heterogeneous Electrocatalysis to Ion Transport with Finite Ion Sizes

Steffen Maaß[1], Jürgen Fuhrmann[2], Stefan Ringe[3]
*[1]Technische Univeristät Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany*
*[2]Weierstrass Institute for Applied Analysis, Mohrenstr. 39, 10117 Berlin, Germany*
*[3]Dept. Of Chemistry, Korea University,145 Anam-ro, Seongbuk-gu, Seoul, South Korea*
*[1]steffen.maass@campus.tu-berlin.de, [2]juergen.fuhrmann@wias-berlin.de, [3]sringe@korea.ac.kr*

CatMAP [1] is a well-established Python package for expressing and solving microkinetic models parametrized by the relative energies of the intermediate states that are obtained from ab initio calculations within the framework of density-functional theory. CatMAP additionally implements scaling relations to reduce the parameter space to a few descriptors for the analysis of the reaction rates. In the case of electrochemical reactions, electric fields influence the kinetics and the selectivity of the reaction, and concentrations of charged reactants are influenced by double-layer effects. This raises the need for coupling the CatMAP microkinetic model to a generalized Nernst-Planck-Poisson system describing the transport of finitely sized, solvated ions in a self-consistent electric field. Ringe et al [2], successfully demonstrated this approach by coupling CatMAP to COMSOL Multiphysics to simulate electrochemical $CO_2$ reduction on gold surfaces.

The contribution presents a pathway to a more robust numerical approach that replaces the iterative coupling between the microkinetic and the transport solvers by a monolithic and more easy-to-generalize implementation realized in the Julia programming language.

We develop the Julia package CatmapInterface.jl which translates a CatMAP specification of a microkinetic model into Julia code which realises a reaction boundary condition to the generalized Nernst-Planck-Poisson solver LiquidElectrolytes.jl [3] realized on top of the solver kernel VoronoiFVM.jl [4] for coupled nonlinear PDE systems. The implementation takes advantage of Julia's automatic differentiation capabilities [5] to generate the full linearization of the coupled nonlinear system as a basis for a robust Newton solver for the fully coupled electrode/electrolyte system.

We present a confirmation of the simulation results from Ringe et al [2] and discuss the application of the approach to other electrode/electrolyte systems.

References:

1. Medford, A. J., Shi, C., Hoffmann, M. J., Lausche, A. C., Fitzgibbon, S. R., Bligaard, T., & Nørskov, J. K. (2015). *Catalysis Letters*, 145, 794-807.
2. Ringe, S., Morales-Guio, C. G., Chen, L. D., Fields, M., Jaramillo, T. F., Hahn, C., & Chan, K. (2020). *Nature Communications,* 11(1), 33.
3. J. Fuhrmann & contributors (2023). https://github.com/j-fu/LiquidElectrolytes.jl
4. J. Fuhrmann & contributors (2023). https://github.com/j-fu/VoronoiFVM.jl, DOI: 10.5281/zenodo.3529808
5. Revels, J., Lubin, M., & Papamarkou, T. (2016). *arXiv preprint* arXiv:1607.07892.

# P65. Modeling In-plane Inhomogeneities of Lithium Iron Phosphate Battery Cells during Shallow Cycling

Alexander Frank, Axel Durdel, Thomas Roth, Andreas Jossen
*Technical University of Munich, School of Engineering and Design, Department of Energy and Process Engineering, Chair of Electrical Energy Storage Technology; Arcisstraße 21, 80333 Munich, Germany*
*alexander.af.frank@tum.de*

Commercial lithium-ion $LiFePO_4$/Graphite cells can show a recovery effect of more than 10% total cell capacity after continuous shallow cycling. Differential voltage analysis and post-mortem experiments suggest that these capacity losses are caused by strongly non-uniform lithium distributions in the electrodes [1]. However, the complete mechanism behind this recovery effect is not yet fully understood. Here, we present a novel modeling approach using a 2D Doyle-Fuller-Newman model [2] which allows for an in-depth analysis of the cell behavior during cycling to better understand the root causes. Preliminary results suggest that the geometric asymmetry at the cell's edge, namely the anode overhang and the edge area of the cathode, is responsible for the relocation of lithium inventory in lateral directions. The model suggests the possibility of unexpected lithium plating during diagnostic CCCV (Constant current constant voltage) full cycles during/after shallow cycling and can help improve the cycling procedures to minimize the aforementioned recovery effect and provide protection from unexpected lithium plating.

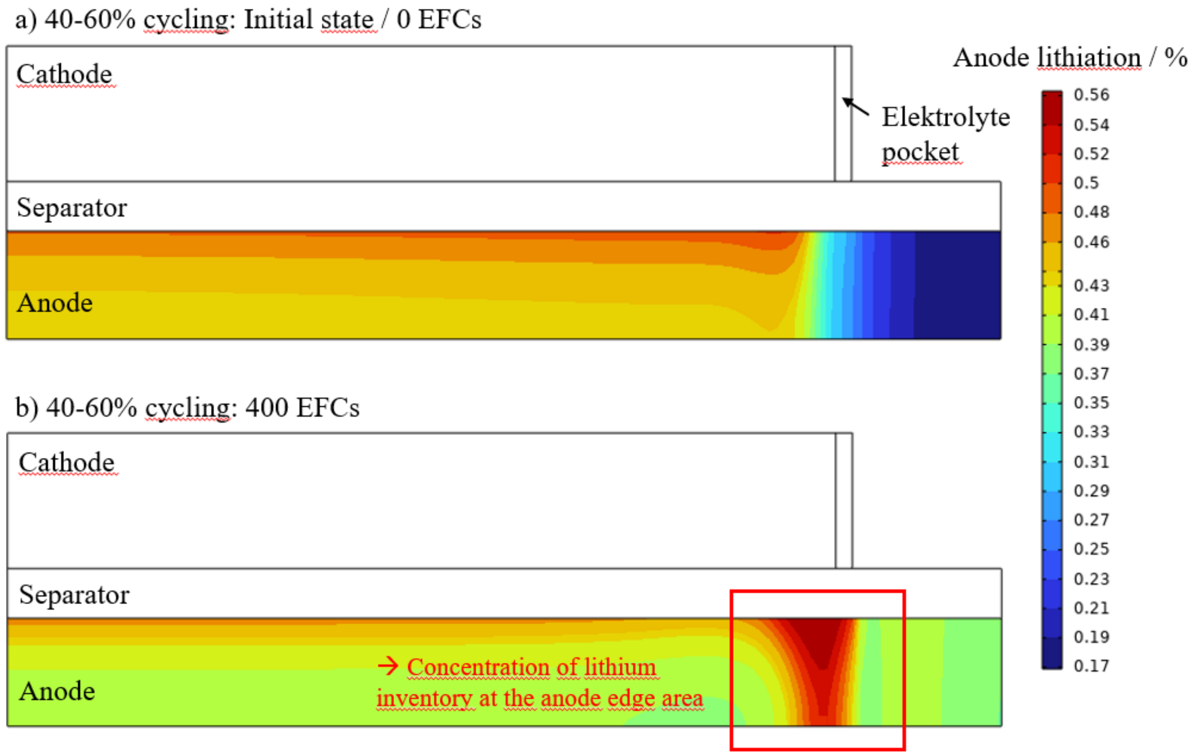


Figure 1: Distribution of lithium inventory in the anode after the first partial cycle a) and after 400 EFCs of partial cycling between 40-60% cell SoC.

References:
1. Franz B. Spingler *et al.* 2020 *J. Electrochem. Soc.* **167** 040526
2. Marc Doyle *et al.* 1993 *J. Electrochem. Soc.* **140** 1526

# P66. Effect of Thermal Gradients on Mechanistic Model-based Degradation Diagnosis in Lithium-ion Cells

A. Singh[1], A. Ghosh[2], P. Nakhanivej[1], Y. Monaghan[1], S. Puravankara[3], M. Loveridge[1], A. Barai[1]
[1]*Energy Innovation Centre, WMG, University of Warwick, Coventry, United Kingdom, CV4 7AL*
[2]*Department of Metallurgical and Materials Engineering, IIT Kharagpur, West Bengal, India, 721302*
[3]*School of Energy Science and Engineering, IIT Kharagpur, West Bengal, India, 721302*
*Anubhav.Singh@warwick.ac.uk*

The increasing scale and operational demands of Li-ion batteries have led to a rise in emphasis on battery diagnostics. Upon optimal implementation, battery diagnostics can significantly improve the safety and longevity of batteries. A popular battery diagnostics approach called ‘*alawa* based on a mechanistic model was proposed by Dubarry et al. [1]. The model provides insight into internal battery phenomena and decouples multiple degradation modes, thus enabling improvements in battery operation as well as identification of safety critical damage. However, majority of the results presented thus far are based on single cell data collected in the laboratory under steady state conditions. This is not realistic because real-life battery packs have several cells connected in parallel. These strings are referred to as supercells. Ideally, the current flowing into a supercell is equally distributed across the cells, thus allowing direct scale-up of the ‘*alawa* model using the voltage and current data collected at supercell level. However, non-uniform operating conditions could result in significant variation in the cells' properties. Consequently, the cells in a supercell are exposed to unequal currents throughout their usage. The resulting heterogeneous degradation across the supercell is not visible in the supercell level data, thus potentially affecting the diagnostic predictions of an upscaled ‘*alawa* model.

Aimed at tackling the problem identified above, the presented work is a part of an ongoing study is to understand the effect of a thermal gradient in a supercell on the degradation diagnosis performed using the ‘*alawa* model. A thermal gradient was deliberately introduced in a supercell composed of four cells through restricted airflow in 50% of the cells via a Perspex cover (Figure 1). Regular charge-discharge cycling of the supercell is ongoing with Reference Performance Tests (RPTs) performed at regular intervals. The ‘*alawa* model was parametrised using the C/40 charge data collected from the RPT after 100 cycles for the supercell as well as individual cells. The results (Table 1) indicate that the ‘*alawa* model's predictions at supercell level tend to align with the least degraded cell in the supercell, thus obscuring actual cell-level degradation. Further cycling is being conducted and the results will be presented in due course.

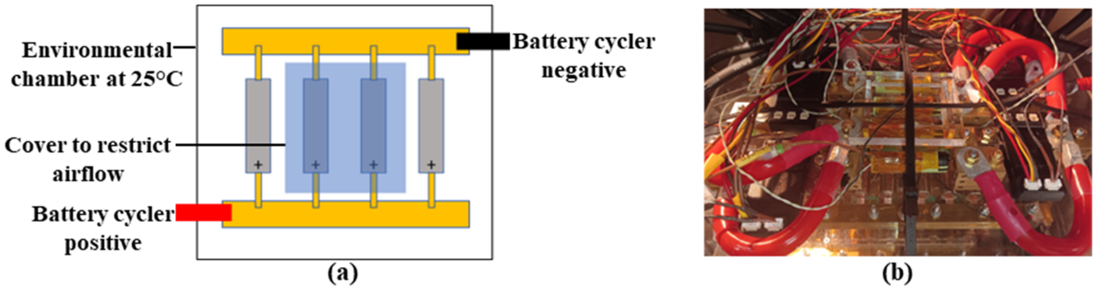


Figure 1: Laboratory setup used to induce thermal gradient in supercell with 4 cells in parallel: (a) schematic and (b) actual.

Table 1: ‘*alawa* model results listing contribution of two degradation modes towards capacity loss calculated from C/40 charge data corresponding to single cells and supercell.

| | **Uncovered cells** | **Covered cells** | **Supercell** |
|---|---|---|---|
| **% Capacity loss** | 2.89 | 4.02 | 3.01 |
| **%Loss of Lithium inventory** | 3 | 3.5 | 3 |
| **% Reduction in negative electrode kinetics** | 150 | 220 | 150 |

References:
1. M. Dubarry, C. Truchot, B. Y. Liaw, J. Power Sources 219 (2012), 204-216.

# P67. Novel Flow Structures for Additive Manufacturing of Gas Diffusion Layers for PEM Fuel Cells

S. Hoffmann, J. Haußmann
*Institute of Product Engineering, Karlsruhe Institute of Technology, Germany*
*Kaiserstr. 10, 76131 Karlsruhe, Germany*
*sarah.hoffmann@kit.edu*

The use of additive manufacturing for the fabrication of gas diffusion layers (GDL) opens up a wide range of new options for their design in contrast to the typically used randomly positioned fibers [1]. A section of the cathode side of a PEM fuel cell consisting of two bipolar plate channels and their connecting land, a GDL and a membrane layer was selected for this study. With the simulation software GeoDict the movement of gas particles through this structure was simulated for two different types of GDL: a paper GDL with randomly positioned fibers and a GDL built from three perforated layers with increasing pore radii (23 µm, 48 µm, 98 µm) toward the bipolar plate (BPP). The latter is designed for additive-subtractive fabrication using laser sintering and laser perforation. A previous study of Balakrishnan et al. [2] showed that gas flow structures with a pore size gradient can be beneficent for the PEM fuel cell performance, while maintaining a continuous material connection from the bipolar layer (BPP) to the membrane. In the simulations this direct material connection was found to lead to an increase in electrical and thermal conductivity by a factor of 2 compared to the fiber structure.
The analysis of the gas particle distribution at the interface between GDL and membrane revealed a more even particle distribution for the perforated layer structure in comparison to the fiber structure. This indicates to a more evenly distributed reaction and thus to an improved performance of the PEM fuel cell. These results show the possible improvements by applying additive manufacturing on GDLs and its effect on electrical and thermal conductivity as well as gas transport.

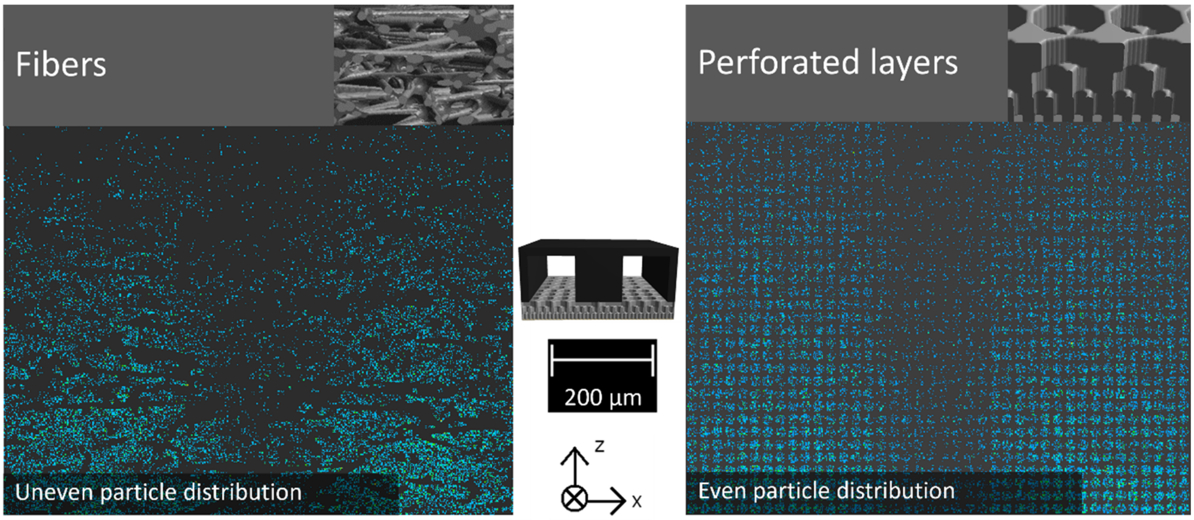


Figure 1: Comparison of the gas particle distribution after 2.5 ms under a gas diffusion layer made of randomly distributed fibers and a gas diffusion layer made from three perforated continuous layers.

References:
1. S. Park, J.W. Lee, B. N. Popov, *A review of gas diffusion layer in PEM fuel cells : Materials and design*, International Journal of Hydrogen Energy. **37** (2012), 5850-5865
2. M. Balakrishnan, *Tailored Electrospun Gas Diffusion Layers for Polymer Electrolyte Membrane Fuel Cells : Design and Durability,* Thesis, 2019, University of Toronto.

# P68. Multiscale-Multidomain Modeling and Validation of Commercial 18650 Cylindrical Cells

Tanmay Dev[1], Michele Spinola[1], Thomas Reichbauer[2], Christoph Weißinger[1]
[1] *Virtual Battery Design, CoE Battery, Capgemini Engineering, Munich, Germany.*
[2] *Battery Testing, CoE Battery, Capgemini Engineering, Munich, Germany.*
*tanmay.dev@capgemini.com*

Li-ion batteries are crucial for the continued development of electric mobility and energy storage. They are among the best choices to accomplish our goal of creating lightweight electric mobility systems because of their high energy and power density. The top choices among various commercial form factors are cylindrical cells in a range of sizes because of their excellent mechanical and thermal characteristics and ease of manufacturing. The current research project intends to develop an electrochemical-thermal model based on the widely used Samsung INR18650-35E cell and parameterize it in order to validate it using experimental data.

Throughout their operation, commercial cylindrical cells are exposed to varying loads and current densities. A Multiscale Multidomain model for cylindrical cells was developed to study the electrical and thermal fields during slow and fast charge-discharging. A multidomain model has the advantage of being computationally efficient by decoupling the domains of particle level, electrode level, and cell level.[1,2] Correct Multiphysics upscaling from microscale to the full cell level is made possible by the inter-domain exchange of solution variables. Lithium diffusion in solid particles of Gr-Si anode and NCA cathode, ion and charge diffusion in electrode pairs,[3] heat flow and electrical current in the cell domain were solved. The electric field and electrochemical-resistive heating were upscaled to the cell level to validate the multiscale model framework.

Test data have been used to validate the Multiphysics model. Low current density exhibits better approximation of cell voltage and capacity, while high current density exhibits deviation. Higher characterization accuracy of conductivity and diffusivity can improve the simulation of field variables at high current density. Thermal characterization is highly impacted by the condition of the test bench and hence also influences the validation of the thermal model. It would be suitable to extend this model framework to include mechanical coupling.

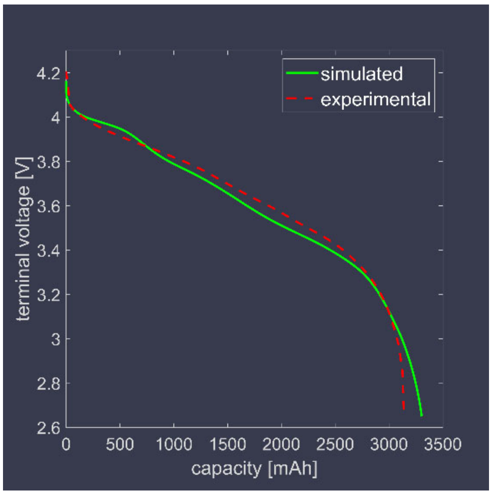


Figure 1: V vs Q at 0.5C

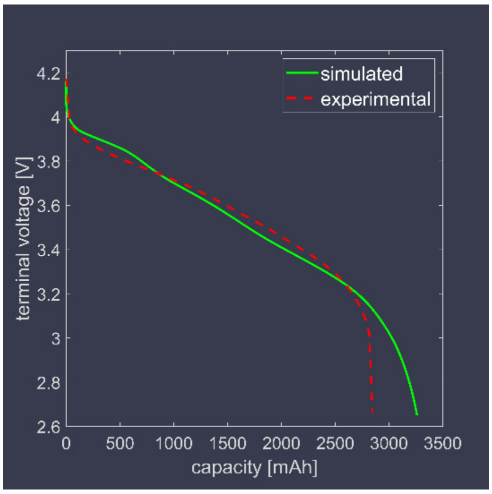


Figure 2: V vs Q at 1C

References:
1. K-J Lee, K Smith, A Pesaran, G-H Kim. *J Power Sources* 241 (2013) 20-32.
2. A Schmidt, D Oehler, A Weber, T Wetzel, E Ivers-Tiffée. *Electrochimica Acta* 393 (2021) 139046
3. T Dev, JL Schaefer, A. Salvadori. *J Energy Storage* 73 (2023) 108927.

# P69. On the Anode Exhaust Gas Recirculation of PEM Fuel Cells Using Passive Ejectors

N. Lindacher, L. Weiß, S. Rieß, M. Wensing
*Friedrich-Alexander-Universität Erlangen-Nürnberg, Professorship for Fluid Systems Technology*
*Cauerstraße 4, 91058 Erlangen/Germany*
*nicklas.lindacher@fau.de*

In PEMFC systems, ejectors are used to recirculate the anode exhaust gas - which consists of a mixture of unconsumed hydrogen, nitrogen and water - from the anode outlet to the anode inlet (cf. Fig. 1 left). The ejector is a passive component in which only flow processes take place. This means that no electrical energy is required to compress the anode exhaust gas. The pressure increase between the inlet for the anode exhaust gas (point s in Fig. 1) and the ejector outlet (point a in Fig. 1) is made possible by the available energy of the compressed, fresh hydrogen, that is supplied at point p (cf. Fig. 1) to the ejector. Figure 1 on the right shows a more detailed structure of the investigated ejector. It is a single choking ejector consisting of a convergent primary nozzle, a suction chamber, a throat and a diffuser.

Our work focuses on the modeling and experimental validation of the thermodynamic processes in this ejector type to identify potentials and limitations regarding its application in PEMFC systems. In order to analyze the operating behavior of the ejector, a simulation model has been implemented in Matlab®, which is described in [1]. Based on a stationary, zero-dimensional and single-phase assumption, the ejector is calculated at specified state points. The ejector model enables the calculation of specific operating points and reveals the sensitivity of relevant parameters like temperature, stoichiometric factor etc. on the ejector performance. For example, heating the fresh hydrogen (with the waste heat from the FC) leads to both a higher ejector performance and a better prevention of water condensation in the ejector due to the increase in temperature. In general, the ejector performance depends on the operating conditions of the fuel cell stack and on the ejector geometry, especially on the primary nozzle throat diameter.

The remaining experimental validation will serve to check the simulation results and to determine suitable calibration values for the simulation model in order to obtain quantitatively exact simulation results. The aim is to develop a design tool for ejectors by combining modeling and experimental validation.

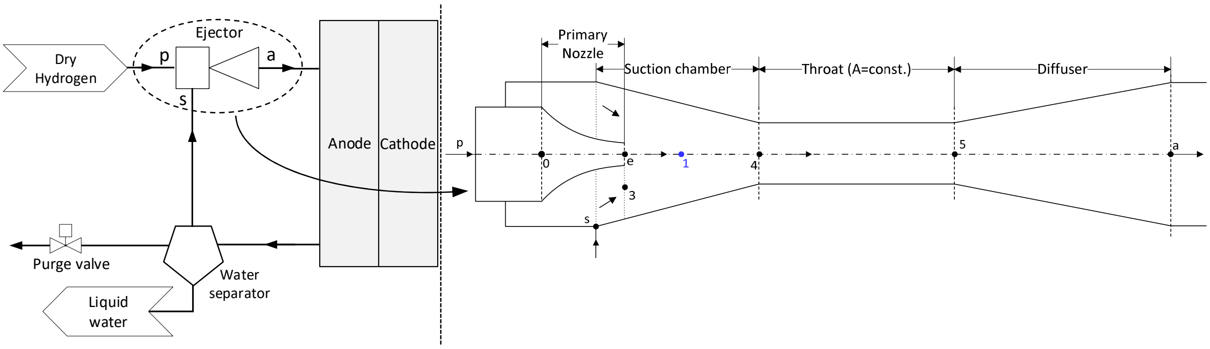


Figure 1: Left: Simplified scheme of the anode circuit with passive recirculation. Right: Sketch of the considered single choking ejector (according to [1]).

Reference:
1. Lindacher N, et al. *Development of an Ejector Model for PEMFC Systems*. Submitted to Fuel Cells: From Fundamentals to Systems. Paper is still in review; 2024.

(contribution by M. Jałowiecka et al. moved to Oral Presentations section)

# P71. Zero-Excess Lithium Metal Anodes in Next-Generation Sulfide-Based Solid-State Batteries

R. Wullich, L. Gubler, M. El Kazzi
*Electrochemistry Laboratory, Paul Scherrer Institute, Villigen PSI, Switzerland.*
*robin.wullich@psi.ch*

All-solid-state batteries (ASSBs) are considered to be the next generation of safe and high energy-storage technology replacing the carbonate-based liquid electrolytes by a solid-state electrolyte with comparable conductivity. The use of an inorganic, non-flammable solid-electrolyte (SE) holds the promise to enable the use of a lithium metal anode, which could increase the energy density above 500 Wh $kg^{-1}$ compared to state-of-the art Li-ion batteries (LIB). [1] However, the demand on Li metal has been growing rapidly over the past years increasing concern of its availability in the future. [2] The further replacement of the micron-thick Li metal anode by a sub-micron thick inorganic nucleation and barrier layers deposited on a thin copper current collector (CC) (Figure 1.a) not only reduces the amount of used lithium but also simplify the manufacturing making the production safer. [3] In this technology, which is better known as “zero-excess” (ZE-LMB) anodes, the Li metal anode is formed *in situ* during the first charge using exclusively the available Li from the cathode.

The nucleation layer acts as a seed for homogeneous and highly reversible Li platting/stripping while the barrier layer protects the solid electrolyte from the highly reactive Li metal preventing potential side reactions and therefore, the combination of both interlayers promises to enable stable long cycling with a high-capacity retention.

In this work we are presenting preliminary results on the electrochemical performance of ZE-LMB using silver thin films acting as a nucleation layer and compare it to the performance of bare current collector. Figure 1 (a) shows a schematic illustration of the applied technology in comparison with the state-of-the-art Li-ion battery. On the right-hand side Figure 1 shows critical-current density tests in asymmetric cells (CC|SE|Li) using bare Cu CC (b) and 100 nm Ag thin film (c). By simply implementing a thin nucleation layer the critical current could be doubled from 0.3 mA $cm^{-2}$ to 0.6 mA $cm^{-2}$.

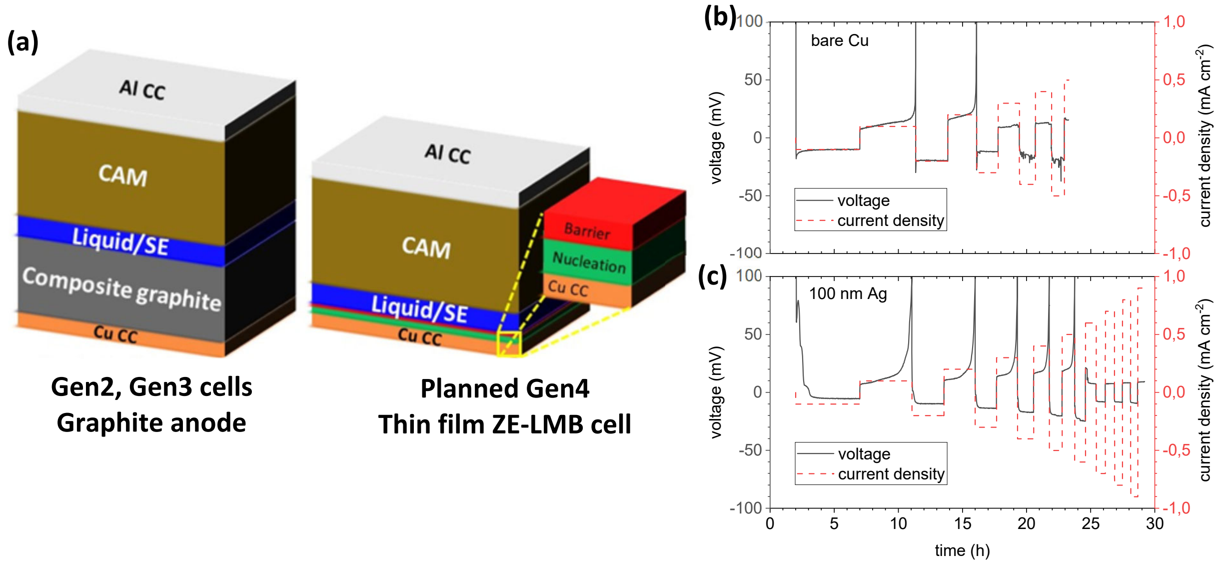


**Figure 1: (a) schematic illustration of the applied ZE-LMB technology. Critical-current-density tests in asymmetric cells using (b) bare Cu CC and (c) 100 nm Ag thin film.**

References:
1. Zizheng Tong, Behrouz Bazri, Shu-Fen Hu, Ru-Shi Liu, *J. Mater. Chem. A*, 2021, 9, 7396-7406
2. Hanna Vikström, Simon Davidsson, Mikael Höök, *Applied Energy*, 2013, 110, 252-266
3. Teklay Mezgebe Hagos, Hailemariam Kassa Bezabh, Chen-Jui Huang, Shi-Kai Jiang, Wei-Nien Su, Bing Joe Hwang, *Acc. Chem. Res.*, 2021, 54, 24, 4474-4485

# P72. Investigation of Internal Temperature Distribution in Lithium-ion Battery Cell and Module Using a 3D Electrothermal Model

Erwan Tardy, Pierre-Xavier Thivel, Florence Druart, Pierre Kuntz, Didier Devaux, Yann Bultel

*Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI,*
*F-38000 Grenoble, France*
*erwan.tardy@grenoble-inp.fr*

In recent years, lithium-ion batteries (LIBs) have been massively developed in many applications, especially for the transportation associated with the rapid growth of electric vehicles (EVs). They provide high energy and power densities, high efficiency and long lifespan compared to other battery technologies. Despite remarkable improvements, Li-ion batteries still face thermal issues, which cause performance drop, limited calendar life, safety concerns and degradation [1]. Therefore, proper thermal management for a LIB is necessary to control its temperature and to extend its lifetime. In particular, internal temperature needs to be known for improving the safety and limiting premature ageing of LIBs as a remarkable difference between the external and internal temperatures can be observed [2].

In the present work, the internal temperature distribution of a large commercial prismatic NMC-type lithium-ion battery (Table 1) is investigated using a 3D electrothermal model developed with the COMSOL Multiphysics® software. The internal geometry is modeled from a large number of X-ray tomograms performed on the corresponding cell. The study is extended to a module of 12 cells in series (12S) to evaluate the heterogeneities of internal temperatures considering the real geometry of each cell. In addition, the cell and module are experimentally charged and discharged at several currents at 25°C in a climatic chamber to determine the temperature changes. Finally, the numerical results are compared to the experimental data at both cell and module scales to validate the model.

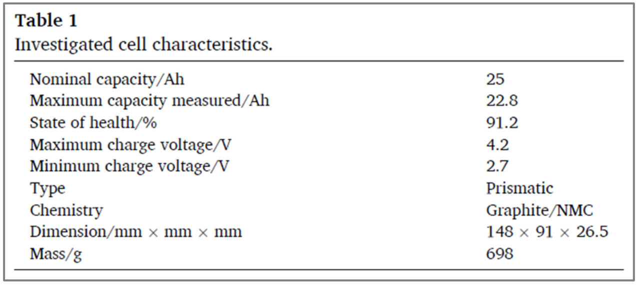


**Table 1**
Investigated cell characteristics.

| | |
|---|---|
| Nominal capacity/Ah | 25 |
| Maximum capacity measured/Ah | 22.8 |
| State of health/% | 91.2 |
| Maximum charge voltage/V | 4.2 |
| Minimum charge voltage/V | 2.7 |
| Type | Prismatic |
| Chemistry | Graphite/NMC |
| Dimension/mm × mm × mm | 148 × 91 × 26.5 |
| Mass/g | 698 |

The results show a cooling process due to entropy change at low C-rate while at higher C-rate the Joule effect is predominant. Therefore, entropy change can act as an active cooling process at low C-rate [3]. In addition, the anisotropic properties considerably influence the internal temperature distribution as well as the inert gas which insulates the inner part of the cell by acting as thermal resistance [3]. Finally, higher internal temperatures are observed in the module because of its architecture (Figure 1).

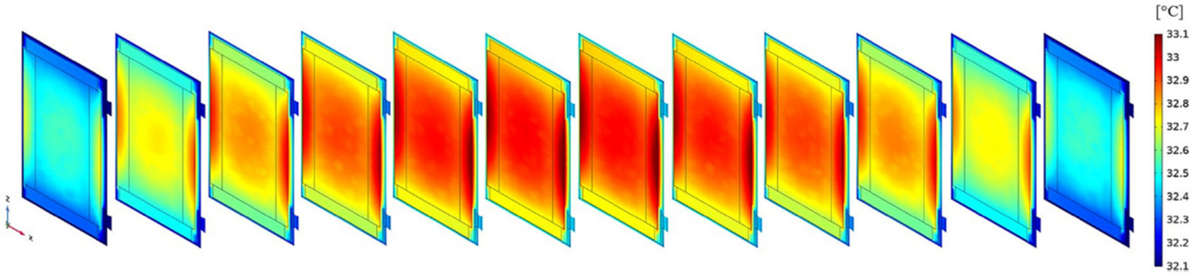


Figure 1. Temperature distribution in a module 12S at the end of 1C discharge at 25°C considering the real geometry of each cell [3].

References:

1. Chidambaranathan Bibin, M. Vijayaram, V. Suriya, R.Sai Ganesh, S. Soundarraj, Materials Today: Proceedings 33 (Part 1) (2020) 116–128, https://doi.org/10.1016/j.matpr.2020.03.317.
2. Zhongbao Wei, Jiyun Zhao, Hongwen He, Guanglin Ding, Haoyong Cui, Longcheng Liu, Journal of Power Sources 489 (2021), 229462, https://doi.org/10.1016/j.jpowsour.2021.229462.
3. Erwan Tardy, Pierre-Xavier Thivel, Florence Druart, Pierre Kuntz, Didier Devaux, Yann Bultel, Journal of Energy Storage, Volume 64, 2023, 107090, https://doi.org/10.1016/j.est.2023.107090.

(abstract withdrawn)

(abstract withdrawn)

# P75. A New Distribution Based Approach to Modelling of Hysteresis in Electrochemical Systems

Franz Pichler, Florian Feyersinger
*Virtual Vehicle Research GmbH*
*Inffeldgasse 21a, 8010 Graz*
*Franz.pichler@v2c2.at*

A novel approach to the thermodynamically consistent simulation of phase-separating materials, (e.g. iron phosphate) will be presented. This innovative model builds upon the foundational principles of the state-of-the-art yet exceeds its performance in both computational cost and result consistency.

The state of the art in this context, is given by the many-particle approach, pioneered by Dreyer et al. [1] and Bazant et al. [2]. It utilises non-monotonic potential curves and the simulation of many (i.e. thousands [1]) of particles that spontaneously transform between lithium poor and lithium rich states. These individual transformations show up as unwanted peaks in the voltage response that can only partially be suppressed by an increase in number of simulated particles. In addition to the high number of simulated particles, the fast individual state transformations, necessitate small simulation time steps, which renders these simulations computationally expensive.

Despite the elegance of these models, their drawbacks have hindered broad adoption. The presented model addresses these issues by describing the evolution of a many-particle system from a unique perspective. Instead of simulating the evolution of individual particle concentration states, the model describes the evolution of particle populations cluster in certain concentration states, based intercalation rates and size of itself and its adjacent classes. This eliminates spontaneous state changes and yields smooth transitions in particle class populations. As a result, individual peaks in the voltage response vanish, as shown in Figure 1, reducing degrees of freedom compared to many-particle models and allowing the use of larger time steps. Additionally, the model's thermodynamic foundation offers fundamental advantages over Plett's empirical hysteresis model[3], which, while unable to explain hysteresis occurrence, incorporates it empirically.

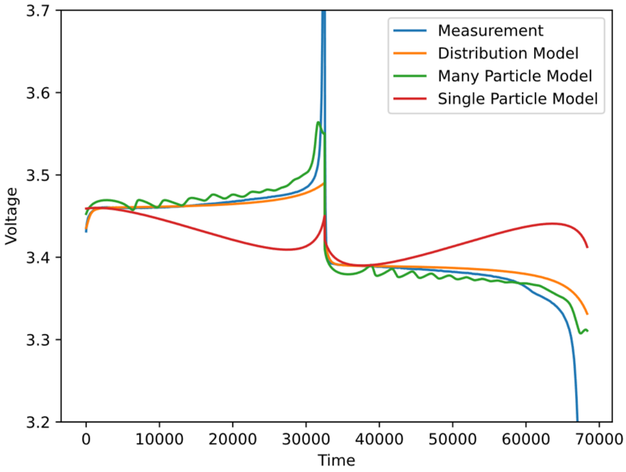


Figure 1: Measurement and simulation of a LiFePO electrode charge and discharge cycle. The single particle model shows the shape of the underlying chemical potential curve. The many particle model shows the typical “noisy” hysteresis (20 particles). The distribution model yields a smooth hysteresis.

References:
1. Guhlke, C., Gajewski, P., Maurelli, M. et al. Stochastic many-particle model for LFP electrodes. Continuum Mech. Thermodyn. 30, 593-628 (2018). https://doi.org/10.1007/s00161-018-0629-7
2. Raymond B. Smith and Martin Z. Bazant 2017 J. Electrochem. Soc. 164 E3291
3. C. P. Graells, M. S. Trimboli and G. L. Plett, "Differential hysteresis models for a silicon-anode Li-ion battery cell", 2020 IEEE Transportation Electrification Conference & Expo (ITEC), Chicago, IL, USA, 2020, pp. 175-180, doi: 10.1109/ITEC48692.2020.9161591.

(abstract withdrawn)

# P77. Numerical Investigation of Bubble Growth and Detachment Characteristics in Electro-chemical Systems

Wiebke Schrader[1], David Müller[1], Pooria Hadikhani[2], Alexander Stroh[1]
[1] *Institute of Fluid Mechanics (ISTM)*
[2] *Institute for Applied Materials – Electrochemical Technologies (IAM-ET)*
*Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany*
*wiebke.schrader@kit.edu*

Chemical process industries are energy intensive, with energy often being obtained from fossil fuels. Therefore, an electrolyzer represents a sustainable and cost-effective alternative for synthesis process. In the case of the electro-organic Shono-reaction, hydrocarbons are oxidated at the anode, while hydrogen is produced at the cathode. Evolving hydrogen generates gas bubbles and hence affects the species transport in the liquid electrolyte. The limiting transport mechanism in such electrolysis cells is the diffusion of the educts to the respective electrodes. While a bubble is attached to the electrode, educts are hindered from getting in contact with the electrode and thus the cell's productivity is reduced. To increase productivity, the two-phase flow and in particular the hydrogen bubble dynamics require further research. For the Shono-reaction oxidation occurs at the anode and the produced, long-chained hydrocarbon molecules dissolve in the electrolyte. Since the effect of the motion of these molecules on the species transport is yet to be determined, a simplified water electrolysis cell was chosen to examine the two-phase flow. Thereby, the simulation domain is firstly based on an existing design of a membrane-less electrolysis cell to enable validation in a later step [1].

This study focuses on the modelling of two-phase flow of hydrogen bubbles in a liquid electrolyte with respect to bubble growth, departure diameter and eventually detachment of the bubble with an interface-capturing Volume-of-Fluid (VoF) Method. The third-party framework *geoChemFoam* based on the open-source library OpenFOAM provides the solver *interTransferFoam*, being able to model bubble formation due to specie diffusion [2]. In the conference contribution, this solver is extended by a suitable contact angle model to describe the bubble detachment from the electrodes. Furthermore, a parameter variation of the contact angle is conducted regarding the corresponding departure diameter and resulting wake flow behind the bubble. The main objective of this work is the identification of dominant factors affecting bubble detachment such as contact angle, coalescence and flow rate as well as the investigation of bubble-induced mixing in the bubble wake.

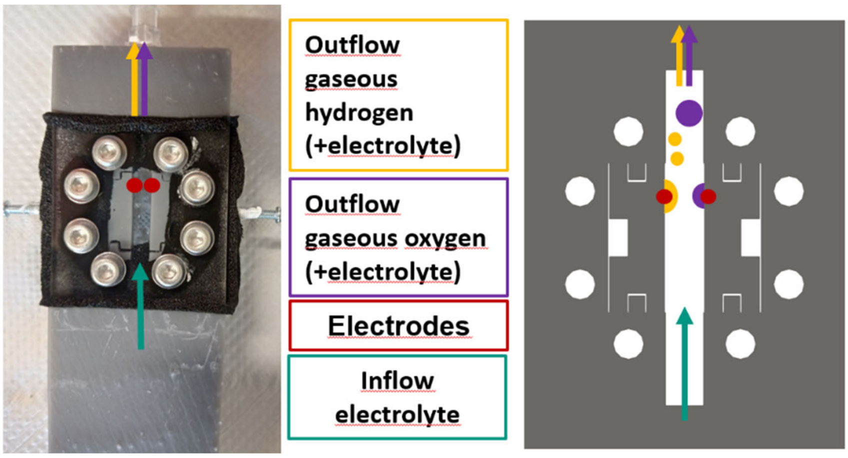


Figure 1: Manufactured and schematics of the reference electrolysis cell design [1]

References:

1. P. Hadikhani et al. "A membrane-less electrolyzer with porous walls for high throughput and pure hydrogen production." Sustainable Energy & Fuels 5(9) (2021), 2419-2432.
2. A. Patsoukis-Dimou & J. Maes "Volume-Of-Fluid Simulation of Gas Dissolution in Liquid: Rising Bubbles and $CO_2$ Trapping", 14th International Conference on Computational Dynamics in Oil and Gas, Metallurgical and Process Industries (CFD2020), Oct 2020.

# P78. Numerical Study of a Hydrogen Dilution Effect on the Performance of PEMFC Fuel Cell

Maha Benhamad, Erwan Tardy, Konakpo Parfait Kamara, Florence Druart,
Lenka Svecova, Jonathan Deseure
*Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble-INP, EIP- LEPMI,*
*38000 Grenoble, France*

PEM Fuel cell (PEMFC) systems require pure hydrogen as anodic fuel for its operation. Only few papers focused on the effects of the presence of an inert gas in the hydrogen on the performance of a PEMFC can be found in the literature based either on experimental or numerical studies [1-3]. In this study, the hydrogen dilution with different concentrations of inert gases, such as $CO_2$, $CH_4$, Ar and $N_2$, has been studied by a numerical simulation. A single cell with a 25 $cm^2$ electrode area and GDLs covered by a microporous layer (MPL) and two catalyst layers (CLs) was simulated. The fuel cell operates at 70°C and 1 atm with relative humidity of 100%. A three-dimensional, steady-state model for a PEMFC cell was simulated using COMSOL Multiphysics 6.1. In this work, the secondary current distribution interface was used for modelling the conservations equations in the ionic and electrode phases. Free and porous media flow and transport of concentrated species interfaces are considered for modelling the gas flow channel, GDL, MPL and CLs in the anode and cathode sides.

The simulation results were validated by a comparison with an experimental study performed in parallel to the modelling under the same operation conditions. Figure 1 presents the numerical results of the developed model for hydrogen dilution ($H_2$:70% and $X_i$:30%). Compared to the experimental and numerical results for pure hydrogen, the current density decreases when hydrogen is diluted as shown in the figure. The polarization of $H_2$ diluted with $N_2$ is significantly higher than the $H_2$ diluted with the other inert gases (approx. 1.3 $A/cm^2$). The dilution of hydrogen with $CO_2$ results in the minimum current density.

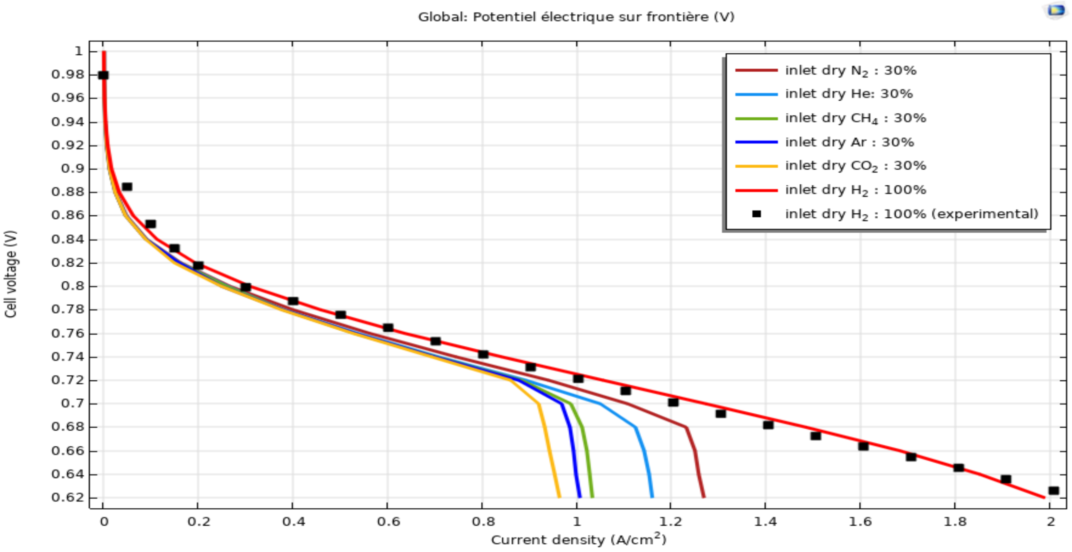


Figure 1: Comparison of Experimental data with the Secondary Current Distribution (cd) interface results (with dilution: $H_2$:70% and $X_i$:30%).

Keywords: PEMFC, hydrogen dilution, microporous layer (MPL), catalyst layers (CL), COMSOL Multiphysics.

References:

1. Y. Bultel, K. Wiezell, F. Jaouen, P. Ozil, G. Lindbergh, Electrochimica Acta 51 (2005), 474-488.
2. M. Boillot, C. Bonnet, N. Jatroudakis, P. Carre, S. Didierjean, F. Lapicque, Wiley Online Library, Fuel Cells Vol 6 (2006), 31-37.
3. Sunhoe Kim, S. Shimpalee, J.W. Van Zee, Journal of Power Sources 137 (2004), 43-52.

# P79. Optimal Control of a Coupled Electrical-thermal Equivalent Circuit Model for Li-ion Batteries with Applications to Fast Charging

M. Spinola[1], T. Dev[1], T. Reichbauer[2], C. Weißinger[1]
*[1] Virtual Battery Design, CoE Battery, Capgemini Engineering,*
*[2] Battery Testing, CoE Battery, Capgemini Engineering,*
*Frankfurter Ring 81, Munich, Germany.*
*michele.spinola@capgemini.com*

With the proceeding emergence of electrical applications as electrical vehicles, smartphones, etc., the importance of mathematical models and simulations which adequately describe the behavior of batteries increases. In this context, also the question of suitable charging protocols rises, focusing on to reach a desired state of charge (SOC) in minimal time with a given maximal power input while guaranteeing safety constrains as remaining in comfort zones for battery voltage and temperature. This yields a relevant, however, due to different coupled physicochemical-thermal effects, nontrivial issue to solve. To tackle this in a senseful, manageable manner, this work provides an equivalent circuit model (ECM) - and gradient-based optimization framework to elaborate promising charging protocols for Li-ion batteries in a numerically efficient way.

Here, the ECM coupling the electrical and thermal domain is used to describe battery voltage and temperature as satisfactory compromise between accuracy and computational complexity. The SOC is calculated via Coulomb counting. Further, due to the therein defined system of ordinary differential equations, the mentioned optimization task is represented as a so-called optimal control problem with state inequality and equality constraints (cf. [1,2,3,4]). Discretizing the model in the time domain results in a high-dimensional system to optimize. For this, a gradient-based optimization method is used since it allows to reach the optimum in a more efficient way compared to gradient-free methods. In this work, the sensitivities of voltage and temperature with respect to current are recursively calculated over time. The mentioned procedure leads to a further substantial speed-up of the optimization routine compared to typically used finite difference (FD) approximations. This is given by the fact that the proposed recursive calculation needs to solve the electrical-thermal model only once per gradient step whereas an FD approximation requires to solve it as many times as the number of time discretization points. The derived optimized load profiles are compared to different, typically used charging protocols as CCCV, MCCCV. Finally, simulatively obtained results are complemented by validation with a commercial 18650 cylindrical cell.

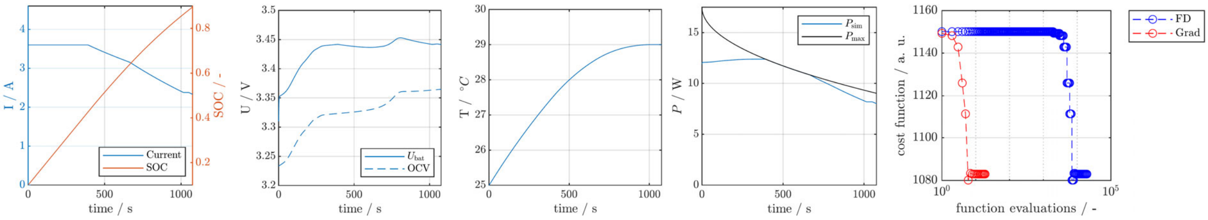


Figure 1: Obtained, simulated fast charging protocol from 10 % SOC to 90 % for an LFP cell with 1.2 Ah battery capacity with corresponding voltage, temperature and power output. The rightmost figure shows that significantly less function evaluations are needed with the described Grad-method compared to FD.

References:

1. K. Altmann, S. Stingelin, F. Tröltzsch, *International Journal of Circuit Theory and Applications*, *42*(8), 2014, 808-830.
2. F. Lam, A. Allam, W. T. Joe, Y. Choi, S. Onori, *IEEE Control Systems Letters*, *5*(6), 2020, 2066-2071.
3. S. Park, D. Lee, H. J. Ahn, C. Tomlin, S. Moura (2020, December). In *59th IEEE Conference on Decision and Control (CDC)*, 2020, 3506-3513.
4. H. E. Perez, X. Hu, S. Dey, S. J. Moura (2017). *IEEE Transactions on Vehicular Technology*, *66*(9), 7761-7770.

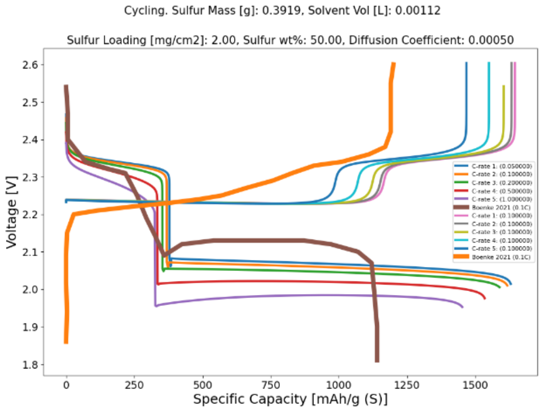
# What is Missing from Current Li-S Models to Predict Coin-Cell Behaviour?

Elizabeth Olisa[1, 2], Monica Marinescu[1, 2], Michael Cornish[1, 2]
[1] *Imperial College London, London, UK*
[2] *Faraday Institution, London, UK*
*Department of Mechanical Engineering, Imperial College London, SW7 2AZ*
*l.olisa20@imperial.ac.uk*

To meet the growing demand for batteries, alternative battery chemistries beyond lithium-ion (Li-ion) are required. A promising alternative is lithium-sulfur (Li-S). As most of the materials and morphology development in Li-S batteries is conducted at coin-cell level, understanding the mechanisms that limit coin-cell performance and how they translate to larger cell form factors is essential. The ability to test assumptions and predictions through a model saves experimental time and cost, and enables simulation of behaviour under different conditions. Physics-based models are being used successfully for Li-ion cell design, and has created an opportunity to achieve this level of maturity with Li-S models. One key difference is that, for Li-S batteries, the mechanisms governing cell performance depend on factors such as electrolyte-to-sulfur, and electrolyte-to-cathode ratios, which change significantly when scaling-up from coin-cell to pouch-cell.

Li-S battery models are predominantly designed for pouch-cell batteries. Whilst these models provide the fundamental tool to analyse the behaviour of a pouch-cell, they have not been tested for coin-cells. The physical differences between coin and pouch-cells result in differing mechanisms, leading to the question: *can a pouch-cell model be re-parameterised to accurately predict coin-cell behaviour?* To answer this question, published zero-dimensional (0D) pouch-cell models [1], [2], [3] were analysed and upgraded. The experimental data published by Boenke et al.[4] were used for parametrisation and validation.

The new model is able predict all behaviour as tested by Boenke [4], including both charge and discharge mechanism, and varying parameters such as sulfur loading and sulfur weight percent. To improve predictions further, several features were changed from existing models, including the porosity derivation based on concentration of precipitated sulfur. Unlike existing Li-S models, this model can retrieve C-rate dependence in terms of both capacity and voltage changes. This is achieved via transport of species between the cathode and a reservoir of excess electrolyte, and the influence of area, rate of change of species and precipitation dynamics on one another during cycling.



Despite its simplicity, these changes have significantly improved the model's accuracy when compared to experimental data. From here, further mechanisms or dimensionality can be added, when needed, to capture additional features, such as cell degradation, with the confidence that the correct causality for coin-cell behaviour is captured.

References:

[1] M. Marinescu, T. Zhang, and G. J. Offer, "A zero dimensional model of lithium-sulfur batteries during charge and discharge," *Physical Chemistry Chemical Physics*, vol. 18, no. 1, pp. 584–593, 2016, doi: 10.1039/c5cp05755h.

[2] M. Cornish and M. Marinescu, "Towards Rigorous Validation of Li-S Battery Models," Dec. 2021, [Online]. Available: http://arxiv.org/abs/2112.08722

[3] K. Kumaresan, Y. Mikhaylik, and R. E. White, "A Mathematical Model for a Lithium–Sulfur Cell," *J. Electrochem. Soc.*, vol. 155, no. 8, p. A576, 2008, doi: 10.1149/1.2937304.

[4] T. Boenke *et al.*, "Sulfur Transfer Melt Infiltration for High-Power Carbon Nanotube Sheets in Lithium-Sulfur Pouch Cells," *Batter Supercaps*, vol. 4, no. 6, pp. 989–1002, Jun. 2021, doi: 10.1002/batt.202100033.

# P81. Development of 3D-Printed Gas Diffusion Layers for Enhanced Liquid Water Transport in Polymer Electrolyte Fuel Cells

Tim Dörenkamp[1], Ambra Zaccarelli[2], Felix N. Büchi[1], Thomas J. Schmidt[1,3], Jens Eller[1]
[1] *Electrochemistry Laboratory, Paul Scherrer Insitut, Villigen, Switzerland*
[2] *Department of Materials, ETH Zürich, Zürich, Switzerland*
[3] *Department of Physical Chemistry, ETH Zürich, Zürich, Switzerland*
*tim.doerenkamp@psi.ch*

Recent work has shown that structured gas diffusion layers (GDLs) can enhance the performance of polymer electrolyte fuel cells (PEFC) [1] and that additive manufacturing (AM) has been identified as a viable method to fabricate just such [2,3]. In this work we explore the use of projection µ-stereolithography (PµSL) as a method to manufacture porous structures which can meet the requirements of commercialized GDLs regarding feature size (~10 µm fiber diameter) and build volume (several tens of mm$^2$ for differential cell tests). Initially, GDLs prepared by AM were coarse with finest structures of about 120 µm [3] which is in the range of typical GDL thickness. The 3D printed structures are designed to guide the product water through the GDL by adjusting the throat size [4] and therefore the capillary pressure, which is required in the water phase to percolate through the throats to the neighboring pore as described by Young-Laplace law. Figure 1 shows (a) one of the structures tested and (b) the pressure measurement during its drainage. The filling of the structures is monitored by employing X-ray radiography as well as X-ray tomography and the results are compared to the capillary pressure curve computed by GeoDict (Fig.1 c). Furthermore, we will discuss how to exploit the relationship between throat size and break-through pressure to achieve desired water pathways for enhanced water transport and present a pathway towards integration of these materials into operating fuel cells (e.g., printing, carbonization & hydrophobic treatment).

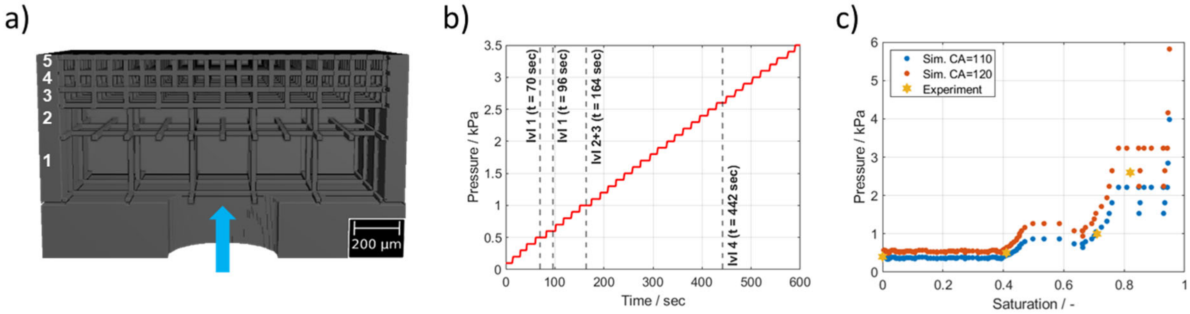


Figure 1: a) Designed pore size gradient b) Capillary pressure vs. time during drainage c) Measured vs. simulated pressure for different contact angles (CA)

References:
1. C. Csoklich et. al., *Energy & Environmental Science*, 2022, 15, 1293-1306
2. D. Niblett et. al., *Journal of the Electrochemical Society*, 2020, 167, 013520
3. D. Niblett et. al., *International Journal of Hydrogen Energy*, 2022, 47, 23393-23410
4. D. Niblett et. al., *Journal of Power Sources*, 2020, 471, 228427

# P82. Aqueous Interfaces for Sustainable Electric Energy Storage

Vasily Artemov
*École Polytechnique Fédérale de Lausanne (EPFL),*
*1015, Lausanne, Switzerland*
*vasily.artemov@epfl.ch*

The demand for short-term electrical energy storage is growing rapidly with the development of renewable energy systems. However, current technologies rely on environmentally unsafe materials and cause enormous $CO_2$ emissions during manufacturing and recycling. I will discuss possible alternatives using anomalous electrical properties of water confined to the nanoscale (including naturally abundant) materials. I will discuss the atomic-level electrodynamics of water and aqueous electrolyte solutions in bulk and at strong confinement based on the wide range of experimental data [1, 2]. I will highlight the distinction between the bulk and confined water states in terms of molecular structure and dynamics [3, 4]. I will show a prototype of a supercapacitor for sustainable electrical energy storage using confinement-controlled water that can become a game changer in renewable energy storage [5]. I will outline perspectives for the research of confined fluids for a better understanding of atmospheric and natural phenomena and innovative critical raw materials for energy applications.

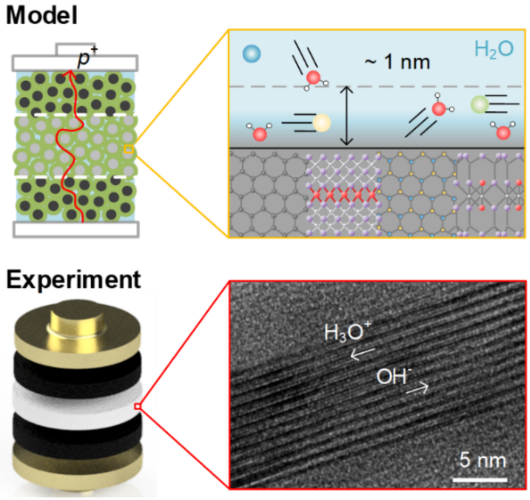


Figure 1: The model (top) and experimental (bottom) concepts of sustainable electric energy storage system (supercapacitor) using strongly confined water properties.

References:
1. Artemov, V. The Electrodynamics of Water and Ice, Springer, **2021** (book).
2. Artemov, V.; Ryzhov, A.; Ouerdane, H.; Stevenson, K. J., J. Phys. Chem. C **2023**, 127, 261
3. Artemov V.; Uykur, E.; Kapralov, P.; Kiselev, A.; Stevenson, K. J.; Ouerdane, H.; Dressel, M., J. Phys. Chem. Lett. **2020**, 11, 3623
4. Artemov V.; Frank, L.; Doronin, R.; Stärk, P.; Schlaich. A.; Andreev, A.; Leisner, T., Radenovic, A.; Kiselev A., J. Phys. Chem. Lett. **2023**, 14, 4796
5. Melnik, S.; Ryzhov, A.; Kiselev, A.; Radenovic, A.; Weil, T.; Stevenson, K. J.; Artemov, V. J. Phys. Chem. Lett. **2023**, 14, 6572

# P83. Preparation of Titanium Multilayer Porous Transport Layers (PTLs) for Polymer Electrolyte Water Electrolysis (PEWE)

Z. Turtayeva, C. C. Weber, M. Ammann, F.N. Büchi
*Electrochemistry Laboratory, Paul Scherrer Institute*
*Villigen PSI, Switzerland.*
*zarina.turtayeva@psi.ch*

Polymer electrolyte water electrolysis (PEWE) converts stochastic, renewable electricity into transportable and storable hydrogen energy. However, the use of expensive catalysts such as iridium oxide and platinum for the oxygen and hydrogen evolution reactions leads to high production costs and restriction of widespread commercialization. To overcome this issue, one of the goals is the reduction of catalyst loading and enhance catalyst utilization. Therefore, the elucidation of the relevant design of porous transport layers (PTL) for high catalyst utilization is a key requirement in the field of PEWE [1]. Good interfacial contact at the catalyst layer (CL) and PTL interface is necessary to achieve high catalyst utilization during water splitting. Therefore, two-layer PTL/MPL NovElyTi™ materials for PEWE have initially been developed that allowed to improve the anode catalyst utilization for conventional $IrO_2$ loading [2].

The present study investigates the concept of creating a 3rd and finer Ti powder layer (few microns particle size) using spray coating on the surface of actual NovElyTi™ material and it's sintering (Fig. 1). Spherical, sponge and hydrogenation–dehydrogenation titanium powders are used as starting materials. A systematic study is conducted to find the processing parameters, which can demonstrate the potential of the multilayer PTL development to reduce the contact resistance between Ti structures and the CL and aiming to use very low loadings of $IrO_2$.

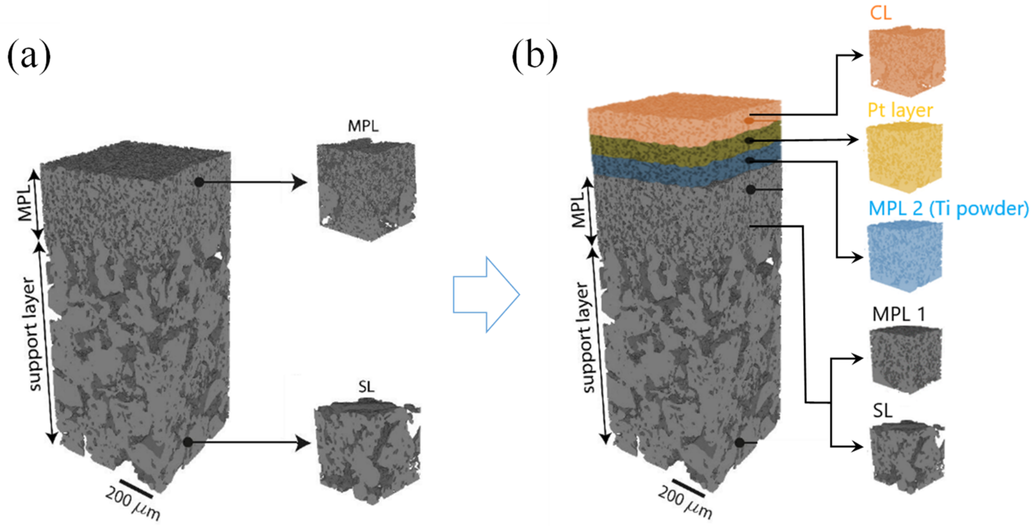


Figure 1: (a) NovElyTi™ sintered material with support and micro porous layer and (b) aimed multilayer PTL and catalyst layer.

References:
1. Schuler, T. Towards a Generic Understanding of Porous Transport Layers in Polymer Electrolyte Water Electrolysis., PhD Thesis (2020).
2. Weber, C. C. *et al.* Microporous Transport Layers Facilitating Low Iridium Loadings in Polymer Electrolyte Water Electrolysis. *RSC Energy Environ. Sci. Catal.* (2023).

# P84. Advantage of Spatially Resolved 3D Simulations for Analysis of Local Effects and Gradients along the Channel in a PEM Fuel Cell

Nick Raue, Johannes Schall, Dietmar Gerteisen
*Fraunhofer Institute for Solar Energy Systems ISE*
*Heidenhofstraße 2, 79110 Freiburg, Germany*
*nick.raue@ise.fraunhofer.de*

Spatially resolved studies of PEM fuel cells represent an important tool for analyzing and better understanding the behavior of PEM fuel cells and have been carried out experimentally and numerically with models in 1-3D format for many years [1]. Supporting the experimental part, numerical models provide more detailed insights into cell processes and reactions, where 3D models specifically illustrate local effects in each dimension like channel-rib variations or through-plane gradients in the GDL and electrodes and thus enable the most detailed, numerical insight related to the geometric aspect.

At Fraunhofer ISE, the CFD code AVL-FIRE M is used for the 3D simulations of PEM fuel cells, which offers a wide range of electrochemical reaction and transport processes in the porous layers as well as general flow effects in a fuel cell [2]. To validate the model, measured values for the local current density and HFR (range 0.9 - 0.25V) were used, which were obtained with a segmented ATC (along the channel) PEM fuel cell, developed and operated at Fraunhofer ISE with an active area of 50 cm² and 25 segments. For validating the model, this work shows the comparison of experimental and simulated local current density and HFR values at selected potentials and for variations e.g., of the inlet humidity. In addition, local effects and their driving forces, such as the water transport mechanisms in the porous layers, were investigated. With the aim of highlighting the advantages of 3D models, these investigations are carried out along the channel and in through -/in-plane direction. As an example, at high potentials it could be observed that the current decreases stronger towards the air outlet, which was found to be a result of the water transport through the membrane. The back diffusion, influenced by the asymmetric humidification and operation in counter flow, shows a strong increase near the air outlet where the current drop starts. Following this the membrane locally dries out and in combination with the oxygen consumption the current decreases stronger than in the mid segments (Fig. 1 (b)).

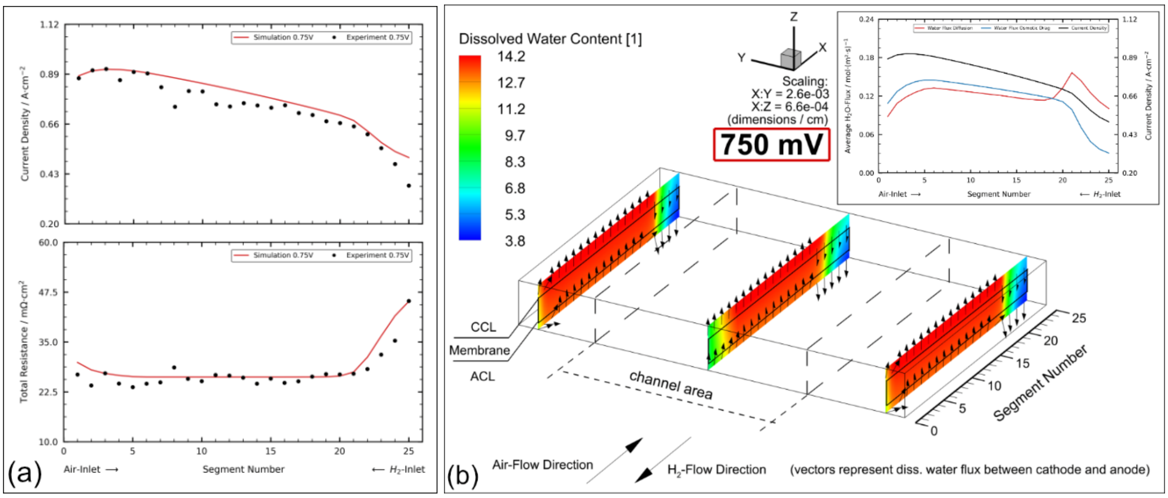


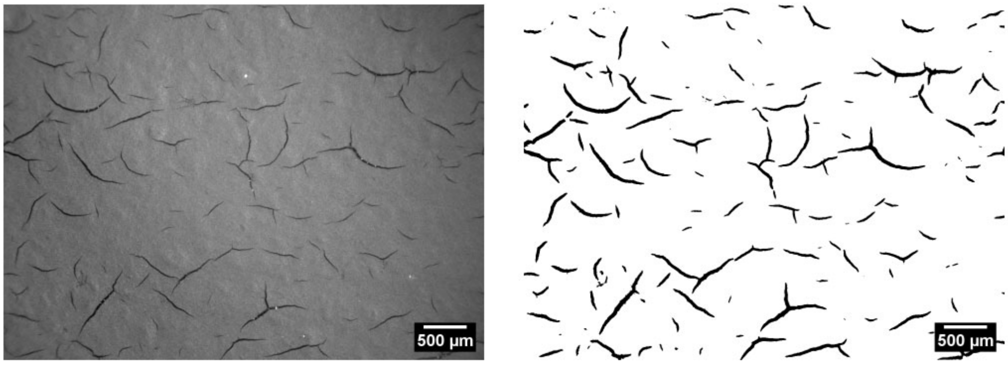
Figure 1: (a) Experimental and simulated local current density and HFR development along the channel, (b) influence of water transport mechanisms on water content in through-plane direction in MEA (both for: inlet humidity anode/cathode = 30/70 %, cooling temperature = 80 °C, outlet pressure = 2 bar (a))

References:
1. C. Kalyvas, A. Kucernak, D. Brett, G. Hinds, S. Atkins, N. Brandon, WIREs Energy Environ 3 (2014) 254-275. doi: 10.1002/wene.86
2. C. Fink, S. Gößling, L. Karpenko-Jereb, P. Urthaler, Fuel Cells 20(4) (2020), 431-452, doi: 10.1002/fuce.201900197

# P85. Methods for Cracks Analysis in MPLs

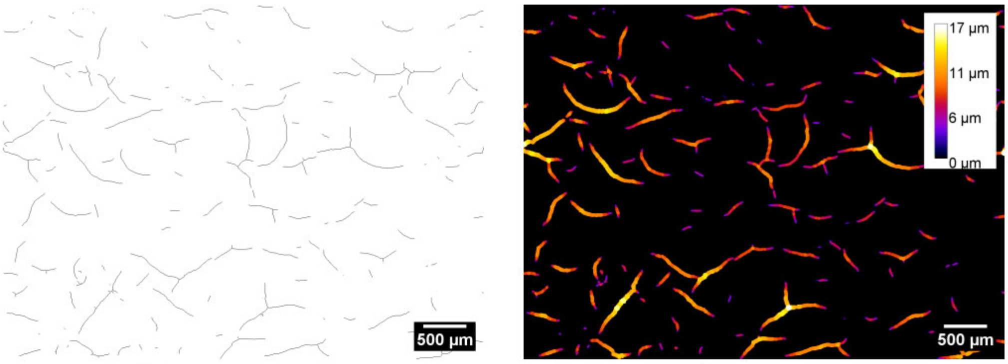
B. Galante[1], J. Herranz[1], F.N. Büchi[1], R. Gilardi[2], A. Guglielmi[2], B. Buades[2], J. Eller[1]
*[1] Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*
*[2] Imerys Graphite & Carbon, 6804 Bironico, Switzerland*
*Bruno.galante@psi.ch*

The role of cracks in Micro Porous Layers (MPL) in Polymer-Electrolyte Fuel Cells (PEFCs) has captured increasing attention due to its possible beneficial impact on cell performance [1–4]. Numerous studies have begun to address the crack formation processes and analyze the morphology of the cracks [2-4]. In this contribution, a method for an in-depth characterization of the surface cracks in an MPL is proposed. This method is based on optical microscopy images and image processing steps for segmenting images of the MPL surface and labeling the cracks using "ImageJ-Fiji" [5]. Labeling all the cracks allows for the calculation of the overall cracked area and the individual crack size. The identified cracks are further analyzed addressing the crack length, shape, and thickness as illustrated exemplarily in Figure 1. The combination of this characterization of the MPL cracks and fuel cell testing will allow the assessment of how the cracks influence cell performance.



(a) Optical microscopy image of MPL cracks.

(b) Segmented image.



(c) Skeleton of the cracks.

(d) Cracks width.

Figure 1: Overview of the crack analysis workflow.

References:
1. Z. Chen et al. "Crack evolution during the film drying process of fuel cell microporous layer ink", Colloids and Surfaces A - Physicochemical and Engineering Aspects 650 (2022) 129283.
2. J. Dai et al. "Analysis on the influence of crack structure on MPL transmission properties", Journal of Power Sources 562 (2023) 232790.
3. S. Wang et al. "Enhancing the properties of water and gas management for proton exchange membrane fuel cells via tailored intersected cracks in a microporous layer", Journal of Power Sources 533 (2022) 231402.
4. Z. Chen et al. "Interrelation between ink viscoelasticity and crack structure of fuel cell microporous layer", Fuel 360 (2024) 130629.
5. https://imagej.net/software/fiji/

# P86. Modeling of Transport in Alkaline Electrolyzers Using Open-source Computational Fluid Dynamics

Andreas N. Jacobsen[1], Ehsan Mahravan[1], Jacopo Catalano[2], Pourya Forooghi[1]
[1]*Department of Mechanical and Production Engineering, Aarhus University*
*Katrinebjergvej 89 G-F, 8200 Aarhus N, Denmark*
[2]*Department of Biological and Chemical Engineering, Aarhus University*
*Gustav Wieds vej 10 D, 8000 Aarhus C, Denmark*
*anj@mpe.au.dk*

Detailed 3-dimentional modeling of transport phenomena is an effective tool in design and optimization of water electrolyzers, and in understanding the underlying physical mechanisms [1, 2]. In this work, we have developed a computational fluid dynamics (CFD) solver for modeling of multiphase flow and mass transfer in an alkaline water electrolyzer at cell level. The solver is developed in OpenFOAM, an open-source library for development of partial differential equation solutions, most widely used for CFD problems. The modular nature of the solver and availability of the source allows unlimited extension of the model and inclusion of different sub-models. Moreover, excellent parallelization capabilities of OpenFOAM for very large computational domains can be an advantage.

The developed tool employs the finite volume method to solve the governing transport equations for species concentration distribution, current/ion distribution in the fluid and electrodes, and fluid momentum in porous and non-porous regions. Two phase flow is modeled as mixture where bubble drift relative to the mixture, thus only one momentum equation needs to be solved. Coverage sub models are introduced to capture related ohmic losses [2]. This enables reproducing polarization curves to be compared with experiments and to be used in optimizing the design, for example for the design of inlet and outlet channels and the electrode.

A new bubble growth model was introduced, the model both captures the growth of moving bubbles and attached bubbles. The sensitivity of mass transfer mechanisms is presented.
The model is validated against a series of polarization curves, with varying temperatures from in-house experiments. The solver is then utilized to study the effect of different operational and design parameters on performance of a zero-gap cell.

References:

1. Jaeseung Lee , Afroz Alam , Chungi Park , Soobin Yoon , Hyunchul Ju, *FUEL,* **315** (2022), 123273
2. J.S. Lopata, S-G. Kang, H-S. Cho, C-H. Kim, J.W. Weidner, S. Shimpalee*, Electrochimica Acta*, **390**, 2021, 138802
3. H. Vogt, R.J. Balzer, *Electrochimica Acta* **50** (2005), 2073-2079

# P87. Nonlinear Frequency Response Analysis for the Proton Exchange Membrane Water Electrolysis Model Validation

Tamara Miličić[1], Thanh Vu Hoang[2,3], Kasun Muthunayakage[1,2], Luka A. Živković[1],
Tobias K. S. Ritschel[4], Tanja Vidaković-Koch[1]
*[1] Electrochemical Energy Conversion, Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstraße 1, 39106 Magdeburg, Germany*
*[2] Otto von Guericke University, Universitätplatz 1, 39106 Magdeburg, Germany*
*[3] IEK-13, Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*
*[4] Department of Applied Mathematics and Computer Science, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*
*milicic@mpi-magdeburg.mpg.de*

For the advancement of any technology, experimental investigation is invaluable. However, mathematical models contribute significantly to the understanding and are often necessary for the interpretation of experimental data. This is especially the case for complex systems such as electrochemical reactors where the interplay of the electrochemical kinetics, mass, and heat transport is present. Nevertheless, sufficient information from experiments is crucial for obtaining realistic model predictions. In electrochemical engineering, macroscale models are usually parametrized based on the polarization curve and/or electrochemical impedance spectroscopy (EIS) data. The polarization curve contains a steady-state characteristic and as such lacks any information about the dynamics. In contrast, EIS is a dynamic method but is limited to the linear range. Since the coupling of electrochemical reactors and renewable resources is foreseen, the reactors will operate highly dynamically. Thus, both dynamic and nonlinear information should be taken into consideration for the model validation.

In this work, we suggest a nonlinear frequency response (NFR) analysis [1] for model parametrization and validation. The proton exchange membrane water electrolyzer (PEMWE) is used as an example system. First, experimental measurements on a lab-scale PEMWE were performed under different operating conditions. Subsequently, a simple model was developed and a maximum likelihood estimation approach [2, 3] was applied for the model parameter estimation. The reliability of the obtained model and parameters was discussed, as well as the advantage of the NFR analysis compared to the studies based on the polarization curve and EIS.

References:

1. T. Vidaković-Koch, T. Miličić, L.A. Živković, H.S. Chan, U. Krewer, M. Petkovska, *Cur. Opin. Electrochem.*, 30 (2021), 100851
2. A. van den Bos, Parameter Estimation for Scientists and Engineers, Wiley, 2007
3. D. Boiroux, T.K.S. Ritschel, N.K. Poulsen, H. Madsen, J.B. Jorgensen, *IEEE 58th Conference on Decision and Control (CDC)*, Nice, France, December 11-13, 2019, 6983-6988

(abstract withdrawn)

# P89. Parameters Estimation Fitting Loop for Enhanced Physical Based Model

Y. Aymon, P. Caliandro
*BFH ESREC*
*Aarbergstrasse 46*
*2503 Biel/Bienne*
*yohan.aymon@bfh.ch*

The measurement of specific physical and geometrical parameters of lithium-ion cells presents difficulties, making it challenging to obtain accurate values. Using available voltage measurements from a tested cell, a fitting procedure was implemented to approximate parameters ordinarily hard to obtain. By combining the result of a Doyle–Fuller–Newman model implementation in COMSOL and a fitting procedure running on MATLAB, an estimation of the parameters is realized. Then the results are integrated in a fitted physical based model, where it can be integrated in a simulation bench using MATLAB Livelink. This work's primary objective is to reduce measurement time and resources spent without hindering the reliability of the battery model, thus contributing to more cost-effective performance analysis and design in the field of lithium-ion batteries.

The initial parameter sensitivity analysis[1] yielded to a classification of importance in the parameters to estimate. Then, the optimization process involves two main stages: parameters fitting and model simulation. A combination of MATLAB and some voltage measurements made on a real cell is employed for the parameter fitting procedure. Taken as references, these measurements are compared with simulated voltage in COMSOL by applying strictly the same current on the model and the tested cell. The RMSE cost function is implemented between a given measured voltage and a simulated voltage outputted from COMSOL. This process runs on an HPC server and uses a Particle Swarm algorithm to enhance the search of an optimal set across the solution space. This method also brings the opportunity to run models in parallel, thus improving the total simulation time as well. A two-step optimization approach is also applied and improves the overall precision, especially during long profiles.

The results showcase the effectiveness of the optimization strategy, with 11 parameters successfully fitted. The Root Mean Square Error (RMSE) between the simulated voltage and the measured curve is varying from 157 mV down to 5.2 mV at best.

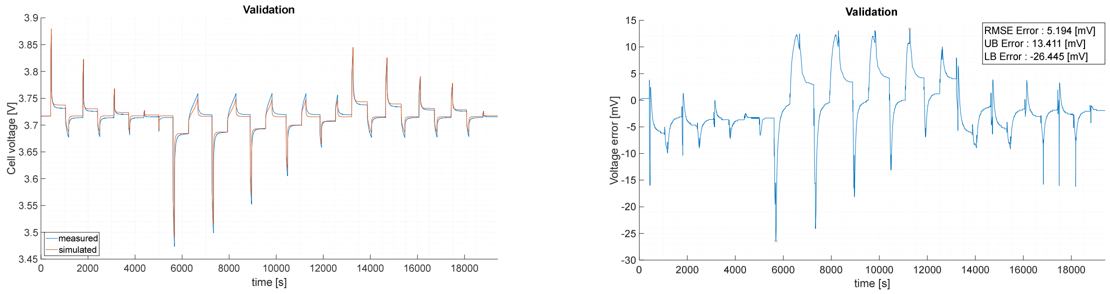


Figure 1: (Left) Simulated potential output from COMSOL and measured voltage (Real cell potential); (Right) Error curve representing the difference between measured and simulated voltage.

References:
1. Luder, Daniel (15 October 2020). Enhanced Physics-Based Models for State Estimation of Li-Ion Batteries In: COMSOL Conference 2020. online. 14./15. October 2020.

# Organizing Committee

**Dr. P. Boillat**

Senior Scientist, Fuel Cell Systems and Diagnostics Group & Laboratory for Neutron Scattering and Imaging

**Dr. Felix N. Büchi**

Senior Scientist, Fuel Cell Systems & Diagnostics Group

**Dr. Mario El Kazzi**

Group Head, Battery Materials and Diagnostics

**Dr. Jens Eller**

Senior Scientist, Fuel Cell Systems and Diagnostics Group

**Cordelia Gloor**

Staff, Electrochemistry Laboratory

**PD Dr. Lorenz Gubler**

Group Head, Membranes & Electrochemical Cells

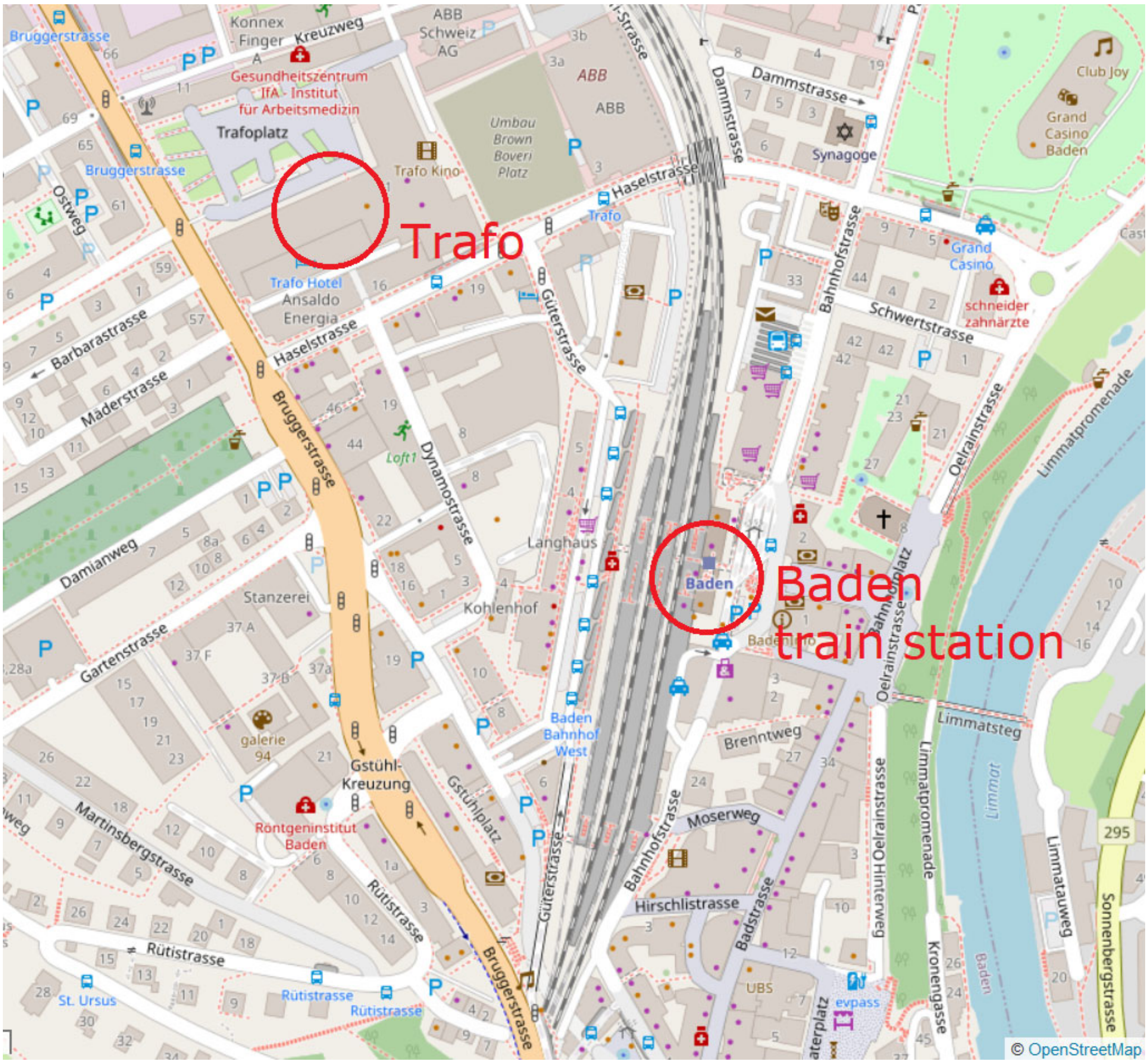
**Dr. Juan Herranz**

Group Head, Fuel Cell Systems & Diagnostics

**Dr. Sigita Trabesinger**

Group Head, Battery Electrodes & Cells

# Map Baden



**Conference Venue**

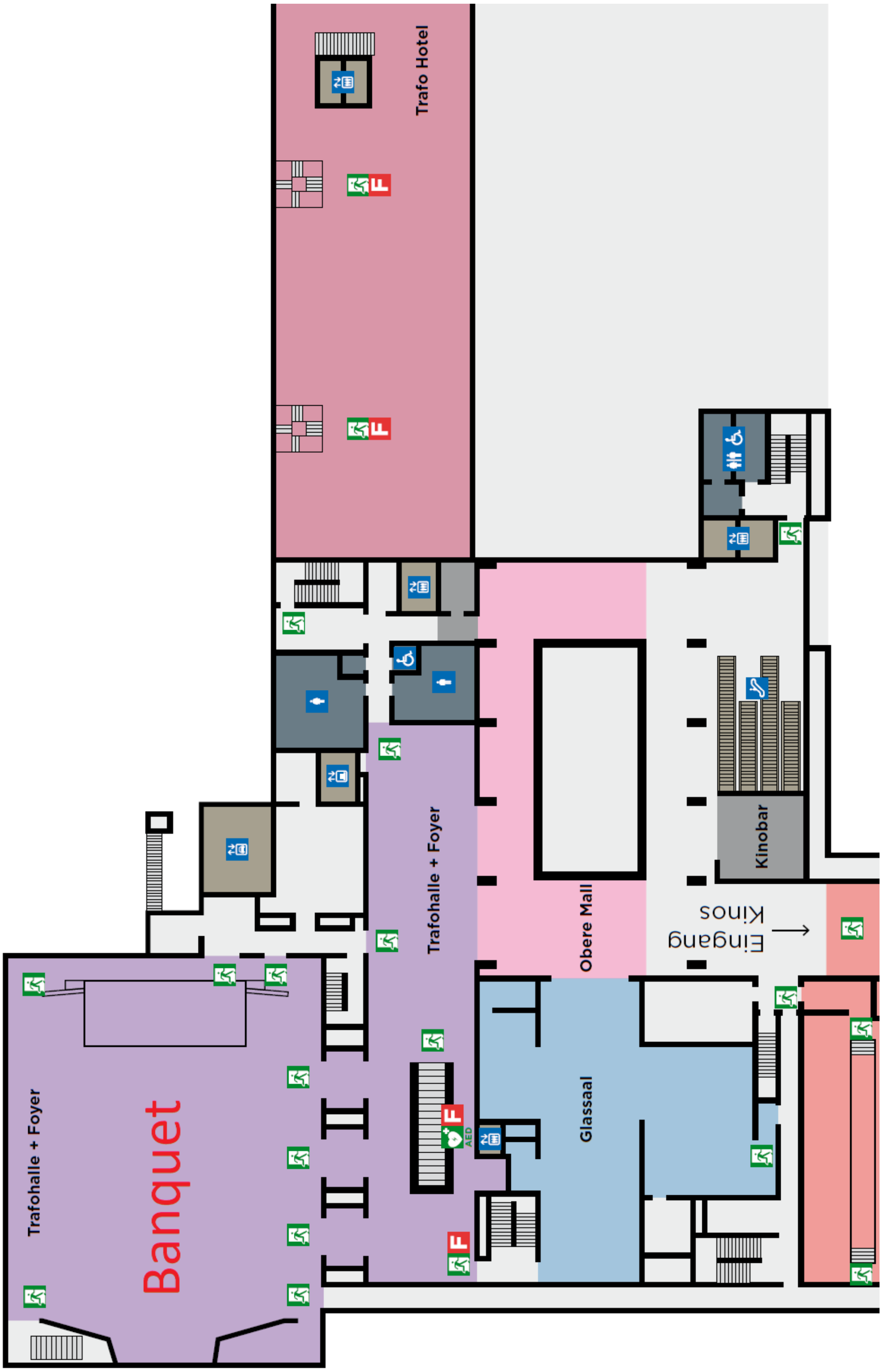
Trafo Baden
Brown Boveri Platz 1
5400 Baden

Web: www.trafobaden.ch
Phone: +41 (0)56 204 08 88

Walking distance between Trafo and Baden train station: 5 min.

# Trafo Floor Plan, Ground Floor

# Trafo Floor Plan, First Floor



# Trafo, Venue Layout