Electrocatalysis

Bifunctional Perovskite Oxide Catalysts for Oxygen Reduction and Evolution in Alkaline Media


Sustainable Electrochemical Energy Technologies

Electrochemical Energy Conversion and Storage

Fuel Cell

Oxygen Electro Catalysis

Water Electrolyzer

Metal-Air Battery

Highly efficient chemical-to-electrical energy conversion

$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

$4\text{OH}^- + 4\text{e}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$

Oxygen Reduction Reaction (ORR)

Oxygen Evolution Reaction (OER)

Perovskite Oxides as Bifunctional ORR/OER catalysts

Bifunctional perovskite oxide catalysts derived from earth abundant elements hold great promise to replace the precious metals (e.g., Pt, Ir) for clean electrochemical energy applications
Abstract: Oxygen electrocatalysis, namely of the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER), governs the performance of numerous electrochemical energy systems such as reversible fuel cells, metal–air batteries, and water electrolyzers. However, the sluggish kinetics of these two reactions and their dependency on expensive noble metal catalysts (e.g., Pt or Ir) prohibit the sustainable commercialization of these highly innovative and in-demand technologies. Bifunctional perovskite oxides have emerged as a new class of highly efficient non-precious metal catalysts (NPMC) for oxygen electrocatalysis in alkaline media. In this review, we discuss the state-of-the-art understanding of bifunctional properties of perovskites with regards to their OER/ORR activity in alkaline media and review the associated reaction mechanisms on the oxides surface and the related activity descriptors developed in the recent literature. We also summarize the present strategies to modify their electronic structure and to further improve their performance for the ORR/OER through highlighting the new concepts relating to the role of surface redox chemistry and oxygen deficiency of perovskite oxides for the ORR/OER activity. In addition, we provide a brief account of recently developed advanced perovskite–nanocarbon hybrid bifunctional catalysts with much improved performances.

1. Introduction

Innovative electrochemical energy storage and conversion such as metal-air batteries, alkaline fuel cells, and direct solar water splitting are capable of simultaneously storing and converting electrical energy generated from renewable sources (e.g., solar, wind, and hydraulic power) with much improved efficiency. Among others, the performance of these technologies greatly depends on four electrochemical reactions: oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) at the cathode, and oxygen evolution reaction (OER) and hydrogen oxidation reaction (HOR) at the anode (Figure 1).[1] However, the ORR and OER are a pair of sluggish electrochemical reactions and require a large amount of precious metals as the catalysts to enhance activity and durability.[2] In particular, while the most active catalysts for the ORR are Pt alloys, the Pt catalyst is not active for the OER, because the formation of Pt oxide surface film at high potentials decreases their ability to catalyze the OER. Oppositely, IrO$_2$ is the most active catalyst for the OER due to its good electrical and ionic conductivities, but not effective for the ORR. These problems along with the prohibitive cost and scarcity of these precious metals represent a grand challenge to widespread application of these electrochemical energy technologies. Therefore, the development of a single high-performance nonprecious metal catalyst (NPMC) simultaneously active for the ORR and the OER is desperately needed to replace these precious metals. In addition, issues of corrosion and stability with electrodes based upon NPMCs in acidic media drifted research interest in oxygen electrocatalysis toward alkaline media, targeting the alkaline fuel cells, metal-air batteries, and electrolyzers. Although nitrogen-doped carbon based NPMCs have shown remarkable ORR activity,[3–10] their activity and durability for the OER remain significantly insufficient. As a matter of fact, compared to the ORR, electrocatalysis of OER is more challenging due to the extremely oxidative conditions at high potentials (> 1.4 V vs. RHE), where most of currently studied carbon-based catalysts degrade due to the rapid oxidation of carbon.[2,11,12] It is well known that carbon can thermodynamically corrode above 0.207 V to carbon dioxide and corrosion currents reach significant levels around 1.0 V and above. However, the standard reduction potential for oxygen evolution is 1.229 V versus the standard hydrogen electrode (SHE). Also, even with the best OER electrocatalysts such as RuO$_2$, IrO$_2$, etc., above 1.5 V versus SHE is required to generate a noticeable oxygen evolution current density.[13] As a result, under such an oxidative environment, most of carbon-based catalysts suffer from significant performance degradation during the OER.

Relative to conventional carbon materials, transition metal oxide/sulfide catalysts are inherently more stable than carbon in oxidizing environments.[14–17] Among the various studied oxides, perovskites with a general ABO$_3$ formula hold the greatest promise to be efficient bifunctional ORR/OER
Recently, highly efficient double perovskites and oxygen-deficient perovskites have even surpassed the activity of state-of-the-art IrO$_2$ catalysts in alkaline media. Compared to other type of oxides, a major advantage of perovskite oxides is the flexibility of tuning their physical-chemical and catalytic properties of the ABO$_3$ formulation (Figure 2), where A sites are rare earth or alkali metal ions and B sites are transition metal ions. In an ideal unit cell, the A-site cations tend to be larger and more electropositive with twelve-fold oxygen coordination, whereas B-site cations are smaller and more electronegative with six-fold oxygen coordination. Due to high versatility in their electronic structure and choice of metal cations, advanced perovskites have been progressively developed and modified to yield a typical $\text{A}_x\text{A}'_1\text{A}^{1/3}_0\text{B}_x\text{B}'_1\text{B}^{1/3}_0\text{O}_3$ structure in order to achieve desired properties. The substitution of the A-site and B-site metal cations and generation of oxygen deficiency/vacancy have large characteristic effects on their electronic structures and coordination chemistry. As a result, their ORR/OER activity is highly correlated to measurable pa-

Figure 2. A unit cell in perovskite showing relative positions of different ions. (Reprinted from Ref. [25] with permission, copyright 2015 Elsevier)
parameters, including number of 3d $e_g$ electrons and their spin state in transition metals, covalency of transition-metal-oxygen bond, positions of d-band center of transition metal, and p-band center of oxygen relative to Fermi level. These measurable parameters depend heavily on the type and distribution of cations and their oxidation states as well as on the concentration of oxygen vacancies.

In this review, after a brief description of the important reactions mechanisms on oxides surface, we discuss the established structure–activity correlation of the perovskite oxide catalysts in terms of their ORR and OER activities. We then discuss the strategies, including effective substitutions of metal cations and oxygen vacancy formation, responsible for their improved performance. We also try to elucidate the dominant role of less studied surface redox active centers, which essentially include transition metal cations and oxygen vacant sites in terms of their bifunctional performance. Next, recently developed advanced perovskite–carbon hybrid nanomaterials with synergistically improved performance over individual perovskite oxides and carbon based catalysts are highlighted. Finally, we conclude with a discussion of future directions to further improve the ORR/OER performance of perovskites oxide catalysts.

2. ORR and OER Mechanisms on Perovskite Oxide Catalysts

In 1977, Tseung and Jasem[35] first studied the criteria for semiconductor oxide electrodes for the OER. They proposed that the oxides having a transition metal redox couple at potentials below the theoretical oxygen electrode can form more active metal sites with higher oxidation state, which would be very promising electrocatalysts. Higher ORR activity and a good electrical conductivity are also likely desired to form active ORR catalysts. In the following years (1980–1984), Trasatti published a series of interesting papers[36, 37] on the ORR activity of rutile, spinel, and perovskite oxides based upon these rules. Most notably, he discovered and emphasized a volcano-type relationship between the enthalpy of transition from a lower to a higher oxidation state and corresponding OER overpotential. On the other hand, Bockris and Otagawa[38, 39] (1983, 1984) attempted to elucidate the mechanism and rationalize the specific property–activity relationships. They performed a systematic investigation for eighteen different perovskite oxides[38] and found the current density at constant overpotential to be inversely dependent on the enthalpy of Mo(OH)$_2$ hydrogen formation. Subsequently, they concluded that these oxides share a common rate-determining step (RDS), that is, desorption of OH$^-$ intermediates. The aforementioned activity descriptors laid the foundation for the efficient design of oxide electrocatalysts over the next 25 years.

Figure 3 illustrates some of the proposed reaction mechanisms on oxide surfaces that were rationalized from different perspectives. Man et al. extended the mechanisms which were originally determined from extensive computational work on metal surfaces[40, 41] to oxide surfaces,[41] in order to rationalize the trends in the ORR activity of perovskites and rutile oxides (Figure 3a). This mechanism, sometimes alternatively referred to as acid–base mechanism,[43, 46] essentially proceeds through a series of acid–base steps, in which OH$^-$, an oxygen nucleophile (Lewis acid), attacks a metal-bound electrophile oxygen surface species (Lewis base). An identical reaction mechanism was proposed by Goodenough et al. for the ORR on pyrochlore and rutile oxides (Figure 3b).[42] Computational work on the OER by Mavros and co-workers found that this reaction mechanism is also the most favorable in dimeric metal “oxide” molecules with early transition metal ions (Figure 3c).[43] Note that the mechanism shown in Figure 3a involves a step with a bare catalyst surface, while mechanisms 3b and 3c do not. Surface pH of zero charge (pHpzc)[47, 48] governs the adsorption of species (e.g., H$_3^+$, OH$^-$, O$^-$, etc.) on oxide surface. Generally, binary metal oxides[49] and perovskites[50] have pHpzc values between 7 and 11, whereas, during electrocatalysis of oxygen in alkaline media, the surface of these oxides encounters a pH of 13–14. Since the pH value (13–14) at which testing of OER/ORR activities of oxides is performed is much higher than their pHpzc values (7–11), oxide surfaces are expected to accumulate negatively charged adsorbates such as OH$^-$ in alkaline solution,[31] thereby being more favorable to the OER over the ORR. Suntivich et al. proposed that the RDS in reaction mechanisms of OER/ORR may be different for different perovskites depending on the $e_g$ orbital filling of the transition metal cation.[32, 44] For example, during OER, for $e_g$ filling greater than 1, RDS is the formation of the O–O bond in OOH$^-$ adsorbate on B-site cations, whereas for $e_g$ filling less than 1, the deprotonation of the oxyhydroxide group to form peroxide ions may be the RDS (Figure 3d).[44] Similarly, during the ORR, for $e_g$ filling more than 1, the rate of O$_2^-$/OH$^-$ exchange is the RDS due to insufficient energy gain in O$_2^-$/OH$^-$ and for $e_g$ filling less than 1, the RDS is the step of surface OH$^-$ regeneration due to insufficient destabilization of B-O$^2^-$ (Figure 3e).[52] Due to the diversity in these mechanisms, it is highly complicated to assign a single reaction mechanism to oxygen electrocatalysis on oxide surfaces. Moreover, as these mechanisms involve several common intermediates, future research is required to clearly distinguish them on oxide surfaces during the ORR/OER.

3. Perovskite Oxide Catalysts

The ORR/OER performance of some of the recently developed perovskites in alkaline have matched or even surpassed that of the catalysts based on noble metals, namely, Pt, Ir, and Ru.[52–54] The preparation of such potentially promising perovskites requires synthesis routes to accommodate for effective diffusion of different metal cations and oxygen defects while preserving the essential perovskite lattice structure. Moreover, these synthesis routes should have a good scope for adequate control over the morphology, size, and phase to generate desired ORR/OER activity in the obtained perovskites. In this part, we review the most effective synthesis methods to prepare highly active ORR/OER bifunctional perovskite catalysts along with the effective strategies to improve their ORR and OER activities in alkaline media.
3.1. General Synthesis Routes

Conventional solid-state ceramic preparation methods require extremely high temperatures and prolonged process times to overcome diffusional barriers and form lattice structures.\[26, 34\] Generally, the particles obtained by this method are phase impure with reduced surface area due to high temperature agglomeration. An alternative strategy is to synthesize perovskite nanoparticles with bottom-up approaches by sol–gel methods,\[55, 56\] co-precipitation hydrolysis process,\[32, 44\] reverse micelle synthesis,\[57–59\] and hydrothermal routes.\[60, 61\] These processes require lower temperatures due to their better diffusion in liquid solutions, and they may result in nanosize perovskites as small as 10 nm. Nevertheless, dissimilar hydrolysis rates for systems with two or more metals could lead to phase impurities and particle growth of otherwise promising perovskites. To overcome this, recently a unique synthesis approach was invented by Hardin et al.,\[52\] which is discussed in the co-precipitation method below. In this part, we provide a brief summary of these synthesis methods to perovskite oxides with an emphasis on principle understanding.

3.1.1. Solid-state route

As previously mentioned, solid-state reactions are typically brute force ceramic preparation methods that require elevated temperatures and a prolonged process time to overcome diffusional barriers. In a conventional solid-state route, a stoichiometric amount of metal precursors after dehydration is thoroughly ground and fired in desired atmospheres at elevated temperatures. The obtained products are further ground and refined by annealing to obtain target catalysts. The solid-state conditions including temperature and time duration of heat treatment are dependent on the types of metal cations and used precursors. The rate of diffusion is a key to the solid-state synthesis, and generally it can be increased by three ways. The first method is simply increasing the temperature. The second option is to introduce defects by starting with reagents/precursors that decompose prior to or during reaction, such as carbonates or nitrates. The final route involves pelletizing the mixer powder before annealing. An initial heating cycle to lower the temperature can help to prevent spillage and volatilization. The heating atmosphere (e.g., inert, air, or vacuum) is also of great importance and can affect the phase purity, atomic defects, and particle size and shape.\[34\] One example was demon-

Figure 3. OER/ORR mechanisms proposed for oxide surfaces. (a) Four-step reaction mechanism proposed by Rossmeisl and co-workers for the OER on noble metal catalyst surfaces\[40\] and later applied to oxide surfaces.\[41\] (b) Four-step reaction mechanism proposed by Goodenough et al. for the ORR on perovskite surfaces.\[42\] (c) Acid–base mechanism proposed for dimeric molecules.\[43\] (d) Four-electron OER reaction mechanism on perovskite surface; the RDS are the O–O bond formation and proton extraction of the oxy-hydroxide group.\[44\] (e) Four-electron ORR mechanism for perovskite surface; the RDS are either the surface hydroxide displacement or the surface hydroxide regeneration.\[32\] (Reprinted with permission from above-mentioned references)
strated by Grimaud et al., who prepared highly active \((\text{Ln}_x\text{Ba}_{1-x})\text{CoO}_y\) (with \(\text{Ln}=\text{Pr}, \text{Sm}, \text{Gd} \text{and Ho}\)) and \((\text{PrBa})_x\text{Co}_{1-x}\text{Fe}_{y}\text{O}_{z}\) catalysts via the solid-state route with varied heating temperature and atmosphere.\(^{[26]}\)

3.1.2. Co-precipitation method

In a typical co-precipitation method, the desired rare and alkali earth metal and transition metal precursors are first mixed in Milli-Q water to form a homogenous solution. The as-prepared solution is then reacted with a suitable organic base to form precipitates followed by filtration and drying. Subsequently, the required heat treatment at elevated temperature and in different atmospheres produces the desired stoichiometry. The heating temperature and duration varies with different metal precursors; the details are described elsewhere.\(^{[52, 62]}\) Although the co-precipitation method is able to yield nanosized oxide particles as small as 10 nm,\(^{[63, 64]}\) their phases usually are not very pure and show relatively low mass activity. The disparities of hydrolysis rates for different metal cations could explain why this happens.\(^{[56]}\) Recently, an advance was made by Hardin et al.,\(^{[52]}\) wherein they used reverse-phase arrested growth precipitation to form uniform 25 nm nanoparticle dispersions of hydrolysis products of La\(^{3+}\) and Ni\(^{2+}\) nitrates. A rapid freeze drying was used during the synthesis and yielded highly open, low fractal dimension, and mixed metal hydroxide nanoparticle powders. During subsequent calcination of these powders, highly active phase-pure perovskite nanoparticles within a size range of 20–50 nm with a surface area of 11 m\(^2\) g\(^{-1}\) were prepared.

3.1.3. Reverse micelle synthesis

Reverse micelle (RM) synthesis has been used successfully for the preparation of nanoscale particles for various materials including metal,\(^{[45]}\) metal oxides,\(^{[66]}\) or their precursors,\(^{[67]}\) and recently perovskite oxides electrocatalysts.\(^{[25, 54]}\) It exploits the unique properties of oil–surfactant–water ternary systems that form a stable colloidal dispersion of RM particles under adequate reaction conditions. When a polar phase (typically water) and non-polar phase (typically oil) are mixed together along with a suitable surfactant in appropriate concentrations, phase segregation occurs either to form oil-filled spheres (micelles) in water medium or water-filled micelles in oil medium. The important feature is that the obtained product characteristics (i.e., size, shape, etc.) can be influenced by choice of surfactant, solvent, solvent/surfactant ratio, and temperature and pH of the ternary solution.\(^{[68]}\) Generally, surfactants with larger hydrophobic chains\(^{[67]}\) and solvents with lower molecular weight are used to obtain smaller particle sizes.\(^{[66]}\) A typical procedure to synthesize pure crystalline homogeneous perovskite nanoparticles of the series \(\text{La}_x\text{Sr}_{1-x}\text{CoO}_y\)\(^{[57]}\) starts with the preparation of aqueous mixed metal nitrate solution. Then, two RM solutions are prepared. The first mixed a surfactant (polyoxyethylene(5)nonylphenylether) and an organic solvent (cyclohexane) with the mixed nitrate solution. The size of nanoparticles is controlled by the aqueous phase-to-surfactant ratio \((R_s)\). The second solution is prepared by mixing an aqueous solvent \((\text{NH}_4\text{OH})\), the surfactant, and the organic solvent with same \(R_s\) and hence the micelle size, as the metal nitrate solution filled micelle. On mixing these two solution types, collisions between the two micelle types causes hydroxylation of mixed metal nitrate solution, eventually giving rise to mixed metal hydroxide precipitates with the micelle core. After subsequent centrifugation and filtration, the collected precipitates are finally heat treated to give phase-pure homogeneous perovskite nanoparticles.

3.1.4. Sol–gel method

Sol–gel is one of the most exploited routes to produce nanostructured perovskite oxide catalysts. Citric acid and EDTA are extensively used for a solvent and a polymer, respectively. Thus, sometimes it is also referred to as EDTA–citric process. In a typical procedure, the metal salts/precursors are first dissolved separately in a typical solvent and then mixed slowly to form a homogenous mixed solution. The pH of the solution during this stage is very important and therefore is maintained to facilitate the chemical reactions, especially hydroxylation of metal salts. Subsequent refluxing yields thick gels, which are then either filtered out or centrifuged to separate the precipitates. These precipitates are either oven-dried or freeze-dried followed by calcination in air to form the perovskite oxide catalysts. The specific details can be found in the relevant literature.\(^{[25, 55, 66]}\) More importantly, the calcination temperature and atmosphere are important to yield the desired final catalyst performance.\(^{[67]}\) Progressively, well-dispersed nanoporous \(\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_y\) perovskites with surface area as high as 210 m\(^2\) g\(^{-1}\) have been prepared via a modified amorphous citrate precursor method using Vulcan XC-72R as a pore-forming material.\(^{[80]}\)

3.1.5 Hydrothermal process

The hydrothermal process essentially involves a dissolution/precipitation mechanism driven by the driving force owing to the difference in solubility between the soluble reactant phase and the insoluble product. It has shown a promising potential to produce well-dispersed, fine and homogenous powder with improved calcination and sintering properties for perovskite oxides.\(^{[60, 61]}\) The primary requirements to form an anhydrous oxide are the nature of the starting material, composition of the precursors, and the temperature range used during the synthesis. The main advantage of this method is to significantly reduce the reaction temperature and hence the sintering effects.\(^{[66]}\) It also induces metastable phases which are critical to eventually form phase-pure products. In a typical hydrothermal synthesis, metal salts in the desired stoichiometry (typically nitrates or acetates) are first homogenously mixed in water to form aqueous solutions. An adequate base (often \(\text{NH}_4\text{OH}\)) is then added to maintain the pH in the basic range and to facilitate complete decomposition of the acidic solution through a rapid hydroxylation. This resulting solution is then hydrothermally processed, essentially in a Teflon-lined autoclave. Next,
the insoluble products are thoroughly filtered, washed, and centrifuged to collect precipitates. These precipitates are finally heat-treated in a relatively low temperature range (generally 500–600 °C) to yield the desired perovskite oxides.

3.2. Strategies to Improve Catalyst Performance

Sabatier’s principle, which qualitatively describes that high catalytic activity can be obtained when adsorbed species bind to the surface neither too strongly nor too weakly, has been instrumental to fundamental understanding of OER/ORR mechanisms and the development of highly active perovskite electrocatalysts. However, it is very challenging and unreliable to assess the binding energy of oxygen and intermediate reaction species. Hence, experimental studies in the past have focused on developing correlations between the intrinsic ORR/OER activity of perovskite oxides and their parameters that can be measured experimentally. These measurable parameters are derived from principles of both molecular orbital theory (MOT) and band theory (BT).

The $e_g$ orbitals of transition metal cations participate in $\sigma$-bonding with a surface anion adsorbate and consequently its occupancy greatly influences the binding of oxygen related intermediates on B-site cations and ultimately OER/ORR activity.\cite{32, 44} Recently, Shao-Horn et al. indicated that design principles for enhancing the ORR and OER activity of transition-metal oxide perovskites are linked with the $e_g$-filling of B-sites in perovskite oxides. Generally, a value near 1 of $e_g$ filling corresponds to maximum activity, which can be further improved by increasing the covalency between the metal 3d and oxygen 2p orbitals.\cite{32, 44} In turn, the $e_g$ filling of transition metals is dependent on their oxidation and spin states. In Figure 4\cite{33}, the $e_g$ filling of various transition metal cations with most common oxidation state and possible spin state are given. In principle, during the OER/ORR on perovskite oxides, covalent mixing (hybridization) of the transition metal 3d orbitals and O 2p orbitals occurs due to the spatial overlap and energetic similarity of the electronic states. Consequently, the greater covalency of transition metal cation–oxygen bonds could reduce the charge transfer gap between the two and in-turn promote charge transfer between redox active centers (surface metal cations and oxygen anions) and adsorbates participating in the RDS of the OER/ORR.\cite{32} Apart from the covalency of cation-oxygen bond and 3d $e_g$ filling, the position of oxygen p-band and metal d-band relative to the Fermi level is considered highly important to achieve high ORR/OER activity of perovskites. Density functional theory (DFT) calculations have been used to determine the relative position of these bands. However, the DFT calculation for transition metal cation d-band may result in a large correlation error. Therefore, the delocalized nature of the O p-band is exploited to obtain a more accurate picture of the electronic structure characteristics of oxides critical to catalysis while still reflecting the metal d-character through hybridized density of states.\cite{26} The relative position of these bands determines the hybridization and covalent mixing between the oxygen 2p orbitals and metal cation 3d orbitals.

This further affects the charge transfer between the active redox centers and adsorbates.

More importantly, the above described parameters, that is, $e_g$ orbital filling, transition metal–oxygen covalency, and relative position of metal 3d-band and oxygen 2p-band center can be tailored with various substitutions and oxygen vacancy to improve the OER/ORR performance. These substitutional and vacancy effects along with their origin are described in the following section.

3.2.1. Tuning alkali or rare earth metal (A sites) and transition metal (B sites) cations

Substitutions of alkali or rare earth metals in perovskites play a significant role in modifying the electronic structure of perovskites, thereby affecting their catalytic activity. Alkali earth metals can be combined with rare earth metals to produce alterations in net positive charge contribution by A-site metal cations. This ultimately changes the oxidation state and spin state of transition metal cations (B sites) and may induce oxygen vacancy. After a systematic examination of 10 transition metal perovskite oxides, Suntivich et al. found a volcano-shape dependency of the intrinsic OER activity on the $e_g$ electron occupancy (Figure 5a).\cite{34} They concluded that oxides having an $e_g$ occupancy of near unity with high covalency of the transition metal (B sites)–oxygen bond show maximum OER activity. Based on this design principle, they were able to predict the high activity of $\text{Ba}_0.5\text{Sr}_{1.5}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_x$ (BSCF) with at least one order of magnitude higher than the state-of-the-art IrO$_2$ catalysts. Interestingly, a similar correlation between $e_g$ filling states and the ORR activity was identified by the same authors.\cite{34} They revealed an M-shape relationship between the ORR activity of the perovskites and the d-electron number per B cation with maximum activity attained near $d_A$ and $d_B$. Both high-spin $d_A$ and low-spin $d_B$ have $e_g$ filling closer to unity, and

![Figure 4. Potential transition metal 3d electron configurations for LaMO$_7$ perovskite oxides (M = Cr, Mn, Fe, Co, Ni) for different spin states at room temperature. Orange configurations designate the stable spin state for the bulk oxide at room temperature as determined by magnetic measurements. White configurations are possible spin states observed at other temperatures or under thin film epitaxial strain. Although an intermediate spin state is typically cited as the stable electronic configuration for LaCoO$_3$ at room temperature, this remains controversial and thus the state high- and low-spin state configurations are shown in blue to emphasize the ambiguity of the cobalt spin state. (Reprinted from Ref. [33] with permission from the Royal Society of Chemistry)](Image)

thus this M plot is further supported by the volcano-shape relationship that they obtained between ORR activity and \(e_g\) filling (Figure 5b).

Thus, in principle, any perovskite with unity \(e_g\) filling for B-site transition metal should be simultaneously active for the ORR and OER. However, this is not universally true for perovskite catalysts, due to the fact that most of them are active for the OER, but not for the ORR. Hence, the effect of A sites, especially the ratios of A to A’ along with other important factors cannot be ignored. Furthermore, during the study of several cobalt-based double perovskites with rare earth metals as lanthanides, Grimaud et al. found that the O-p band center relative to the Fermi level linearly increases with increasing cobalt oxidation state from Ho to Pr (Figure 6). This uplift of O-p band center increases the Co-O bond hybridization as observed by the O K-edge XAS measurements in their study.

**3.2.2. Oxygen deficiency/vacancy**

During the ORR electrocatalysis, there is a dynamic reduction of molecular \(O_2\) and a subsequent incorporation into solid-state \(O^2-\) and vice versa. The famous Kroger–Vink notation aptly describes the global oxygen incorporation reaction into lattice vacancies and electron transfer as:

\[
O_2 + 4e^- + 2V^0_0 \leftrightarrow 2O^2_0
\]  

where \(V^0_0\) denotes oxygen vacancies.

These oxygen vacancies can behave as donors or acceptors, augmenting the charge transfer between adsorbent and adsorbate and thus leading to semiconducting behavior over a thin surface layer on catalysts. Thus, in oxygen deficient oxides, there is a simultaneous filling and creation of lattice oxygen vacancies, which also predominantly plays a determining role in their intrinsic ORR/OER activities. Recently, a systematic study conducted by Grimaud et al. on double perovskites showed that the presence of oxygen vacancies induces a stabilization of the \(d_{xz}\) and \(d_{yz}\) and the \(d_{z^2}\) molecular orbitals in the \(t_{2g}\) and \(e_g\)-parentage orbitals, respectively. This leads to a formation of an oxygen-deficient octahedral symmetry that is called square pyramidal symmetry \((C_4v)\) shown in Figure 7. The type of lanthanide was believed to affect the oxygen vacancy content and oxidation state of cobalt, which both impact the OER/ORR activity, and thus the generation of oxygen vacancies is conducive to the electrocatalytic performance of the catalyst.
Recently, we introduced a new strategy to generate oxygen deficiencies by employing synergistic effects of extremely high temperature and vacuum atmosphere during the synthesis of catalysts, in which we successfully prepared highly efficient oxygen-deficient BaTiO$_3$-rich bifunctional catalysts. The oxygen-deficient hexagonal BaTiO$_{3-x}$-rich catalyst exhibited excellent catalytic activity simultaneously for the ORR and OER in alkaline media. Especially, its OER activity exceeds the state-of-the-art IrO$_2$ catalyst at relatively low potential (<1.6 V), evidenced by much more negative onset potentials and higher current densities (Figure 8). The exceptionally improved catalytic activities simultaneously for both oxygen reactions is likely due to the oxygen vacancies in h-BaTiO$_3$ crystal structures, facilitating the adsorption of reactants (OH$^-$) and charge transfer. This work has demonstrated a new type of bifunctional perovskite catalyst through creating oxygen deficiency for oxygen reduction and evolution, holding great promise to be applied in reversible electrochemical energy conversion and storage technologies such as metal–air batteries and regenerated fuel cells. A more detailed understanding of the mechanism for oxygen-deficient BaTiO$_3$ can be further obtained by using theoretical computation and simulation, which is one of our future focuses.

3.3. Importance of Surface Redox Centers

Most of the previous studies on ORR/OER activities of perovskites focused on developing a correlation between bulk properties of redox active centers (metal cations and oxygen anions) and their catalytic activity. The reasons could be any or all of the following: the extreme sensitivity of surface redox states to temperature, gas pressures, or electrochemical reaction conditions. Mueller et al.$^{[14]}$ developed highly advanced surface sensitive operando X-ray absorption spectroscopy to study oxygen incorporation and evolution reactions on the surface of thin film iron and cobalt perovskites as model electrodes. In contrast to the conventional view, which considered bulk metal centers as active redox centers, the surface oxygen anions have played a major role in determining the OER/ORR activity of the electrocatalysts. Further investigations revealed that, similar to the previous activity descriptor, a narrow electronic state of higher O 2p character near the Fermi level exchanges electrons with the oxygen adsorbates.

The vastly improved OER activities of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF82), Ba$_{0.5}$Sr$_{0.5}$Co$_{0.4}$Fe$_{0.6}$O$_{3-δ}$ (BSCF46) and SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (SCF82) over La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ (LSC46), LaCoO$_3$ (LCO) and LaMnO$_3$ (LMO) were primarily due to the increased number of cobalt and iron cations and oxygen vacancies present on their surface. The surfaces of highly active BSCF82, BSCF46, and SCF82 rapidly become amorphous during few cycles of water oxidation.$^{[20]}$ This amorphization (absent in LSC46, LCO and LMO) is essentially accompanied by partial leaching of Ba$^{2+}$ and Sr$^{2+}$ from the surface, thus generating a larger electrochemical active surface area, which considerably increases the pseudocapacitance and OER currents. It is worthwhile noting that BSCF82, BSCF46, and SCF82 have higher O p-band centers relative to the Fermi level when compared with those of LSC46, LCO, and LMO with inferior OER activity.$^{[20]}

3.4. Nanocarbon-Supported Perovskite Oxide Catalysts

Both ORR and OER catalysts require an efficient flow of electrons through the electrodes for generating high respective current density. As a result, the electrical conductivity is vital to prevent energy loss and improve the performance of ORR/OER perovskite electrocatalysts. However, most metal oxides, including a majority of perovskites, show poor electrical conduc-

Figure 7. Double perovskite crystal structure and cobalt crystal field. (a) Schematic representation of (Ln$_{0.5}$Ba$_{0.5}$)$_3$CoO$_3$, double perovskites showing the ordering of Ln and Ba cations and the formation of oxygen deficiency in the LnO$_2$ planes. This ordering is reflected by the doubling of the c parameter compared with ideal cubic perovskites, resulting in ap × ap × 2ap lattice parameters (ap being the lattice parameter of cubic perovskite indexed in Pm-3m space group). The structure has (b) octahedral (O$_6$) and (c) square pyramidal (C$_4$) symmetry for Co ions, with different crystal-field splitting of d-electron states for the different coordination symmetries. (Reproduced with permission from Ref. [26]. Copyright 2013, Macmillan Publishers Ltd.).

Figure 8. Oxygen-deficient BaTiO$_{3-x}$ (BTO-1300VAC) perovskite oxide bifunctional catalyst for the ORR and the OER (the inset shows the crystal structure of h-BaTiO$_3$). (Reprinted from Ref. [25] with permission. Copyright 2015 Elsevier).
tivity at ambient temperatures, thus limiting their bifunctional catalytic performance in oxygen electrocatalysis.

Hence, integrating with the highly electrically conductive nanocarbon (e.g., carbon tubes,[75,76] onion-like carbon,[77,78] and graphene[79,80]) will benefit the activity improvement for the perovskite oxide catalysts.[81] In particular, the intensely exploited nitrogen-doped carbon composite catalysts for the ORR can be used as the active carbon to integrate with perovskite oxide catalysts, due to their high intrinsic electron conductivity and high activity for the ORR.[79,82–84] Typically, the perovskite oxide catalysts have been extensively supported with various types of nitrogen-doped carbon catalysts to increase their overall bifunctional electrocatalytic activity.[52-54,85-87] These ORR active carbons can act as conductive bridges by electrically wiring the metal oxides to the electrodes, which trigger the much needed electron transport. This approach will allow for integrating the ORR-active carbon with the ORR/OER-active perovskite oxides in a bifunctional cathode for reversible electrochemical systems.

Noteworthy, studying the interfaces between nanocarbon and perovskite nanocrystals and their possible synergistic effects will yield novel composite catalysts with much improved activity and durability. A study of interactions between nanosized Pt and metal oxides (WO$_3$ and TiO$_2$) using XPS also suggests that a partial charge transfer from the metal oxide to Pt can result in increased ORR activity.[88] A similar promotional role of these oxides is expected to be the case for the bifunctional nanocarbon/perovskite composite catalysts.

In Figure 9, we propose two types of configurations for graphene-based bifunctional catalyst designs: (i) N-doped graphene-supported oxides, which can further improve the overall performance of perovskite catalysts (e.g., catalytic activity, electron conductivity, and mass transport) and (ii) Compared to other designs, core–shell configurations may be an optimal structure for designing efficient bifunctional catalysts; the ORR-active graphene-rich shells are porous and highly graphitic, so they provide facile electron transfer pathways and mass transport channels for the OER-active perovskite cores. For example, Chen et al.[54] developed a highly active and durable core–shell bifunctional catalyst, wherein highly OER-active LaNiO$_3$ acts as a core surrounded by a highly ORR-active nitrogen-doped carbon nanotube (NCNT) shell component. The geometric confinement of metallic oxide by an NCNT corona component could enhance the interfacial contact between metal oxide and conductive carbon, so it would then suppress the dissolution and agglomeration of oxide nanoparticles, eventually producing better electrocatalytic activity and stability. As a result, this hybrid perovskite catalyst exhibits an exceptional bifunctional capability because it matches the individual activity and durability. A study of interactions between nanosized Pt and metal oxides (WO$_3$ and TiO$_2$) using XPS also suggests that a partial charge transfer from the metal oxide to Pt can result in increased ORR activity. A similar promotional role of these oxides is expected to be the case for the bifunctional nanocarbon/perovskite composite catalysts.
ORR and OER activities of state-of-the-art commercial Pt/C and LaNiO$_x$ respectively.

In addition, Hardin et al.\textsuperscript{[52]} investigated the ORR/OER bifunctionality of nanostructured LaNiO$_3$ supported on nitrogen-doped carbon (nLaNiO$_3$/NC) (Figure 10) and reported an exemplary low total overpotential (1.02 V) between ORR and OER; this matched or even surpassed that observed for investigated noble metal catalysts Pt/C (1.16 V) and Ir/C (0.92 V).

To generate these synergistic activities in hybrid materials, their preparation required modified synthesis routes that were designed to incorporate unique structural and functional properties of the precursor materials into the final obtained catalysts. A simple synthesis of each component separately, followed by the use of mechanical grinding or extensive stirring, has a high probability to compromise the individual activity in each component. Thus, judicious design of the hybrid perovskite catalysts with uniform mixture at nanoscale is crucial for high performance.

4. Conclusion and Outlook

Simultaneously reducing the overpotentials in cathodic ORR and anodic OER processes remains a grand challenge for the reversible electrochemical energy technologies, such as reversible alkaline fuel cells, metal-air batteries, and water electrolyzers. Compared to other oxides, the unique partially substituted A$_1$B$_x$O$_3$ perovskite structure provides a great flexibility to design and synthesize a large amount of catalysts with controlled electronic and geometric structures, which is very valuable for the development of ORR/OER catalysts. Thus, the bimetallic perovskite oxides have shown the most promising potential to be highly efficient bifunctional electrocatalysts, due to continuously improved activity and stability. The OER/ORR activity of these perovskites has been correlated with the measurable parameters that define their electronic structure pertaining to oxygen electrocatalysis. In this review, these structure–activity correlations are discussed in detail along with their origin and impact on electrocatalytic activity. Based on the past experimental studies by various groups, a near unity $e_g$ orbital occupancy in transition metal cation, closer transition metal d-band and oxygen p-band center relative to the Fermi level, high covalency of the metal-oxygen bond, and oxygen deficiency are favorable for the ORR/OER activity of the perovskites. The versatile structures of the perovskites have been progressively modified by various strategic substitutions and ionic defects to alter these parameters in order to enhance their activity. The importance of surface-active redox centers is demonstrated with various recent examples, which further demand a great improvement in characterization techniques to probe the in-situ surface changes in perovskites during OER/ORR testing. The activity and durability of these perovskites require a more unified way to exploit these designed principles in a coherent manner to increase their activity to the next level.

In terms of performance improvement, a great challenge is a simultaneous high performance for the ORR and the OER. Based on recent achievements in developing bifunctional perovskite catalysts, the ORR seems to be even more challenging for these oxide catalysts\textsuperscript{[20, 91]} relative to the OER. Thus, fully elucidating the active sites and the relevant ORR mechanism is required to provide more effective guidance to tune the structures of perovskite allowing enhanced O$_2$ adsorption and subsequent disassociation. Also, current perovskite oxide catalysts still suffer from low electrical conductivity. Appropriate doping and defect control may be effective solutions. In addition, synthesis of high-surface area and robust nanoparticles of perovskite allows for significantly improved mass activity by increasing the active surface areas and enhancing charge/mass transport. Generally, integrating perovskite catalysts with ORR-active nanocarbon will be an effective strategy to improve the electrical conductivity and the ORR activity. However, proper selection of the type of nanocarbon and how to incorporate them together are crucial to overall catalyst performance and durability, due to the possible corrosion of carbon under the OER conditions.

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