Perovskite Oxide Based Electrodes for the Oxygen Reduction and Evolution Reactions: The Underlying Mechanism

Review Article

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Perovskite Oxide Based Electrodes for the Oxygen Reduction and Evolution Reactions: The Underlying Mechanism

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ABSTRACT: One hindrance to the development of fuel cells and electrolyzers are the oxygen electrodes, which suffer from high overpotentials and slow kinetics. Perovskite oxides have been shown to be promising oxygen electrode catalysts because of their low cost, flexibility, and tailorable properties. In order to improve perovskite catalysts for the oxygen reduction (ORR) and oxygen evolution (OER) reactions, a better understanding of their reaction mechanisms is needed. This Perspective aims to inform researchers of the current proposed reaction mechanisms for ORR and OER on perovskites and perovskite/carbon composites in order to guide future catalyst development. Additionally, important experimental practices will be recommended. A recent development for OER is the lattice oxygen evolution reaction, which is a possible addition to the conventional four consecutive proton-coupled electron transfer mechanism. Carbon additives are consistently added to perovskites to enhance conductivity and ORR/OER activity. However, carbon plays an active role in ORR, and there is evidence of a synergistic relationship between perovskite and carbon in perovskite/carbon composites.

KEYWORDS: *perovskite, oxygen reduction, oxygen evolution, reaction mechanism, composite, alkaline*
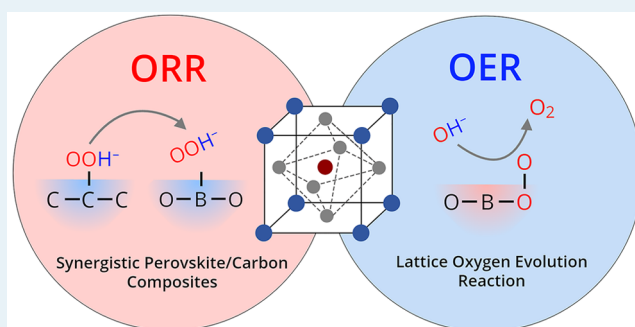
1. INTRODUCTION

Renewable energy usage has increased over the past 20 years in response to environmental pollution issues.[1] However, renewable energy sources suffer from intermittency[2,3] and cannot satisfy the global energy demand without being coupled to a reliable energy storage system. A hydrogen-based system is one solution to this problem,[3,4] where electrolyzers convert the surplus of renewable energy into chemical energy stored in chemical bonds of H_2 and fuel cells convert H_2 back into electricity when and where it is needed. The reactions occurring at the oxygen electrodes, oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), are significant hindrances to the further development of fuel cells and electrolyzers, respectively, because they suffer from high overpotentials and slow kinetics. To overcome this, novel catalyst materials for the ORR and OER have been widely investigated over the last few decades. Under low-temperature conditions, fuel cells and electrolyzers can operate using an acidic or alkaline electrolyte. In acidic media, expensive noble metal catalysts are usually required, such as Pt and IrO_2. An alkaline environment is particularly advantageous because a wide variety of materials present adequate chemical stability.[5,6] In particular, perovskite oxides have shown promising ORR and OER activity as catalysts for alkaline fuel cells and water electrolyzers. Perovskite oxides are a group of complex oxides with the formula ABO_3 and contain abundant, relatively low-cost elements. The development of perovskite catalysts in alkaline media for ORR and OER began around the 1970s to 1980s with the work of researchers such as Matsumoto et al.[7] and Bockris and Otagawa.[8] Since then, the reaction mechanisms for ORR and OER still are not completely understood. Understanding these reactions is crucial for overcoming the high overpotentials associated with these electrochemical reactions and developing highly active catalysts.

One disadvantage of many perovskite oxides is their relatively low electrical conductivity. To increase the electrical conductivity pathways within the perovskite electrode and to boost the electrode performance, carbon conductive additives are commonly added to both ORR and OER perovskite-based electrodes. However, recent findings have shown that carbon is not just a conductive additive but is an active participant in ORR. Furthermore, carbon addition can influence perovskite
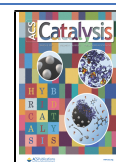
properties, and thus, physical-chemical characterizations of perovskite/carbon composites do not necessarily represent the intrinsic properties of the perovskites. Therefore, it is important to recognize and understand the non-negligible impact of carbon on perovskite ORR activity. For OER perovskite-based electrodes, the influence of carbon on the OER mechanism and activity seems to be less significant but also not sufficiently understood. However, carbon oxidizes at the potentials where OER occurs, and thus, it should be avoided to ensure electrode stability.

Recently, developments in the understanding of a new OER pathway involving perovskite's lattice oxygen, the so-called lattice oxygen evolution reaction (LOER), have occurred.[9−14] Before, the oxygen evolution reaction was thought to occur solely through four consecutive proton-coupled electron transfer (PCET) steps. Particularly for perovskite oxides, some evidence has suggested that LOER is the preferred reaction mechanism for water oxidation, opening new perspectives in perovskite catalyst optimization. Indeed, understanding the OER and ORR reaction mechanisms can lead to the fast design of the best catalyst because it reveals the key perovskite properties for maximizing the electrocatalytic activity.

This Perspective is focused on explaining the current understanding of the oxygen reduction and evolution reaction mechanisms for perovskites in alkaline environments. Due to the participation of carbon in the ORR mechanism, perovskites are discussed separately from perovskite/carbon composites. Currently, carbon's influence on the OER reaction mechanism is not as clear, and thus, carbon presence in perovskite OER electrodes is not discussed in depth. However, this Perspective will detail the recent understanding of the LOER mechanism. Open questions and theories are also mentioned in order to facilitate further research. Finally, suggestions are given on good experimental practices when measuring the ORR or OER activity of perovskites or perovskite/carbon composites. These practices are important for accurate measurements and for comparison of results within the scientific community.

2. REACTION MECHANISMS

2.1. ORR Mechanism. Although the oxygen reduction reaction (ORR) has been widely investigated with the development of fuel cells, the exact reaction mechanism is still under debate. The overall four-electron reaction is given in eq 1.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E_0 = 0.40 \text{ V}_{SHE} \quad (1)$$
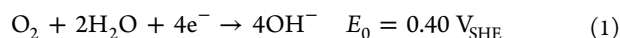
This general reaction can then be broken down into single-electron reaction steps. However, depending on electrolyte pH and catalyst, there are multiple possible reaction pathways. Two possible reaction pathways for the ORR mechanism are the so-called dissociative and associative pathways. In the dissociative pathway, the O−O bond is broken as O_2 adsorbs onto two metal active sites. As a result, no peroxide intermediate is formed. The O−O bond in oxygen molecules requires a high amount of energy to break,[15] making the dissociative pathway rather unlikely for most catalysts.[16−18] In the associative pathway, the O_2 molecule adsorbs onto a single metal site. A peroxide intermediate is formed (eq 2), and via this pathway, the O−O bond is easier to break.[15,19] In alkaline media, hydrogen peroxide takes the form HO_2^-.[20]

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad E_0 = -0.07 \text{ V}_{SHE} \quad (2)$$
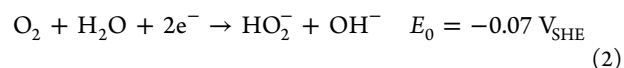
Then, the peroxide intermediate can electrochemically react on the catalyst surface (eq 3) or desorb from the catalyst surface. At the same time, the peroxide can also react chemically (eq 4) in the electrolyte or at the catalyst surface. If the peroxide escapes into the bulk electrolyte, only two electrons are transferred, making this pathway less energetically efficient than the four-electron pathways.

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad E_0 = 0.87 \text{ V}_{SHE} \quad (3)$$

$$2HO_2^- \rightarrow 2OH^- + O_2 \quad (4)$$

If the oxygen produced by the chemical disproportionation of peroxide (eq 4) is further reduced via eq 2, more electrons can be transferred. Rotating ring disk electrode (RRDE) is frequently used to determine the number of electrons transferred by measuring the amount of hydroperoxide detected at the ring. In this way, it is possible to determine if two or four electrons have been transferred. However, it is not possible to know with RRDE if four electrons have been transferred via the dissociative or associative pathways (i.e., with or without the formation of peroxide intermediates). An overview of the possible reaction pathways described so far is shown in Figure 1.
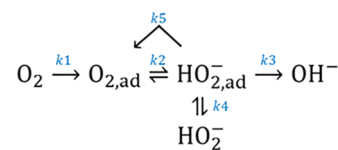

Figure 1. Possible ORR reaction pathways. Adapted with permission from ref 18. Copyright 2003 PCCP Owner Societies.

Often in literature, the ORR activity of a perovskite catalyst is evaluated with carbon added to the catalyst layer. However, in this case, the measured activity is that of the perovskite/carbon composite and not the intrinsic activity of the perovskite. Carbon's presence will convolute any mechanistic studies on perovskite catalysts. Therefore, to evaluate the true activity of the perovskite oxide, carbon should be excluded from the electrodes. However, this may also cause issues. Many perovskites lack sufficient electrical conductivity without carbon.[21] In addition, carbon often helps to disperse catalyst particles on the substrate.[22] Solving these issues and finding the true activities of the perovskites are imperative for future catalyst development. Indeed, given the carbon corrosion issue at fuel cell cathode operating conditions,[23,24] the development of a perovskite catalyst that is intrinsically conductive and highly active for ORR would represent a breakthrough in the field.

In the following sections, the detailed ORR reaction mechanisms on perovskites, carbon, and perovskite/carbon composites are discussed. Particularly, section 2.1.3 details the significant influence of carbon on the perovskite ORR activity. Although in literature studies the presence of carbon in ORR perovskite-based electrodes is often not explicitly stated, in this Perspective, it is always specified if carbon was added to the catalyst layer.

2.1.1. On Perovskites. As mentioned above, in order to probe the ORR reaction mechanisms on perovskite surfaces, carbon should not be added as a conductive additive. Indeed,

only by using perovskite single-material electrodes can the ORR mechanism occurring on the perovskite surface be studied. To date, a small number of researchers have published the ORR activity of perovskites without carbon and a few examples are given here.[25−28] One way that perovskites have been successfully studied without carbon is by using epitaxial thin films.[29−33] With physical vapor deposition techniques, the perovskite's structure and composition can be precisely tailored.

Regarding the ORR mechanism for perovskite single electrodes, a possible catalytic cycle (without carbon) is shown in Figure 2. At the reducing potentials required for the
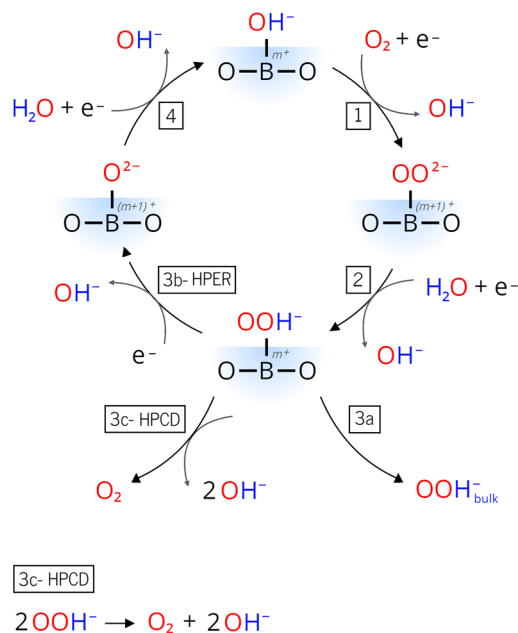

Figure 2. An ORR reaction mechanism on perovskite surfaces. Step 3 has three different possible pathways: (3a) the release of peroxide from the surface; (3b) the electrochemical reduction of peroxide; and (3c) the chemical disproportionation of two peroxide molecules, which leads to the formation of an oxygen molecule. From there, the oxygen produced by HPCD has the possibility to re-enter the catalytic cycle. Adapted with permission from ref 37. Copyright Nature Publishing Group.

oxygen reduction reaction, in alkaline media, the perovskite surface is covered by hydroxide ions.[34,35] Therefore, hydroxide adsorbs onto the perovskite surface before oxygen reduction. Then, the first step is to replace OH_{ads}, as shown in step 1 in Figure 2. For perovskites, the associative pathway is more likely (as discussed in section 2.1), and therefore, O_2 adsorbs onto one metal site,[36,37] replacing OH_{ads}. This metal active site is generally considered to be the B site of the ABO_3 perovskite structure.[38] In step 2 of Figure 2, a peroxide intermediate is formed. This peroxide can desorb from the surface (step 3a), react electrochemically in the hydrogen peroxide electrochemical reduction reaction (HPER) (step 3b), or chemically decompose in the hydrogen peroxide chemical disproportionation reaction (HPCD) (step 3c). Regardless of the fate of HO_2^-, the last step in the catalytic cycle is regeneration of the hydroxide surface (step 4).

Which reaction pathway the peroxide will take is dependent on a variety of factors such as perovskite composition and electrode parameters. For example, Aoki et al.[39] changed the

ratio of Mn to Ni in the $La_{0.7}Sr_{0.3}Mn_{1−x}Ni_xO_3$ perovskite series and used RRDE to measure the number of electrons transferred (n). They found that $La_{0.7}Sr_{0.3}Mn_{1−x}Ni_xO_3$ with x = 0, 0.1 was able to transfer close to four electrons. Alternatively, the perovskites with x = 0.3 and 0.5 exhibited n values between two and four, indicating the simultaneous occurrence of both two and four electron reaction pathways.

As the ORR on perovskite surfaces most likely occurs via a peroxide intermediate, it is interesting to investigate the possible reaction pathways following peroxide formation (steps 3a−3c). The possible hydrogen peroxide reaction pathways are summarized schematically in Figure 3. At present, it is not clear which pathway is dominant for perovskites. In addition, the peroxide reaction pathways most likely change with perovskite composition. When the perovskite composition changes, the binding energy of peroxide intermediates also changes. The binding energy affects whether hydrogen peroxide is released into the electrolyte (weak binding energy) or if the peroxide reacts on the catalyst surface.[40,41] Therefore, the binding strength of the hydroperoxide will influence if a two- or four-electron reaction occurs. If HO_2^- is released into the bulk electrolyte (step 3a), it can still undergo chemical decomposition away from the electrode surface. However, the uncatalyzed decomposition of HO_2^- in solution can be considered negligible compared with the rates of HO_2^- decomposition on catalyst surfaces.[42,43] If the peroxide stays near the perovskite surface, it can undergo electrochemical (HPER, step 3b) or chemical decomposition (HPCD, step 3c).

The reaction mechanisms for hydrogen peroxide decomposition catalyzed by perovskites are still open questions. One method for determining the reaction pathway occurring on a perovskite oxide is by evaluating the perovskite's activity for the hydrogen peroxide reduction reactions, HPCD and HPER. HPCD activity can be assessed by measuring a product of the reaction, oxygen. An oxygen sensor is placed into an alkaline solution containing hydrogen peroxide and dispersed perovskite particles. Then the oxygen concentration is measured over time. Using this experimental method, many perovskites have been shown to be active for HPCD in alkaline solution,[42,44−49] making pathway 3c a valid reaction mechanism. Figure 3 shows one example of HPCD activity measurements for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3−δ}$ (BSCF) measured by Fabbri et al.[42] BSCF was active for HPCD but also less active than a well-known HPCD catalyst, MnO_2, which suggests reaction pathway 3c via HPCD is possible for BSCF perovskites. In other studies, perovskite HPCD activity trends have been correlated with B-metal valency,[45,46] oxygen vacancies,[47] or oxygen adsorption/desorption.[49] For example, Yang et al.[46] found a higher Mn oxidation state (Mn^{4+}) in $La_{1−x}Sr_xMnO_3$ led to increased HPCD activity. In contrast, a mixed Mn^{3+}/Mn^{4+} valence with mostly Mn^{3+} is preferred for maximizing the ORR in the $La_{1−x}Sr_xMnO_3$ perovskite series.[32,50] Stoerzinger et al.[51] proposed for Mn-containing perovskites that Mn^{3+} catalyzes oxygen reduction to peroxide while Mn^{4+} catalyzes HPCD.

One common method for measuring the HPER (hydrogen peroxide electrochemical reduction) activity is by recording the current produced as a result of the electrochemical reduction of hydrogen peroxide. The perovskite catalyst, acting as the working electrode in a three-electrode cell configuration, is placed in an alkaline solution saturated with an inert gas, with or without rotation (RDE). Then, hydrogen peroxide is
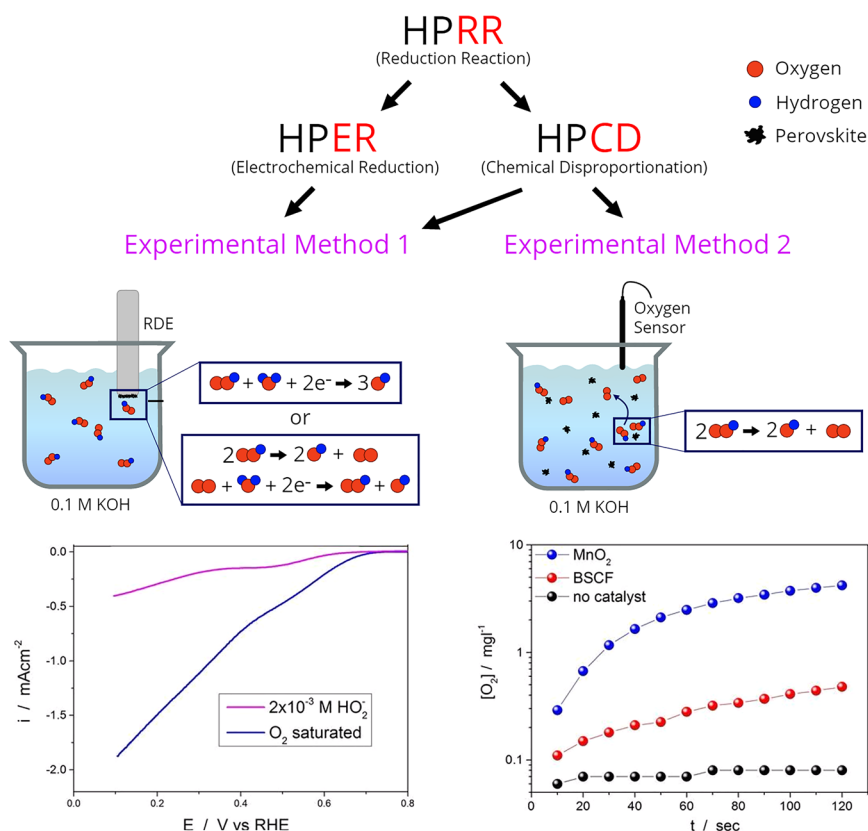
Figure 3. Hydrogen peroxide reduction can occur by either electrochemical reduction (HPER) or chemical disproportionation (HPCD). To differentiate between these two reactions, two experimental methods are typically used. In both methods, hydrogen peroxide is added to the electrolyte. Method 1 is used to determine if HPCD is occurring by measuring the oxygen produced over time. Method 2 measures the current produced as the potential is changed. However, this method cannot conclusively differentiate between HPER and HPCD. Graph insets reproduced with permission from ref 42. Copyright 2014 American Chemical Society.

injected into the solution, and the current is measured while an increasingly negative potential is applied. However, it should be noted that a pathway that includes chemical disproportionation of HO_2^- to oxygen (step 3c in Figure 2) followed by reduction of the produced oxygen, would also contribute current in this situation. Accordingly, this method of measuring current in a solution of hydrogen peroxide cannot be used to definitively differentiate between HPER (step 3b in Figure 2) and HPCD (step 3c in Figure 2). Using this method, a variety of perovskites have been assumed to be active for HPER.[27,42,52] Additionally, the combination of chemical and electrochemical steps (HPCD plus subsequent oxygen reduction) has also been assumed by several researchers.[38,53,54] Therefore, this method will be described generically as measuring hydrogen peroxide reduction reaction (HPRR) activity. An example of this HPRR activity measurement was also performed by Fabbri et al.[42] for BSCF and is shown in Figure 3. Using RRDE measurements, the hydrogen peroxide reduction activity is compared to the ORR activity. BSCF shows relatively high activity for the HPRR. Interestingly, the shape of the potential vs current density curve for HPRR matched that of ORR, however with lower current. Although, again, it is not clear if the HPRR current is from oxygen reduction after chemical disproportionation (HPCD) or from electrochemical reduction (HPER) or, perhaps, both.

Malkhandi et al.[54] investigated the hydrogen peroxide reactions in depth for $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ by dispersing 10 mg of perovskite particles in 100 mL of 0.1 M hydroperoxide in

1 M KOH and applying a fixed potential of approximately 0.3 V_{SHE} to a glassy carbon working electrode. At this potential, the hydrogen peroxide oxidation reaction (HPOR) occurs. They found that the addition of perovskite particles to the electrolyte solution led to a decrease in HPOR current over time. Therefore, they concluded that $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ chemically disproportionated the peroxide, which meant less peroxide was available for HPOR. In the same study, Malkhandi et al.[54] found $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ was active for hydrogen peroxide reduction but contributed the current to the combination pathway, HPCD followed by reduction of the produced oxygen. Although the results by the previous studies are good first approaches to investigating the reaction mechanisms of hydrogen peroxide reduction on perovskite surfaces, further analysis is needed on a wide variety of perovskites.

Recently, significant effort has been put into finding properties that can be used to predict or explain ORR activity trends in perovskites. These activity descriptors include chemical, structural, and magnetic properties.[35] However, correlations between structural properties and ORR activity have not been successfully applied to a broad category of perovskites. One reason for this is because structural changes have extensive effects on electronic properties and reactant surface adsorption and, thus, it is very challenging to uniquely correlate structural changes with ORR activity. Even though the A site is not predicted to be an active site, it can influence the ORR activity of the perovskite by changing physicochem-

ical properties, such as conductivity or the oxidation state of the B site. Partial substitutions of the A and B sites can further influence the ORR activity. Risch et al.[35] reviewed several studies that changed the B-site metal in $LaBO_3$. They found overall that B = Mn or Co led to higher ORR activity than B = Cr or Fe. However, there was no consensus on which B-site metal led to the highest ORR activity because of other conflicting parameters between studies. Alternatively, another method for altering the perovskite structure and ORR activity is to introduce strain. Petrie et al.[31] introduced lattice mismatch strain into $LaNiO_3$ thin films grown by pulsed laser epitaxy (PLE). They found the compressed films had increased ORR and OER activities, which they attributed to splitting of their e_g orbitals. Given the immense number of possible perovskite compositions, systematic studies looking at different perovskite composition properties under operative conditions are essential to finding the keys to perovskite ORR activity.

Oxygen vacancies are a common occurrence in perovskites and can alter electronic conductivity and the cation oxidation state.[55] Unlike for OER (section 2.2), oxygen vacancies do not regularly trend with ORR activity.[56] Lee et al.[28] carefully varied the oxygen vacancy concentration of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ and observed that the higher the oxygen vacancy concentration the lower the Co oxidation state of $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$, measured using X-ray absorption spectroscopy (XAS). By performing density functional theory (DFT), it was found that the Co oxidation state decrease results in a shift of the Co metal d-band center closer to the Fermi level, which suggests that the enhanced ORR activity could be attributed to the underlying electronic changes rather than the structural changes. A few researchers have suggested surface oxygen vacancies can be an active site for ORR.[35,55,57] In this scenario, the O_2 molecule can adsorb onto two sites, the metal B site and the oxygen vacancy, leading to a weakening of the O−O bond, which represses the formation of peroxide.[35] While similar mechanisms have been suggested for some solid oxide fuel cell (SOFC) perovskites[58] and other catalysts,[59] this oxygen vacancy reaction mechanism has not been confirmed for perovskites in alkaline media. However, a similar mechanism has been identified for OER (section 2.2). In addition, oxygen vacancies have also been suggested to play an active role in the chemical disproportionation[47] and electrochemical reduction of hydrogen peroxide.[7] In these two cases, a high concentration of oxygen vacancies would be required for fast reaction rates.

The intrinsic conductivity is important for ORR activity and can be an indicator of performance.[27,60] Some perovskites and other transition metal oxides suffer from low electrical conductivities.[21] High resistances within the electrode layer are detrimental and lead to high overpotentials. However, the ORR activity does not always follow the same trend as measured perovskite conductivity.[61] Although it is clear that perovskites with very low intrinsic conductivities perform poorly as ORR catalysts, conductivity by itself has not been shown to be an ORR performance indicator. However, it should be noted that the conductivity of a powder sample is highly dependent on microstructure. Accordingly, conductivity measurements of samples with different microstructures should be considered carefully. In addition, perovskite conductivity can be altered by modifying the A or B site cations, introducing oxygen vacancies, or adding conductive additives such as carbon.

2.1.2. On Carbon. To enhance electrical conductivity, ORR performance, and catalyst dispersion, carbon is frequently added to perovskite oxygen electrodes. These carbon additives are usually carbon black because of its electrical conductivity and high surface area. Some common carbon black additives are acetylene black, Vulcan XC-72, Ketjen black, and Super P/C65. Pyrolytic carbon (Sibunit carbon) is also sometimes used. Glassy carbon (GC) is usually used as a current collector and substrate for RDE measurements. Although GC is not supposed to be directly in contact with the electrolyte, imperfect thin-film catalyst layers (e.g., resulting from low catalyst loadings) can lead to (partial) exposure of the GC surface to the electrolyte; thus, the GC may participate in the oxygen reduction reaction.

Overall, it is acknowledged that carbon is active for the ORR but can only catalyze the first two-electron reaction of oxygen to peroxide (eq 2). This is evidenced by the almost 100% peroxide yield when carbon, as a single material electrode, is measured by RRDE for ORR in alkaline solution.[42,62] However, the type of carbon and treatments to the carbon surface can change the ORR reaction mechanism and activity.[63] Carbon nanotubes have been shown to also have some activity for hydrogen peroxide reduction (HPRR).[64] Nitric acid treatments can increase the surface area[65] and the number of surface functional groups, leading to enhanced ORR performance.[42,65] Maldonado et al.[66] has proposed that nitrogen-doped carbon can chemically disproportionate peroxide after the two-electron reduction of oxygen to peroxide. An in depth discussion of the reaction steps on different carbons can be found in the following sources.[63,67,68]

Although adding carbon to oxygen electrodes can be advantageous, carbon has stability issues in the cathodic operating conductions of real fuel cells.[24] In addition, for any bifunctional applications, where the catalyst is subjected to ORR and OER potentials, carbon oxidation is even more significant.[69] Therefore, it is of interest to develop perovskite electrodes without carbon or with a more stable conductive additive.

2.1.3. On Perovskite/Carbon Composites. More frequently than not, perovskite oxides are combined with high-surface-area carbon as composite electrodes for the oxygen reduction reaction (ORR). These perovskite/carbon composite electrodes display higher ORR current densities and earlier potential onsets when compared with single material electrodes,[39,70−72] as illustrated in Figure 4 for $LaNiO_3$. Often, researchers state this is because carbon increases electrical conductivity in the electrode.[73,74] In this section, we will provide evidence that carbon's role in perovskite/carbon composite electrodes is more than just to provide electrical pathways within the catalyst layer. Then, current theories on the ORR mechanisms of composite electrodes will be introduced. This will stress the need to acknowledge different ORR mechanisms when investigating perovskites versus perovskite/carbon composites.

Electrical conductivity is an important factor for catalyst activity. Sufficient electrical conductivity is needed for fast charge transfer through catalyst layers. In perovskite/carbon composite electrodes, carbon microparticles with high conductivity are added to perovskite micro or nanoparticles in a homogeneous mixture that is usually drop-casted onto a glassy carbon substrate. Therefore, in the catalyst layer, carbon can only improve the charge transfer between perovskite particles. Carbon cannot change the charge transfer within the oxide particles or the intrinsic conductivity of the perovskite.
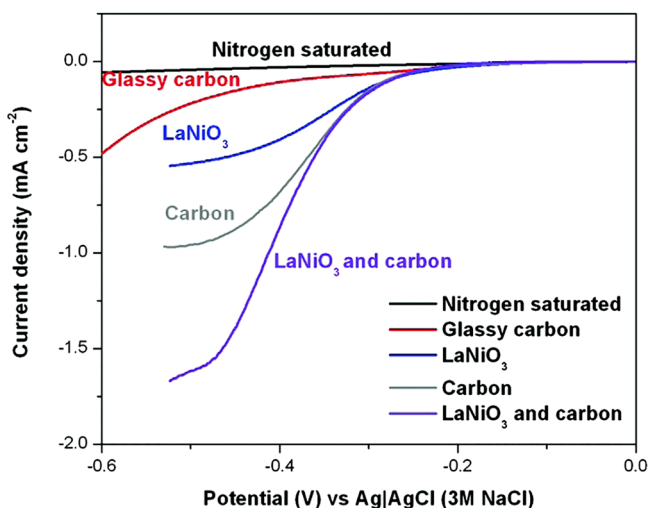
Figure 4. ORR activity of LaNiO$_3$, LaNiO$_3$/carbon, and bare glassy carbon. The perovskite/carbon composite is more active than the perovskite and carbon single materials. Reprinted with permission from ref 70. Copyright 2012 American Chemical Society.
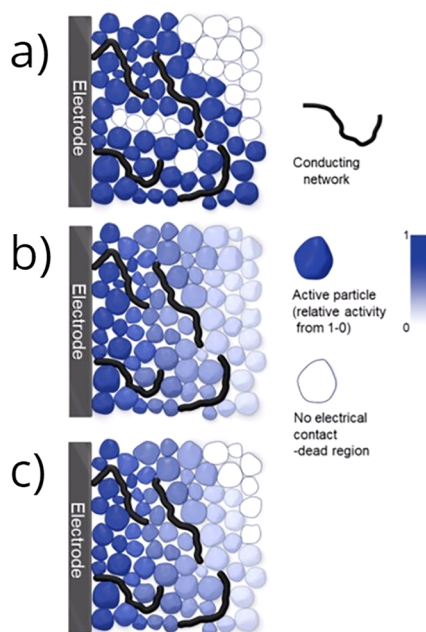

Figure 5. (a) Scenario 1: The catalyst is electrically connected only by a conducting network. (b) Scenario 2: The catalyst becomes less active further from the electrode and is independent of the conducting network. (c) Scenario 3: The catalyst is influenced by both the conducting network and the distance from the electrode. Reprinted with permission from ref 75. Copyright 2020 American Chemical Society.

This is explained well in Figure 5 by Chung et al.[75] They designate three scenarios of insufficient electrical conductivity within an electrode. The first scenario describes a catalyst with poor intrinsic conductivity, where the catalyst particles are only connected to the current collector by external electrical pathways (a conductive additive). Therefore, catalyst particles far from the electrical pathways are inactive and electron transfer can only occur if the perovskite particle is near the network of carbon particles scattered throughout the catalyst layer. The second scenario can be applied to a more intrinsically conductive catalyst without a conductive additive. The catalyst particles become less active the further they are from the current collector (glassy carbon) because of the ohmic drop over each catalyst particle as the electron travels through the catalyst layer. The third scenario is a more realistic model and combines the first two scenarios. External electrical pathways reduce resistance between catalyst particles and ohmic drops occur over each particle. Both of these things should be considered when discussing the electrical conductivity of perovskite/carbon electrodes. In addition, when electrical conductivity is mentioned, a clear distinction must be made between whether one is referring to the intrinsic conductivity of the catalyst or the electrical pathways enhanced by a conductive additive.

The effect of perovskite intrinsic conductivity on ORR performance was discussed in section 2.1.1. Here, the discussion is expanded to composites. Nishio et al.[76] illustrated that adding carbon to several La-based perovskites led to a multifold increase in ORR current density. The same perovskites were then tested for OER, with and without carbon. LaNiO$_3$ and La$_{0.5}$Sr$_{0.5}$CoO$_3$ had reasonable OER performance without carbon, indicating their intrinsic conductivity was sufficient, but their ORR activity without carbon was quite poor. Accordingly, this would imply these perovskites were conductive enough without the need for carbon. Therefore, the question is why would an intrinsically conductive perovskite need carbon for the ORR?

First, the effect of carbon on the electrical pathways between perovskite particles is considered. In the study by Poux et al.,[77] when carbon was added to LaCoO$_3$ and LaMnO$_3$ perovskites,

the capacitance (corrected for carbon contributions) increased, indicating an enhancement in surface utilization and current pathways between oxide particles. However, the increase in ORR activity was several factors higher than the increase in capacitance current. Fabbri et al.[42] investigated the effect of increased surface utilization on ORR current densities for BSCF perovskite composites. This was done by a mathematical manipulation of experimental data. For example, an extreme case was assumed where BSCF was severely lacking in electrical conductivity with only 10% surface utilization. Consequently, its current density would be underrepresented by the common practice of normalizing the measured current by the catalyst surface area because only 10% of the surface area actually participates in the reaction. However, if the measured current is normalized by 10% of the surface area, then this new current density should represent the ORR current of BSCF catalyst with ideal full surface utilization. Therefore, if the role of carbon in the BSCF/carbon composite electrode is only to improve the surface utilization, then the composite's experimentally measured current density should be less than or equal to the single electrode BSCF current normalized by 10% of the surface area. However, this was not the case; the composite electrode's activity was still higher. These results suggest increased surface utilization is not the sole reason for the surge in activity in composite electrodes. The study by Malkhandi et al.[54] further confirms this point. They replaced carbon with gold in a La$_{0.6}$Ca$_{0.4}$CoO$_{3-x}$ electrode. Gold provides external conductivity pathways between oxide particles but is not as active for ORR. The gold/perovskite composite electrode had higher ORR activity than the perovskite electrode but less than carbon/perovskite (Figure 6), implying that adequate electrical contact between

particles, while important, does not fully explain the carbon–perovskite relationship.
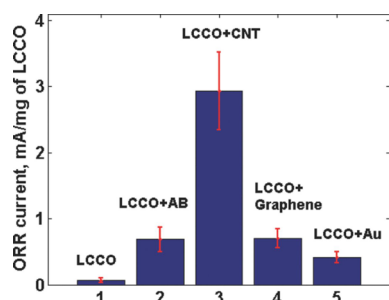

Figure 6. ORR current measured for $La_{0.6}Ca_{0.4}CoO_{3-x}$ with different conductive additives added to the electrode. These include acetylene black (AB), carbon nanotubes (CNT), graphene, and gold. Reprinted with permission from ref 54. Copyright 2013 Electrochemical Society.

Another factor that could influence the utilization of active sites in the electrode layer is the hydrophilicity of the catalyst. The addition of carbon to perovskite particles can change the hydrophilic nature of the electrode layer.[76] If the electrode layer is more hydrophilic, the electrolyte can better infiltrate into the pores, and the number of active sites will increase. Therefore, the hydrophilicity of the electrode layer and how it is changing with carbon is an important factor to be aware of. Although the hydrophilicity of the electrode layer may impact the catalyst activity, there is no direct correlation between ORR activity and hydrophilicity.[78]

The studies discussed so far have suggested that carbon in perovskite/carbon composites is more than just a conductive additive. As discussed in section 2.1.2, carbon is active for ORR in alkaline solution, via the two-electron reaction. When carbon and perovskite are examined separately, the simple addition of their ORR currents is often still less than the composite electrode of the same loading.[42,54] Therefore, the composite's activity is not only due to the combination of two active materials. These results point to a relationship between carbon and oxide. Further demonstrating this connection, the overpotential and current density change with carbon ratio. For BSCF, a volcano plot relationship was found between carbon loading ratio and ORR onset, indicating an optimal perovskite/carbon ratio for BSCF exists. The overpotential decreases with increasing carbon until a certain point. As the electrode becomes carbon rich, the overpotential increases again.[42] In addition, the type of carbon additive has a significant impact on the ORR activity of perovskite/carbon composites,[54,72] emphasizing the significant role carbon plays in oxygen reduction. This is illustrated in Figure 6, where the carbon nanotube (CNT) composite has 3 times as much ORR current as the acetylene black (AB) composite. In the literature, a synergistic relationship between transition metal oxides and carbonaceous materials is occasionally noted but not explained.[79−81] Elucidating the reaction mechanisms on composite electrodes is paramount for further improvement of oxygen electrodes. Currently, there are several theories that attempt to explain the carbon-perovskite synergistic relationship.

As discussed in section 2.1.1, in an oxygen-saturated alkaline solution, oxygen reduction can lead to the production of HO_2^- via eq 2 on carbon or perovskite oxides. The amount of peroxide produced is typically measured by a Pt ring in a RRDE setup. The amount of peroxide produced by single material perovskite electrodes varies for each perovskite composition. However, when carbon and perovskite are combined in a composite electrode, the amount of peroxide detected at the ring decreases.[62,82,83] This is counterintuitive because ORR on carbon exclusively proceeds via a two-electron reaction to HO_2^- (eq 2) in alkaline solution. Therefore, carbon's addition to the oxide should increase the peroxide concentration. Poux et al.[62] attributed the decrease in detected peroxide to enhanced conductivity pathways that increase the number of accessible perovskite sites. As mentioned above, they came to this conclusion after seeing a strong rise in pseudocapacitive charge (corrected for carbon contributions) in perovskite/carbon electrodes. At the same time, they also predicted an electrochemical step was involved because of the change in peroxide yield with applied potential.

One possible theory that would explain these results is that carbon and perovskite catalyze different reactions resulting in a series carbon-2e⁻ + perovskite-2e⁻ reaction, illustrated in Figure 7. The 2e⁻ reaction of oxygen to hydroperoxide is catalyzed by carbon (steps C1−C2). The peroxide is desorbed and subsequently adsorbed onto the perovskite (step C3b). Then, the perovskite catalyzes the electrochemical reduction (step P3b) or chemical reaction (step P3c) of hydroperoxide. This series mechanism would appear as a pseudo four-electron pathway in RRDE as the peroxide would be reacted quickly before it can be detected by the ring. Hermann et al.[84] and Li et al.[83] suggested this mechanism for $La_{0.6}Ca_{0.4}CoO_3$-carbon composites. Savinova's group has investigated this pathway for a variety of perovskites and transition metal oxides.[53,62,77,85] Other research groups have also investigated this pathway extensively.[54,56,86] All of these studies agree that carbon produces peroxide and the perovskite further reacts the peroxide. Although, this does not exclude the possibility that the direct four-electron reaction is also occurring simultaneously. In addition, there is no evidence that this series mechanism can be applied to all perovskite composites. On the contrary, the following evidence suggests that the mechanism changes with perovskite composition. Section 2.1.1 explained how the two- and four-electron reactions can occur simultaneously on perovskite single material electrodes. The scale at which these reactions take place changes with perovskite composition. Similarly, the type of perovskite influences the reaction mechanisms occurring on composite perovskite/carbon electrodes. This is illustrated by examining the work of Poux et al.[77] They measured the ORR activity of $LaCoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$ carbon composites. The carbon loading was kept constant while the perovskite loading was changed, as illustrated in Figure 8. They found that adding perovskite to carbon doubled the current density for both perovskite compositions. However, the changes in the ORR activity of perovskite/carbon electrodes as a function of the perovskite loading were different depending on the perovskite composition. For the $LaCoO_3$ composite, only slight changes in the ORR curves occurred with further increasing perovskite loading, while for the $La_{0.8}Sr_{0.2}MnO_3$/carbon composite, both the onset potential and the shape of the measured current curve changed. From these results, they predicted that for the $La_{0.8}Sr_{0.2}MnO_3$/carbon composite, $La_{0.8}Sr_{0.2}MnO_3$ participated in the first ORR steps. In their subsequent publication,[62] the authors simulated the perovskite contribution and carbon contribution to the total observed composite ORR current. They predicted, through kinetic modeling, that for perovskites
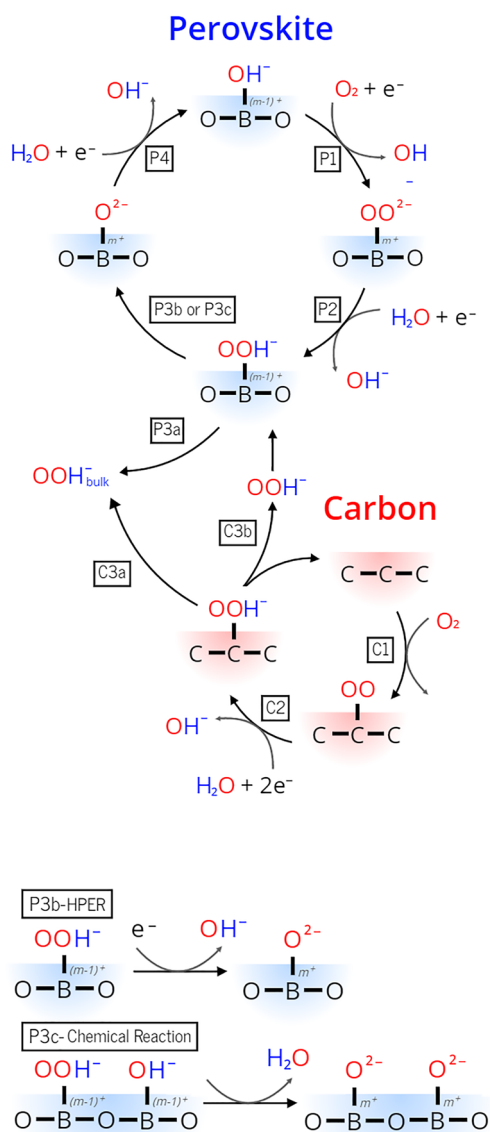
Figure 7. A possible ORR reaction mechanism for perovskite/carbon composites. The notation (P) indicates the step occurs on the perovskite surface and (C) indicates carbon. HO_2^- produced by carbon (C1–C2) has the option to adsorb onto the perovskite surface where HO_2^- can undergo electrochemical reduction (P3b-HPER) or chemical reaction (P3c). The hydroperoxide also can desorb from either the carbon (C3a) or perovskite surface (P3a) and escape into the bulk electrolyte. The perovskite reactions (P1), (P2), (P3b), and (P4) are identical to the perovskite catalytic cycle without carbon (Figure 2). The chemical reaction (P3c) differs from chemical disproportionation and has been suggested for composites by Poux et al.[62] and Mefford et al.[56] Adapted with permission from ref 56. Copyright 2019 PCCP Owner Societies.

with low ORR activity, such as $LaCoO_3$, the carbon contribution to the composite's ORR current is significant and the reaction follows the series carbon-2e$^-$ + perovskite-2e$^-$ pathway. Then, for $La_{0.8}Sr_{0.2}MnO_3$, the carbon contribution was less significant, and they predicted the production and reaction of peroxide both could occur on the perovskite. This would explain why the ORR activity of the $La_{0.8}Sr_{0.2}MnO_3$/carbon composite electrode was influenced more by the perovskite content.

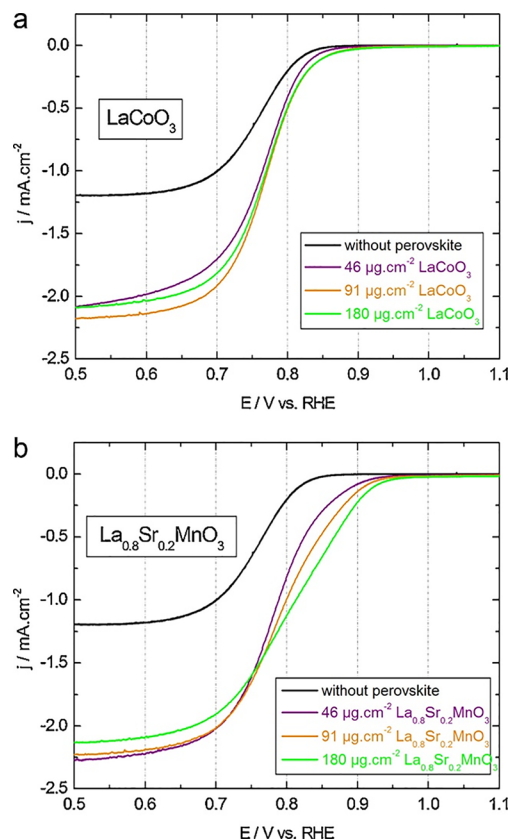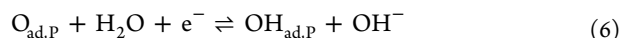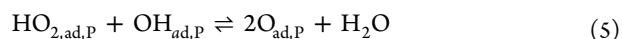**Figure 8.** RDE measurements of two different perovskites/carbon composites ($LaCoO_3$ and $La_{0.8}Sr_{0.2}MnO_3$) where the amount of carbon is constant but the perovskite loading is changed. The two materials react differently to the changing carbon ratio. Reprinted with permission from ref 77. Copyright 2012 Elsevier.

If the series mechanism, where carbon catalyzes the initial peroxide formation and perovskite catalyzes the following peroxide reaction, is assumed, there are still questions to be answered. In the previous section on perovskites (2.1.1), we discussed the possible hydrogen peroxide reactions or pathways that can occur: HPCD, HPER, or peroxide release into the electrolyte. We continue the discussion here for perovskite/carbon composites. Although the mechanistic discussion on perovskites without carbon is important and relevant to the composite reaction mechanism, these two systems must be investigated separately. Several groups have attempted to clarify which peroxide reaction occurs on the perovskite site in perovskite/carbon composites. In their kinetic model, Poux et al.[62] assumed the peroxide produced on carbon was subsequently reacted on $LaCoO_3$ via the chemical reaction of peroxide (eq 5 and step P3c in Figure 7) and the further electrochemical reaction of oxygen (eq 6 and step P4 in Figure 7). The notation (ad,P) is used to indicate adsorption onto the perovskite surface.

$$HO_{2,ad,P} + OH_{ad,P} \rightleftharpoons 2O_{ad,P} + H_2O \qquad (5)$$

$$O_{ad,P} + H_2O + e^- \rightleftharpoons OH_{ad,P} + OH^- \qquad (6)$$

This chemical reaction (eq 5) proposed by Poux et al.[62] differs from chemical disproportionation (eq 4). Via the chemical reaction in eq 5, two oxygen atoms instead of one are produced for every hydroperoxide ion. Therefore, with this pathway (eq 5 + 6), the composite electrode would show an

apparent four-electron reaction with RRDE. Mefford et al.[56] produced a similar kinetic model to reproduce their experimental results on LaCoO$_3$/carbon composites. They modeled peroxide formation on carbon, followed by peroxide spillover to the perovskite. Then they considered two possibilities for the reaction of peroxide on the perovskite site, chemical disproportionation (HPCD) or electrochemical reduction (HPER). They found that modeling the chemical disproportionation reaction of hydroperoxide on the perovskite active sites fit their experimental results for ORR and hydrogen peroxide reduction better than electrochemical reduction. Although, it should be noted that the differences are slight. Hardin et al.[38] found a trend between the HPCD activity of the perovskite LaMO$_3$ and the ORR activity of LaMO$_3$/carbon composites (M = Ni, Ni$_{0.75}$Fe$_{0.25}$, Co, Mn) and hypothesized that a perovskite's ability to disproportionate peroxide could be crucial for active composite catalysts. They predicted that HPER was a rate-limiting step and perovskites able to perform HPCD could overcome this kinetic hindrance. Falcón et al.[48] also correlated ORR and HPCD activity for LaFe$_x$Ni$_{1-x}$O$_3$/carbon composites. Fewer studies have claimed HPER occurs on composites. These include Co$_3$O$_4$/carbon[87] and La$_{0.5}$Sr$_{0.5}$CoO$_3$/carbon gas diffusion type electrodes.[76] As discussed earlier, the type of carbon added to the composite can greatly influence the catalytic activity. Nitrogen-doped carbon is one interesting example because, as mentioned in section 2.1.2, nitrogen-doped carbon is able to chemically disproportionate peroxide.[66] These nitrogen-doped carbon/perovskite composites usually have higher ORR activity than their undoped counterparts.[38,88] Hardin et al.[38] has suggested that LaNi$_{0.75}$Fe$_{0.25}$O$_3$/nitrogen-doped carbon also follows the series carbon-2e$^-$ + perovskite-2e$^-$ mechanism and both the perovskite and the nitrogen-doped carbon participate in HPCD.

Overall, the series carbon-2e$^-$ + perovskite-2e$^-$ pathway is a quite plausible explanation for the experimental results discussed in this Perspective. Indeed, many researchers have used this mechanism to explain their results. However, the current results have not reached a consensus about whether the peroxide is chemically reacted or electrochemically reduced on the perovskite surface. Instead, they illustrate the need for further research to clarify this step. The perovskite composition and carbon type greatly influences the ORR activity and possibly also the reaction mechanism. Perhaps a general ORR reaction mechanism for perovskite/carbon composites does not exist. To find out, more systematic experimental and computational work is needed on a wide range of perovskites.

Carbon−perovskite synergistic relationships have also been observed in hybrid catalysts. These hybrids are synthesized by methods such as chemical vapor deposition, hydrothermal treatment, or electrospinning.[23] These unique synthesis methods lead to a close interaction between the metal oxide and the carbon support, usually graphene, carbon nanotubes (CNT), or other high-surface-area carbons. Therefore, the hybrids must be compared separately from composite electrodes which are prepared by mixing or sonication. The hybrid's reaction mechanisms might differ from those on other perovskite/carbon electrodes. Metal oxide/carbon-based hybrids have been popular because of their high ORR activity. Kéranguéven et al.[72,82] synthesized hybrid-like composites by subjecting the perovskite's metal precursors, carbon, and glycine to high temperatures in an "in situ autocombustion"
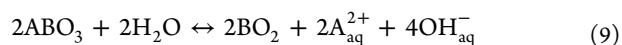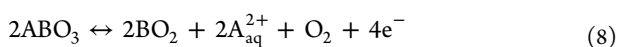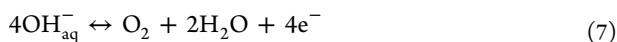
method. The composites synthesized by this in situ method had better ORR performance than the composites that were manually mixed. They attributed this result to a decrease in particle size as well as an enhanced interaction between carbon and perovskite. Liang et al.[89] constructed a hybrid of Co$_3$O$_4$ nanoparticles on reduced, mildly oxidized graphene oxide (rmGO). They hypothesized that there could be bond formation between the transition metal oxide and graphene oxide, which allows for enhanced charge transfer between the two materials. It is interesting to wonder if a similar bond formation could occur on a perovskite−carbon hybrid. Other researchers attribute the hybrid success to electrical conductivity or surface utilization.[90,91] These studies have shown that perovskite/carbon-based hybrids are very promising because of their high ORR performance. Yet, the hybrids and their ORR reaction mechanisms are unknown and relatively unstudied. In addition, perovskite hybrids are less common than other metal oxide hybrids, partly because of synthesis difficulties.[88]

Another important consideration for ORR on perovskite/carbon composites is the oxidation state of the perovskite cations. In section 2.1.1, the oxidation states of the cations in single material perovskite electrodes for ORR were discussed, as well as in section 2.2 for OER. In this section, we will discuss the possible change in oxidation state due to the perovskite's interaction with carbon. Fabbri et al.[92] investigated BSCF/carbon composites by ex situ X-ray absorption near edge structure (XANES). When BSCF was strongly sonicated with carbon (a typical electrode preparation method), a shift in the Co K-edge to lower energies was observed, compared with unmodified BSCF. This leads to the conclusion that carbon acted as a reducing agent and the Co cations in BSCF have a lower oxidation state after sonication with carbon. A similar Co reduction was found by Haas et al.[93] for La$_{0.6}$Ca$_{0.4}$CoO$_3$/carbon composite electrodes. Kéranguéven et al.[82] investigated the oxidation state of Mn in LaMnO$_3$/carbon composites using EELS. They found an increase in the Mn L$_3$/L$_2$ ratio with increasing carbon ratio and accordingly concluded that adding carbon reduced the oxidation state of Mn. However, it should be noted, both Haas and Kéranguéven et al. used post heat treatments on their composite electrodes, most likely forming a (possibly hybrid-like) closer interaction between perovskite and carbon than with sonication or mixing. Additionally, the strong sonication method used by Fabbri et al. could have subjected the ink to high temperatures and pressures. There are several possible reasons why reduced cations could explain the composites' enhanced ORR activities. The first is that the increased electron density of the cation imparts a higher intrinsic conductivity to the perovskite. For BSCF, Co reduction induced by high temperature and observed by in situ X-ray absorption spectroscopy (XAS) was shown to increase conductivity.[94] The second reason could be that reduced Co is more favorable for oxygenated species adsorption. A link between cation oxidation state and oxygenated species adsorption energy was shown by Calle-Vallejo et al.[95] for transition metal oxides. It is clear that the oxidation state of the perovskite's cations, a key property of the material, is influential to their ORR activity. Carbon acts as a reducing agent, possibly influenced by high-temperature processes, leading to higher ORR activity in perovskite/carbon composites versus single material electrodes. Nevertheless, for a clearer, more comprehensive understanding of the impact of carbon on cation oxidation state, more studies using

techniques such as in situ and ex situ XAS and XPS are required.

2.2. OER Mechanism. It has been assumed for a long time that the OER mechanism on oxide catalysts only proceeds via four consecutive proton-coupled electron transfer (PCET) steps, where the metal ion is the active site.[96,97] However, recent findings have questioned if PCET is the only OER mechanism occurring on oxides.[9,98,99] These new findings show that different electrochemical processes can take place simultaneously: oxidation of lattice oxygen toward the production of oxygen molecules (i.e., the lattice oxygen evolution reaction, LOER) and catalyst dissolution. Understanding the electrochemical mechanisms occurring on the surface of a catalyst is of particular importance for the "catalyst optimization strategy". Indeed, if only the PCET mechanism is assumed to occur, the optimization of the adsorption–desorption strength of the reaction intermediates represents the optimal strategy toward the development of highly active OER catalysts. However, if the LOER and catalyst dissolution also play a role in the overall OER mechanism, other catalyst properties or "activity descriptors" must also be considered to find the best catalyst.

The last couple of years have seen an increasing number of evidence, both experimental and theoretical, pointing toward the unexplored complexity of the OER processes. They show that to fully understand the water splitting reaction mechanism, the LOER and metal cation dissolution reactions need to also be considered. Already in the early 1970s to 1980s, a few studies about OER catalysts mentioned the possibility of an alternative pathway to the conventional PCET, where molecular oxygen is generated via the participation of perovskite lattice oxygen.[8,14,100] More recently, Hardin and co-workers[38,101] investigated LaNiO$_3$, LaMnO$_3$, and LaCoO$_3$ as OER/ORR catalysts. For OER, they suggested the participation of lattice hydroxide species in the formation of surface-adsorbed hydroperoxides. However, only in the last five years has a more rigorous formulation of the LOER been provided by different research groups.[10,12,102−106] Binninger et al.,[10] by basic thermodynamic considerations, demonstrated that the conventional OER mechanism, LOER, and metal cation dissolution processes as described by eqs 7−9 are all linked and can concurrently take place on the surface of metal oxides above the OER equilibrium potential. Furthermore, this study[10] postulated that perovskites undergoing LOER and metal cation dissolution (eqs 8 and 9, respectively) would initially leach out the A site cations from the ABO$_3$ perovskite structure, as generally the A site cations are highly soluble in alkaline environment. However, the BO$_2$ metal oxides described as reaction products in eqs 8 and 9 can also undergo LOER and/or metal cation dissolution (eqs 10 and 11, respectively),[9,10] eventually leading to both A and B site cation dissolution from the perovskite structure, as sketched in Figure 9. The A and B site metal cations dissolved as a result of the LOER or chemical dissolution can be released into the bulk electrolyte (thus causing material loss and, most likely, material degradation) or recombine with the OH$^-$ from the electrolyte and redeposit on the catalyst surface as an oxyhydroxide phase as shown in Figure 9.

$$4OH^-_{aq} \leftrightarrow O_2 + 2H_2O + 4e^- \tag{7}$$

$$2ABO_3 \leftrightarrow 2BO_2 + 2A^{2+}_{aq} + O_2 + 4e^- \tag{8}$$

$$2ABO_3 + 2H_2O \leftrightarrow 2BO_2 + 2A^{2+}_{aq} + 4OH^-_{aq} \tag{9}$$

$$BO_2 \leftrightarrow B^{4+}_{aq} + O_2 + 4e^- \tag{10}$$

$$BO_2 + 2H_2O \leftrightarrow B^{4+}_{aq} + 4OH^-_{aq} \tag{11}$$

A similar dissolution and redeposition process has been recently reported for Fe cations in NiFeO catalysts when using
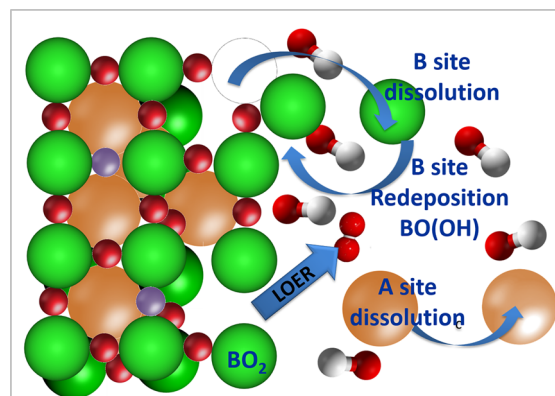

Figure 9. Sketch representing the LOER and cation dissolution on the surface of perovskite oxides. The A and B site cations dissolved from the perovskite surface as a result of the LOER and/or chemical dissolution can further dissolve in the electrolyte or be redeposited on the surface of the perovskite, eventually forming an oxyhydroxide layer.

a Fe-containing electrolyte.[107,108] For the La$_{1−x}$Sr$_x$CoO$_3$ perovskites, it has been demonstrated that the OER activity originates not directly from the perovskite surface but from a few nanometers thick, stable Co hydr(oxy)oxide (CoOxHy) layer formed on the perovskite surface and driven by La dissolution and oxygen vacancy formation. This highly dynamic electrode/electrolyte interface during OER allows the establishment of a dynamic equilibrium between Fe deposition and dissolution rate in the CoOxHy layer promoted by Fe (aq) impurities in the electrolyte. Indeed, DFT analysis shows a strong interaction between the Fe impurities in the electrolyte and the electrochemically formed CoOxHy. Furthermore, DFT reveals a 10-fold gain in stability against Co dissolution for the evolved CoOxHy/LSCO surface system compared with other CoOxHy-based materials.[108] Also, for model LaNiO$_3$ perovskite catalysts with a Ni surface termination, a surface transformation into a Ni oxyhydroxide-type single-layer surface phase was observed.[109] This surface transformation was accompanied by an enhancement in the OER activity. Interestingly, LaNiO$_3$ model catalysts with a La termination do not form an active surface phase even after hours of operation. DFT studies revealed that such evolved surface layers are highly active for OER due to the presence of triply coordinated O* reaction intermediates. DFT calculations also showed that a single-layer of NiO$_2$ would display a considerably larger overpotential than the Ni-oxyhydroxide/LaNiO$_3$ catalyst, which suggests that the underlying perovskite lattice plays an important role in the activity of the topmost layer of Ni oxyhydroxide.[109]

For several OER catalysts, the formation of a superficial oxyhydroxide phase is linked to high OER activity, and many studies suggested a correlation with the occurrence of the LOER and metal dissolution processes. Fabbri et al.[103] showed

by performing operando XAS measurements that one of the most active perovskite catalysts in form of nanoparticles, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), is able to develop under OER conditions a highly active, self-assembled (Co/Fe)OOH phase, as a result of LOER and metal dissolution processes. Furthermore, the BSCF metastability under typical OER conditions in an alkaline environment assures a fairly stable catalyst, via continuous metal cation dissolution and redeposition, with a significant increase in the initial OER current during the formation of the oxyhydroxide layer (see Figure 10).[110]
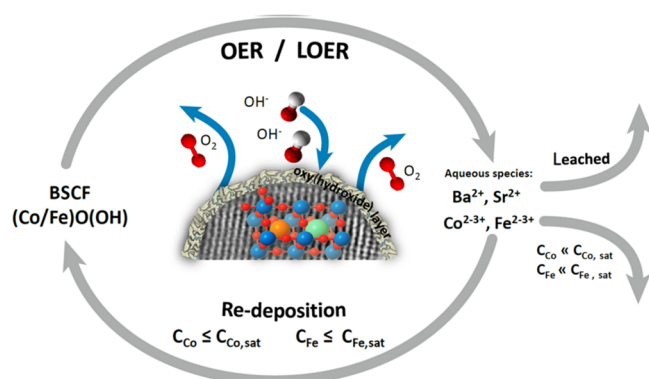

Figure 10. OER/LOER and dissolution/redeposition mechanism leading to the formation of a self-assembled active surface layer on the surface of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite. Ba^{2+} and Sr^{2+} cations are highly soluble, and thus, they can easily leach out from the perovskite structure. Differently, Co and Fe cations, being rather insoluble species, can be redeposited on the catalyst surface, leading to a stable dynamic cycle. Figure readapted with permission from ref 103. Copyright 2017 Nature Publishing Group.

Often, the formation of an oxyhydroxide layer is given as evidence of the LOER mechanism.[103,110−114] According to eq 12, the LOER coupled with metal cation dissolution can lead to the formation of a superficial, electrochemically formed, oxyhydroxide layer, with a poor crystalline structure and, most likely, with a high surface area.

$$2ABO_{3-\delta} + 2OH^-$$
$$\leftrightarrow 2BO(OH) + 2A^{2+}_{aq} + O_2(2-\delta) + 6e^- \quad (12)$$
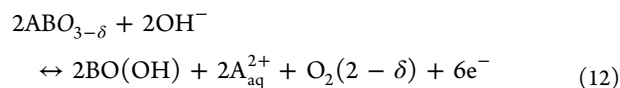
The self-assembled oxyhydroxide layer on the perovskite surface can also undergo LOER and metal cation dissolution, as described in ref 10. Whether the self-assembled oxyhydroxide layer is porous enough to allow the electrolyte to still reach the perovskite surface, or if the oxyhydroxide forms islands or a uniform superficial layer is not clear yet. However, evidence suggests that a catalyst undergoing LOER can also achieve good stability when a dynamic equilibrium between cation dissolution and redeposition can be reached, i.e., when the oxyhydroxide formation breaks at a certain point.[103,107−110,112,113] Interestingly, it has been reported that Co/Fe oxyhydroxide intentionally deposited on the surface of perovskite oxides, particularly on BSCF, shows superior OER activity compared with the same oxyhydroxide deposited on a carbon support.[115]

Vonrüti and Aschauer,[116] using DFT, estimated the OER overpotential for three different perovskites considering a variety of defective surfaces. They reached the conclusion that

metastable materials under OER conditions can display activity improvement because the catalyst surface can reach the greatest diversity of reaction sites and, thus, have the highest chance of finding highly active reaction sites. However, metastable catalysts can benefit from their metastable conditions toward OER enhancement only if the cation dissolution process is slow enough to sustain the electrochemical process without material loss.[116] In other words, dissolution and redeposition seems to be the key process for a highly active and stable OER catalysts, such as NiFeO[107] or BSCF.[103,110]

The great capability of BSCF to create a self-assembled, stable, and highly active oxyhydroxide layer under OER conditions was ascribed to the great flexibility of BSCF to accommodate oxygen vacancies. Indeed, BSCF with Co in a reduced oxidation state, and thus with a high amount of oxygen vacancies, has proved higher OER activity compared to the same perovskite composition with Co cations in a more oxidized state (i.e., with higher oxygen content).[92,103,117,118] More generally, considering the results of different studies on various perovskites, the oxygen vacancy formation energy/content seems to be an established indicator of high OER activity that has a role in the LOER mechanism.[102,103,110,111,119−121] Mefford et al.,[102] for the $La_{1-x}Sr_xCoO_{3-\delta}$ series, found a direct correlation between Co−O bond covalence, oxygen vacancies and diffusivity, and OER activity. The authors reported that for the $La_{1-x}Sr_xCoO_{3-\delta}$ series, the higher the covalent character of the Co−O bond the higher the vacancy concentration, and also the OER activity. Furthermore, they have also indicated a correlation between oxygen diffusivity (measured at room temperature by performing chronoamperometry measurements and RRDE) and OER activity. According to Lopes et al.,[108] who has also investigated $La_{1-x}Sr_xCoO_{3-\delta}$, oxygen vacancies can contribute to faster A-site dissolution and perovskite surface conversion into a highly active CoOOH layer. The role of lattice oxygen vacancy and diffusivity in enhancing the OER activity has been also reported for $La_{0.5}Sr_{1.5}Ni_{1-x}Fe_xO_{4+\delta}$ Ruddlesden−Popper structures.[119] In this catalyst series, Sr and Fe introduction into the $LaNiO_3$ perovskite leads to increased covalency and cross gap hybridization of the transition metal 3d states and the O 2p orbital. This leads to a decrease in the oxygen vacancy formation energy and also increases the oxygen diffusion rate and the OER activity.[119] The relevant role of oxygen vacancy and diffusivity has also been elucidated in two other perovskite-based catalysts, namely, Si-modified $(SrCoO_3)$[111] and a Ruddlesden−Popper/perovskite hybrid system $(LaSr_3Co_{1.5}Fe_{0.5}O_{3-\delta} /La_{0.25}Sr_{0.75}Co_{0.5}Fe_{0.5}O_{3-\delta})$.[121] In the former system, Si incorporation in $SrCoO_3$ has been reported to tune the oxygen vacancy concentration and diffusion rate. The authors claim that high oxygen diffusion rates can facilitate the refilling of the surface oxygen vacancies left by the evolved lattice oxygen, similarly to how it occurs in high-temperature solid oxide fuel cells. Still, without any external source of oxygen, the bulk oxygen content would also decrease as surface lattice oxygen is consumed, until the perovskite structure cannot accommodate any more oxygen substoichiometry and collapses. However, as discussed before, it has been reported that perovskites performing LOER can also show relatively good stabilities. One possibility to conciliate LOER and catalyst stability is to postulate that hydroxide ions from the electrolyte refill the oxygen vacancies left by the evolved lattice
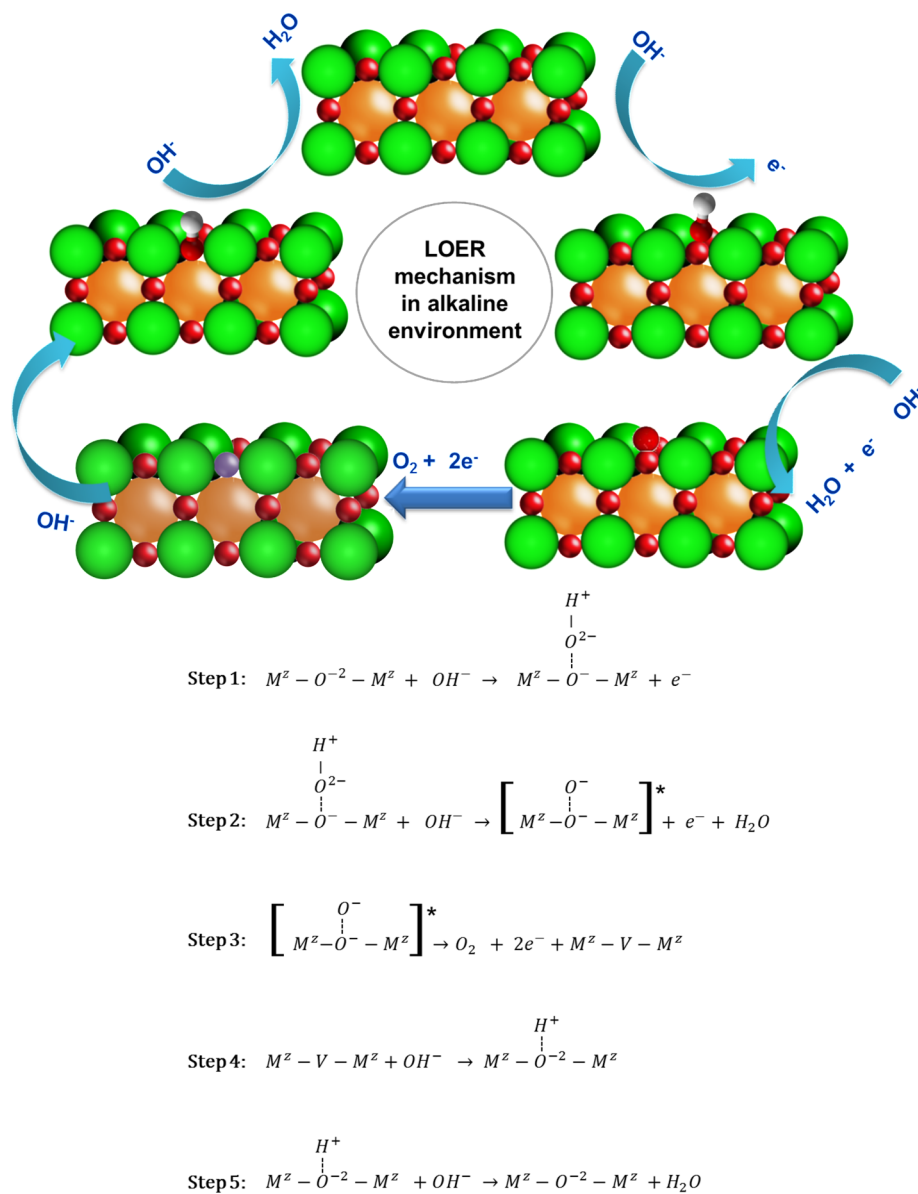
Step 1: $M^z - O^{-2} - M^z + OH^- \rightarrow M^z - \overset{\overset{\displaystyle H^+}{\displaystyle |}}{\underset{\vdots}{O}}{}^{-} - M^z + e^-$

Step 2: $M^z - \overset{\overset{\displaystyle H^+}{\displaystyle |}}{\underset{\vdots}{O}}{}^{-} - M^z + OH^- \rightarrow \left[M^z - \overset{\overset{\displaystyle O^-}{\displaystyle \vdots}}{O}{}^- - M^z \right]^* + e^- + H_2O$

Step 3: $\left[M^z - \overset{\overset{\displaystyle O^-}{\displaystyle \vdots}}{O}{}^- - M^z \right]^* \rightarrow O_2 + 2e^- + M^z - V - M^z$

Step 4: $M^z - V - M^z + OH^- \rightarrow M^z - \overset{\overset{\displaystyle H^+}{\displaystyle \vdots}}{O}{}^{-2} - M^z$

Step 5: $M^z - \overset{\overset{\displaystyle H^+}{\displaystyle \vdots}}{O}{}^{-2} - M^z + OH^- \rightarrow M^z - O^{-2} - M^z + H_2O$

Figure 11. Proposed LOER mechanism in alkaline environment for perovskite oxides. The LOER leads to formation of oxygen vacancies, which are replenished in a final step by reacting with OH⁻ in the electrolyte.[9] Reprinted with permission from ref 9. Copyright 2018 American Chemical Society.

oxygen as shown in Figure 11.[9] Figure 11 describes the LOER as a four-electron process, where decoupled proton electron steps take place (steps 3 and 4). Steps 2 and 3 are likely to occur as a concerted process where H⁺ and O² are released, while in step 4, the oxygen vacancy formed by the oxygen evolution can be replenished by reaction with OH⁻ from the electrolyte. For simplicity, in Figure 11, the metal cation dissolution accompanied by the formation of an oxyhydroxide phase is not considered, but it can also take place simultaneously to the LOER. Recently, besides oxygen vacancy and diffusivity, the distance between surface lattice oxygen has also been proposed to have an influence on the OER activity when lattice oxygen is involved in the electrochemical process, where LOER is favored by a smaller oxygen surface distance.[122]

Despite the beauty of finding a single indicator for the LOER, Cheng and co-workers[117] have shown that the oxygen vacancy is not the only property dictating the perovskite OER activity. Studying the perovskite oxygen content vs OER activity for many perovskite compositions, they found the OER activity increases with the oxygen vacancy content, but several deviation points from the general trend can be observed. This result highlights that by varying the perovskite composition, many physicochemical properties can be modified at the same time, such as crystal structure, electrical conductivity, flat band potential, thermodynamic stability, and so on. All perovskite catalyst physicochemical properties to a certain extent contribute to the OER activity. Therefore, isolating a single perovskite property that fully governs the OER activity is quite complicated. Indeed, the simple variation of oxygen vacancy content also modifies the crystal structure, cation ordering, electronic configuration, and conductivity, as well as surface rearrangement. These are all properties that need to be taken into account when the OER activity vs a single perovskite property is considered. Unfortunately, this makes it very difficult to identify perovskite activity descriptors and also

difficult to understand which perovskite properties favor the occurrence of LOER instead of the conventional PCET OER mechanism.

In addition, providing direct experimental proof that LOER is taking place as the main oxygen evolution mechanism on the surface of perovskite catalysts has proven to be challenging.[9] Grimaud and co-workers[12] have shown by performing isotope labeling experiments that for perovskites with high covalent character (such as $La_{1-x}Sr_xCoO_{3-\delta}$ or $SrCoO_{3-\delta}$), LOER takes place together with the conventional OER mechanism. Differently, for binary oxide catalysts such as RuO_2, isotope labeling experiments have shown that lattice oxygen is not involved in the evolution of oxygen molecules.[123] Recently, more and more often the OER activity dependence on the pH of the electrolyte (vs RHE) has been taken as an indicator of the occurrence of LOER (see Figure 12), assuming that the rate-limiting step in the LOER is a proton trans- fer.[12,111−113,124−127] Generally, higher OER activity has been observed for perovskite-based catalysts, showing pH activity dependence on the RHE scale, leading to the assumption that the LOER can be an effective way to overcome the limitation of the PCET mechanism. In a recent study, where a wide range of pH levels and perovskite compositions have been investigated, it has emerged that while LOER seems to be the dominate mechanism in the alkaline region, in the quasi neutral pH region, OER activity is independent of electrolyte pH, suggesting the occurrence of the PCET mechanism.[127] For $La_{1-x}Sr_xCoO_{3-\delta}$ thin film model electrodes, it has been shown that the OER activity dependence on the pH values is observable only in KOH solution containing Fe impurities.[108] Thus, for this particular system, the linear relationship between OER activity and electrolyte pH values has been ascribed to the increase of Fe impurities in the KOH solution as the pH value increases from 12 to 14.

Regarding the particular steps involved in the LOER mechanism, several detailed reaction mechanisms have been proposed so far. Several key mechanisms are summarized in Figure 13. The main common feature of the LOER process is a decoupled proton−electron transfer mechanism. As discussed above, if the step involving only a proton (specifically a deprotonation step) is the rate-determining step, this would lead to a strong pH dependence of the OER activity on the RHE scale, as observed in several studies (see Figure 12). However, a consensus has been not reached yet, whether the metal cation or the lattice oxygen represents the active site for the LOER. Indeed, proving the reaction steps for an electrochemical process, where only the slowest step is experimentally accessible, is probably one of the greatest challenges. DFT calculations could help in determining the energetics of the intermediates formed during the LOER (after assuming a certain reaction mechanism) and support the experimental evidence of the occurrence of LOER.

Similarly to ORR, carbon is almost always added to perovskite OER catalysts to enhance electrical conductivity and performance, even though carbon's influence on the OER activity of perovskites is not clear. However, unlike for ORR, carbon is not significantly active for the oxygen evolution reaction compared with most perovskite catalysts.[23,128] Although it should be noted that modified carbons, such as nitrogen or oxygen-doped carbons, have been shown to have some activity for OER[129,130] and influence the performance of perovskite/modified-carbon composites.[38] In addition, the type of carbon additive can influence the perovskite OER
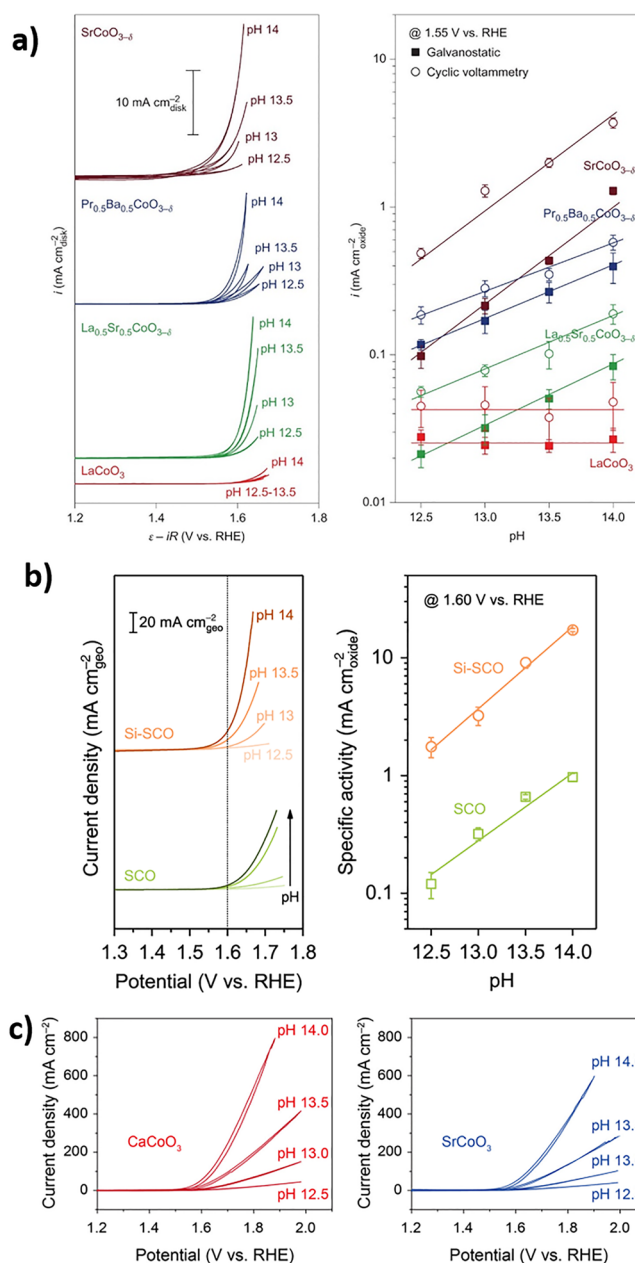

Figure 12. Influence of the electrolyte pH value on the OER activity for different perovskite catalysts as reported by (a) Grimaud et al.[12]. Reprinted with permission from ref 12. Copyright 2017 Nature Publishing Group; (b) Pan et al.[111]. Reprinted with permission from ref 111. Copyright 2016 Nature Publishing Group; (c) Li et al.[124]. Reprinted with permission from ref 124. Copyright 2019 American Association for the Advancement of Science.

activity.[131] Nevertheless, carbon can contribute current at OER potentials because at these potentials carbon can oxidize and produce CO_2 (0.21 V vs SHE).[88,132] This has several negative consequences. Carbon oxidation leads to electrode stability issues.[133] In addition, the current measured for a perovskite/carbon composite includes both the OER activity of the composite as well as the current of carbon oxidation.[134] Interestingly, some metal oxides and perovskites in carbon composites have been shown to influence the rate of carbon corrosion at OER potentials compared with carbon alone.[134−136] In order to avoid carbon stability issues and measure the intrinsic OER activity of the perovskite, it is
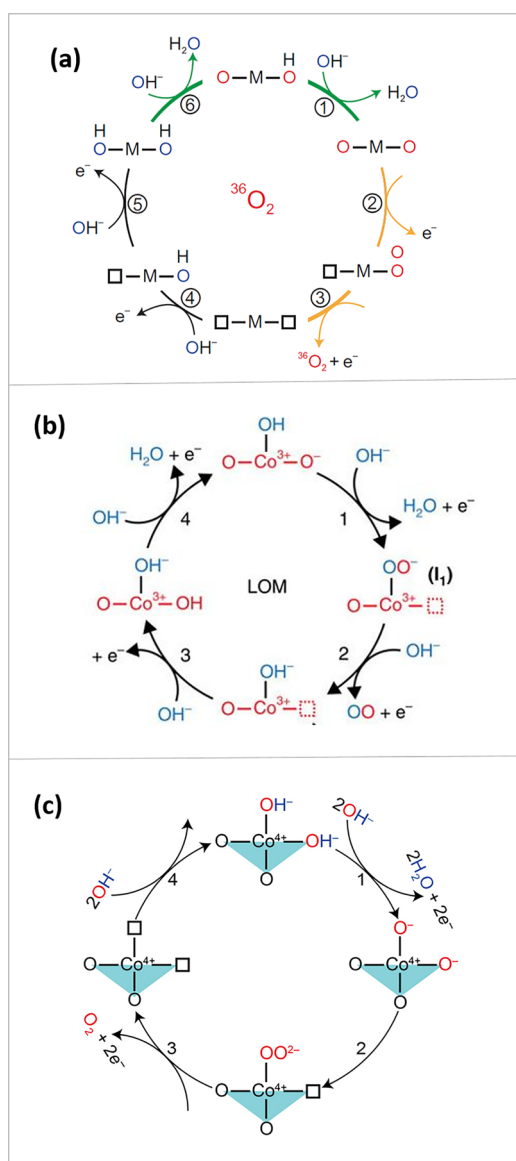
Figure 13. Possible LOER mechanism as reported by (a) Grimaud et al.[12]. Reprinted with permission from ref 12. Copyright 2017 Nature Publishing Group; (b) Mefford et al.[102]. Reprinted with permission from ref 102. Copyright 2016 Nature Publishing Group; (c) Li et al.[124]. Reprinted with permission from 124. Copyright 2019 American Association for the Advancement of Science.

necessary to remove carbon from the electrode. Without carbon, the perovskite electrode may suffer from high resistances and low performance. However, a fair number of perovskites have been successfully implemented in single material electrodes for OER.[33,124,137,138] In addition, conductivity does not always increase when carbon is added to the electrode.[139] Also, the OER performance of perovskite/carbon composites is not always significantly more than perovskite single materials.[128,139] Overall, there are many open questions regarding the carbon influence on the perovskite OER activity and reaction mechanism and further investigation is needed.

3. EXPERIMENTAL PRACTICES AND CONSIDERATIONS

To investigate the oxygen evolution and reduction reaction mechanisms, systematic and controlled experimental methods are required. Cell design, electrochemical measurement techniques, and electrode preparation are all important considerations when designing a rigorous experiment to measure electrocatalytic activity. Several other articles have discussed good practices for general electrocatalysis applications.[140,141] In this paper, we discuss specific experimental considerations that are especially important for perovskites in alkaline media for OER and ORR.

There are several important considerations when designing an electrochemical cell for perovskite ORR or OER measurements. The material of the cell itself is of particular importance when used with alkaline electrolytes. Glass is often used in electrochemical cells and laboratory materials. However, in alkaline solution silicates, metal ions, and other constituents from the glass can leach into the electrolyte.[142−144] Mayrhofer et al.[143,144] investigated the effect of glass corrosion on Pt ORR activity. Overall, the glass cell led to unpredictable results. Pb impurities from the glass increased ORR activity, while silicates inhibited activity. However, they found if a cell made of an inert material, such as Teflon (PTFE), is used instead, no significant amount of impurities are detected in the electrolyte. Glass corrosion should be avoided as the impact of the glassware's varied impurities on perovskite catalytic behavior is not well understood. This also applies to any impurities native to the electrolyte or introduced from other sources. For example, as will be discussed later, Fe impurities have been shown to influence OER activity, but the impact on ORR is not yet understood. Therefore, a suitably high-purity electrolyte and a rigorous cleaning procedure are also required to negate any effects from impurities. Further suggestions on these two aspects can be found in the following reviews.[141,145] Another influential factor is the lifetime of the electrolyte. In alkaline solutions, such as KOH, carbon dioxide from the air reacts with OH⁻ in solution to form carbonates.[146,147] This is detrimental because a decrease in hydroxide ions leads to lower electrical conductivity within the solution, and possible carbonate precipitation can occur on the electrode.[146] In addition, the pH can change which is particularly impactful on catalytic behavior, as is evidenced in Figure 12. Therefore, it is recommended to prepare a fresh electrolyte before performing electrochemical measurements to negate these effects.

Reference electrode (RE) calibration is important for accurate electrochemical measurements. Over time, the RE potential can shift, and therefore, the RE should be calibrated regularly. Potential differences vary between reference electrodes even if they are the same type, and therefore, the potential measured during calibration should always be added when reporting results. In particular, it is helpful to report the potential versus the reversible hydrogen electrode (RHE) scale, as it is independent of electrolyte pH. There are also several important data corrections that are needed when reporting ORR or OER measurements. The first is *iR* compensation, which accounts for ohmic losses due to electrolyte or cell component resistances. Failure to compensate for these ohmic losses may lead to incorrect results.[148] The second is the correction for the contribution of capacitive current from the ORR and OER data. The influence of capacitive current on electrochemical measurements is dependent on the electrode but is more significant for catalysts with higher surface area. When OER activity is measured, via chronoamperometry (CA) measurements (see below), capacitive current correction is not needed.

Glassy carbon (GC) is used as a conductive substrate for perovskite catalysts because of its many attractive properties: chemical inertness, electrical conductivity, and hardness. Although glassy carbon is often considered chemically inert, at OER potentials carbon oxidation occurs. This causes electrode degradation as well as falsely contributes to the overall measured current, especially if the perovskite has low activity. In addition, similarly to carbon black, glassy carbon is active for ORR in alkaline media. For catalysts with low activity or low loadings, the contribution of GC to the ORR current can be significant. This is evident in Figure 4 where the ORR activity of the glassy carbon substrate is half of the total ORR activity of LaNiO$_3$.[70] Surface treatments can significantly alter the activity of the GC (Figure 14). For example, mechanical
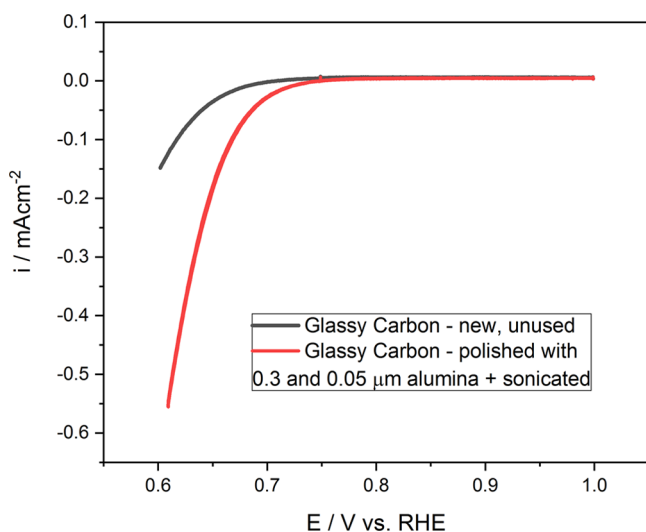

Figure 14. Glassy carbon ORR activity before and after a typical cleaning procedure. The cleaning process has significantly increased the ORR activity of the glassy carbon. RDE measured in 0.1 M KOH using a rotation rate of 1600 rpm and a scan rate of 5 mV/s.

polishing changes the surface area and creates a layer of impurities on the surface, leading to variable activity.[149] Due to the varying ORR activities of glassy carbon, it is difficult to determine the contribution of GC to the overall perovskite ORR activity. Therefore, it is important to measure the ORR activity of the bare GC before the catalyst is drop-casted on the surface. Then, the contribution of GC to the total ORR activity can be estimated. An example is shown in Figure 4. The OER activity of bare GC should also be measured in the same way to ensure the carbon oxidation current is not significant compared to the OER current of the perovskite catalyst of interest.

When the OER or ORR activities of perovskite catalysts are reported, the current is usually normalized by area or mass. This is advantageous because it allows comparison between catalysts with widely different surface areas and loadings. Normalization by mass presents the activity by catalyst weight, which gives an industrial, cost estimate perspective. Normalization by area attempts to describe the intrinsic activity of the catalyst. Three different areas that are often used are the geometric area of the substrate (usually GC), the specific surface area, and the electrochemical active surface area (ECSA). A fundamental explanation of these methods is given in ref 150. The geometric area fails to take into consideration the influence of different catalyst loadings or rough/structured

surfaces and therefore is not suitable for most applications. ECSA is suitable for theoretical applications when the intrinsic activity of the catalyst is needed. The method for determining the ECSA of Pt is tested and proven.[151] However, at the moment, there is no consensus or proven method for determining the ECSA on perovskites. This is an area where further investigations are needed. Currently, for perovskites, normalizing by mass or by the specific surface area measured by Brunauer−Emmett−Teller (BET) analysis are the most reliable options.

3.1. Specific Considerations for ORR. As discussed earlier, low catalyst loadings expose the glassy carbon surface and increase its contribution to the measured current. High catalyst loadings can affect RRDE measurements. When the catalyst loading is increased, the probability of peroxide intermediates reaching the ring decreases.[85,152] A thick catalyst layer increases the chance that the peroxide will be further reacted before it can escape the catalyst layer. This leads to artificially low peroxide yields, and therefore, caution is needed when using high loadings for RRDE. In addition, for high loadings, the surface utilization can be less than 100% if the electrolyte cannot penetrate through the thick catalyst layer. Also, the use of thin-film RDE methods is limited for thick catalyst layers because of mass-transport resistances in the catalyst layer.

As oxygen is the reactant in the oxygen reduction reaction, the reaction rate is highly dependent on the concentration of oxygen in the electrolyte. It is important to check the electrolyte is properly saturated with oxygen during ORR measurements. If O$_2$-saturation is not reached, the oxygen partial pressure is unknown and the equilibrium potential cannot be determined. There is, at the moment, no standardized potential for reporting the ORR current density. For Pt, the activity benchmark potential of 0.9 V$_{RHE}$ is well established.[153] However, it is less clear for perovskites because of their varying onset potentials and activities.

3.2. Specific Considerations for OER. Although all impurities should be avoided for catalytic measurements, Fe impurities are especially influential for OER measurements of oxide and oxyhydroxide catalysts containing Ni and Co.[108,154−157] When Fe impurities are present in the electrolyte, Fe is incorporated onto the catalyst layer, leading to an increase in OER activity.[108,154,157] The Fe impurities can come from a variety of sources including glassware, the electrolyte, or cross contamination from other catalysts. Even seemingly negligible concentrations of Fe ions (as low as 1 ppm) have been shown to effect OER activity.[155] Therefore, the influence of Fe impurities on Co- and Ni-containing perovskites cannot be excluded. To obtain rigorous results without the effect of Fe impurities, a cleaning procedure can be used, as described in ref 145. Although, it should be noted, in an industrial setting, these impurities will be present.

Presently, there is no widely accepted parameter that compares the OER activity of different catalysts. Generally, the current at a given potential or the overpotential at a given current are taken from the Tafel plot as indicators of the OER activity. However, the Tafel plot for the OER is very often built from linear scan measurements rather than on quasi-steady-state current/potential curves. However, linear scan measurements do not properly represent the OER current because they also include capacitive current contributions. A quasi-steady-state current/potential curve can be achieved by holding the potential until a quasi-steady-state current is observed (the

holding time depends on the catalyst material). In this case, it is possible to get rid of capacitive currents, which can be very high for oxide catalysts. Thus, only a quasi-steady-state current vs potential curve can properly describe the OER activity of perovskites. In addition, often the presence of large capacitive current in the low potential range for the OER could lead to a misinterpretation of the OER onset potential. In other words, an apparent early OER onset potential might only originate from capacitive currents and not from true OER current.

Another uncertain point in the OER activity measurement protocol is related to gas saturation of the electrolyte. An O_2-saturated electrolyte might be disadvantageous to dissolve the O_2 generated by the reaction in the electrolyte, leading to formation of bubbles on the catalyst surface, which block reaction sites and influence the apparent measured activity. If the electrolyte is saturated with an inert gas, O_2 molecules are easily dispersed in the electrolyte. However, it would also shift the equilibrium potential of the reaction by continuously changing the oxygen partial pressure in the electrolyte solution, according to the Nernst equation. In this case, the reaction overpotential can no longer be calculated as the difference between the measured potential and the equilibrium potential because the oxygen partial pressure, and therefore the equilibrium potential, is no longer known.

4. CONCLUSIONS AND OUTLOOK

To overcome the challenges faced by alkaline fuel cells and water electrolyzers, further knowledge of the oxygen reduction and evolution reactions is required. With a firm understanding of the reaction mechanisms, the catalysts can be further optimized and developed. Perovskite oxides are promising ORR and OER catalysts, but the mechanistic details of these two reactions on perovskite surfaces are far from understood.

For the ORR, many perovskite properties, such as the perovskite A and B site cations (and their ratio), the oxygen stoichiometry, and the perovskite covalency could affect the reaction mechanism. Indeed, the perovskite physicochemical properties can influence the binding energy of reaction intermediates on the perovskite surface and, thus, determine if the ORR would proceed via a two- vs four-electron pathway. However, since many physicochemical properties can change simultaneously when the perovskite composition changes, a full understanding of the main parameters affecting the ORR activity of perovskite catalysts has not been reached yet. Thus, intensive and systematic studies are still needed to correlate the perovskite properties with ORR activity. Furthermore, the perovskite surface could undergo modification during ORR, resulting in dynamic changes of the surface properties and, thus, of the reaction intermediate binding energy. This suggests that operando characterizations in the ORR operation regime are needed to understand if/how the perovskite surface evolves during ORR. Indeed, if the surface of a catalyst changes during operation, correlating the properties of the as-prepared catalyst with the electrochemical activity could be misleading. Finally, the reaction pathway for hydrogen peroxide is also not known and is expected to be influenced by the perovskite composition, as well as by the hydrogen peroxide binding strength.

The understanding of the reaction pathway and the key parameters affecting the activity of single perovskite ORR catalysts is crucial for moving to more complex systems, such as the perovskite/carbon composites. Carbon is often added to perovskite electrodes in order to provide conductive pathways

between oxide particles, leading to increased surface utilization. However, enhanced surface utilization by itself cannot fully explain the significant increase in ORR activity observed for perovskite/carbon composites compared to perovskite electrodes. Instead, there is evidence of a synergistic relationship between perovskite oxide and carbon. The series carbon-2e$^-$ + perovskite-2e$^-$ pathway on perovskite/carbon composites is one plausible explanation. However, additional studies are required to substantiate and further elaborate this plausible mechanism. As it was shown that the reaction mechanisms occurring on perovskites and perovskite/carbon composites may differ, any study attempting to discover the intrinsic properties of the perovskite should not add carbon to the catalyst layer. To evaluate the intrinsic activity of a perovskite with low conductivity, instead of adding carbon, it would be best to find a conductive additive without any ORR activity or to further develop kinetic models. However, a relatively high ORR activity for perovskite-based electrodes has been so far only be achieved when carbon is added to the perovskite catalyst. As state-of-the-art fuel cell cathodes are currently made of Pt nanoparticles supported on carbon, a perovskite/ carbon electrode would not present major disadvantages compared with a Pt/carbon electrode. However, the perovskite oxides can be considered unique catalysts because they can be active both for the ORR and for the OER (i.e., bifunctional catalysts). This allows operating a fuel cell device both in fuel cell mode and in electrolyzer mode, saving materials costs and space. For OER electrodes, carbon is not recommended, as carbon tends to degrade at high positive OER potentials. Therefore, for the development of perovskite catalysts it is important either to develop intrinsically conductive perovskites, which can show high ORR and OER activity without carbon or to introduce a more stable conductive additive.

For the OER, a breakthrough in the understanding of the reaction mechanism recently occurred with the development of the lattice oxygen evolution reaction (LOER) mechanism. Although, it is still not clear yet what the active site is for LOER or how the lattice oxygen is refilled. Furthermore, along with LOER, several other reactions can also occur on perovskites, possibly simultaneously, including metal cation dissolution and redeposition and the proton-coupled electron transfer (PCET) mechanism. Overall, both ORR and OER mechanisms on perovskite catalysts represent a great challenge for the research community and the development of advanced techniques, such as operando characterizations, coupled with computational studies can possibly give new insights into these electrochemical reactions.

Overall, for both OER and ORR perovskite catalysts, the reaction mechanism most likely changes with perovskite composition and the pursuit of one overarching pathway may be futile. Therefore, further research is needed on a wide variety of perovskite compositions. When conducting these studies, good experimental practices should be used, as detailed in the present Perspective. In order to find activity trends in the vast number of possible perovskite compositions, systematic and comprehensive studies would be very beneficial in pointing researchers to promising perovskite compositions as well as for gaining further insights into the perovskite reaction mechanisms. For bifunctional perovskite catalysts, alternative conductive additives or intrinsically conductive perovskites are needed to boost catalytic performance without the need for carbon.

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Notes

The authors declare no competing financial interest.

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