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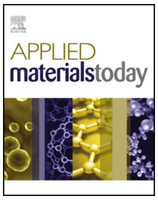

Review

Perovskite oxides as bifunctional oxygen electrocatalysts for oxygen evolution/reduction reactions – A mini review

Haizhen Wang[a], Meng Zhou[a], Pabitra Choudhury[b], Hongmei Luo[a,*]

[a] *Department of Chemical and Materials Engineering, New Mexico State University, Las Cruces, NM 88003, United States*
[b] *Chemical and Materials Engineering Departments, New Mexico Tech, NM 87801, United States*

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ABSTRACT

Energy crisis due to the depletion of fossil fuel as well as the increased population has stimulated researchers to search for new energy resources and energy storage and conversion systems, including fuel cells, electrolyzers and metal–air batteries. Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are two reactions that dominate the overall performance of these devices. However, the sluggish kinetics of these two reactions still impedes the practical application of these devices. Therefore, electrocatalysts, especially non-noble metal oxides are needed to expedite the reactions. Perovskite oxides, as a member of the mixed metal oxide family, show promising electrocatalytic performance toward both ORR and OER. However, there are only a few articles regarding the recent progress of perovskites as bifunctional electrocatalysts till now. In this mini-review, we summarize the recent research status and progress of perovskite oxides as electrocatalysts for ORR/OER, including the basic mechanism behind the catalytic reactions, different approaches to synthesize perovskites as well as the various strategies that researchers have developed to promote their electrocatalytic activities. Besides, the related theoretical calculation method, density functional theory (DFT), which is used to understand the mechanism behind these reactions, has also been discussed. It is believed that this mini-review can not only offer researchers guidance to synthesize perovskite oxides as demanded, but also provide researchers more insights into how to rationally design new perovskite-based catalysts with improved bifunctional electrocatalytic properties.

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* Corresponding author.
E-mail address: hluo@nmsu.edu (H. Luo).

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1. Introduction

The increasing energy crisis and environmental pollution caused by the economic development and human activities has motivated researchers to search for new sustainable energy resources and the corresponding energy conversion and storage devices, such as fuel cells [1], electrolyzers [2] and metal–air batteries [3]. Fuel cell is a device that converts the chemical energy into electricity via a chemical reaction with oxygen and hydrogen and oxygen reduction reaction (ORR) takes place on the cathode side; while conversely water electrolyzer is a device to split water to produce hydrogen and oxygen and oxygen evolution reaction (OER) happens on its anode side. Furthermore, metal–air batteries, composed of metal anode, air cathode and electrolyte, have been regarded as the next-generation electrochemical energy storage systems due to their high theoretical energy density. On their cathode side, oxygen from the surrounding air is reduced (ORR) during the discharging process while OER takes place during the charging process. It is critical requirement for the catalysts to be bifunctional in these rechargeable/reversible systems, including metal–air batteries. However, both OER and ORR are kinetically sluggish [4], which requires extra energy (overpotentials) to overcome the kinetic barrier of these reactions and the energy efficiency of these devices is highly reduced and thus limits the commercialization of these energy devices. Therefore, it is imperative to develop electrocatalysts to facilitate both reactions and minimize this overpotential, and thus to reduce the extra energy needed to drive these reactions in those devices.

At present, platinum (Pt) and palladium (Pd) are the mostly widely used effective electrocatalyst for ORR [1,5] while has poor activity toward OER; and IrO_2 and RuO_2 are regarded as the best OER catalyst but exhibit poor ORR activity [5]. Besides, the scarcity and thus the high cost as well as the poor stability of these noble metal catalysts under reaction conditions hinder their wide applications [1,4,6], which makes the development of effective bifunctional catalysts the primary objective for these electrochemical energy storage and conversion technologies. Therefore, great effort has been devoted to the development of new electrocatalysts, especially those with bifunctional activity toward both ORR and OER, based on non-noble metals with low-cost and high activity and stability.

Extensive research has been carried out to explore new electrocatalysts for OER and ORR up to now and several materials, including carbon-based materials [7–9] and non-noble metal oxides [5,10–12] show promising performance. However, due to the inferior stability, especially under oxidative environments, of carbon-based materials to metal oxides [1], researchers have paid more and more attention to metal oxide catalysts. Mixed metal oxides, such as spinel structures have aroused great interest due to their good catalytic performance originated from the synergistic effect among the metal ions [10,13]. While some progress has been made regarding spinel structured mixed metal oxides as electrocatalysts, their performance as bifunctional electrocatalysts are still relatively limited and thus researchers are trying to develop more efficient low-cost bifunctional cocatalysts toward ORR/OER.

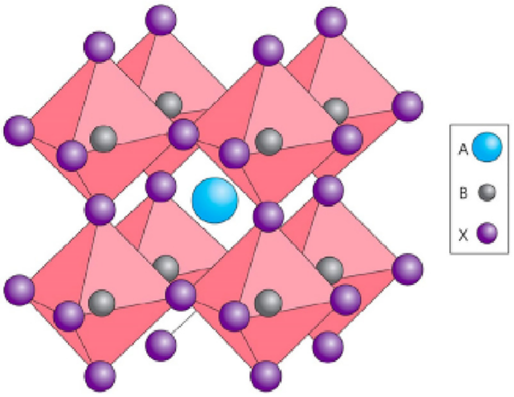

Fig. 1. Schematic illustration of an ideal perovskite oxide unit cell. Reprinted from Ref. [15] with permission, copyright 2016 Taylor & Francis.

Perovskite oxides have attracted great attention recently and found applications in a variety of fields due to their unique electronic, ionic, magnetic, catalytic and environmentally friendly properties [14]. Besides, perovskites can be synthesized easily with relatively low-cost. Perovskites have a general formula of ABO_3, where A is usually rare-earth or alkaline earth metal and B is a transition metal. As indicated from the crystal structure of perovskites (Fig. 1) [15], B stays at the center of the octahedron and A fills the space among the octahedrons. As a new class in the mixed metal oxide family, perovskites with versatile elemental compositions and different crystal structures can be possibly achieved through the A-site/B-site cation substitution or deficiency creation in these sites which renders perovskites to have a new formula of $A_aA'_{1-a}B_bB'_{1-b}O_{3-x}$. It has been reported that more than 90% metallic elements in the periodic table can form perovskite crystal structures [16]. Besides, their physicochemical properties can be widely altered, which can further tune their catalytic activities. The great flexibility in both the composition and crystal structures of perovskites [17–19] leads to the tunable electronic structure of perovskite oxides, which makes them possess diverse physical and chemical properties and thus ideal candidates as electrocatalysts for OER and ORR in alkaline media [14].

Till now, several categories of reviews regarding perovskite oxides as electrocatalysts have been published. These reviews either focuses only on OER [20] or ORR [21,22] of perovskites or one specific topic, such as perovskites/carbon as oxygen electrocatalysts [23,24], while other reviews highlight nanostructure engineering of perovskites for catalyzing reactions in metal–air batteries, water splitting and solid oxide fuel cells [14]. Besides, some reviews have provided a comprehensive overview of various materials, including metal oxides, carbon-based materials and hybrid materials as bifunctional electrocatalyst for metal–air batteries [25] while other reviews have covered the preparation and characterization of perovskite oxides as catalysts for the electrochemical conversion of oxygen (ORR/OER) and heterogeneous reactions, e.g. CO/CH_4 oxidation, methanol/NO/N_2O conversion as well as volatile organic compounds (VOC) combustion and organic dyes removal in aqueous solution [26,27]. It was also highlighted that the extreme flexibilities of perovskites in terms of their structures and compositions, perovskites and their derivatives lead to diverse applications in electrocatalysis, photocatalysis and photovoltaics [28].

Among these previous reviews, there are only a very limited review papers regarding perovskites as bifunctional electrocatalysts for both OER and ORR [1,29]. However, they either did not cover the possible strategies to improve the catalytic activities of these materials or have covered various materials including carbon-based materials, transition metal hydroxide and sulfide, metal-N, etc., as electrocatalyst for OER/ORR in their paper [29].

In this mini-review, the recent progress of perovskites oxides as electrocatalysts for both OER and ORR is summarized, which includes the proposed possible mechanism behind the reactions, the synthetic approaches to prepare perovskite oxides as well as different strategies to improve the electrocatalytic activities. Especially, polymer-assisted approach, an environmentally friendly route, to synthesize perovskites which was not covered in any previously reported reviews, has been covered in this paper. Based on these discussions, the current challenges that researchers are facing in perovskites synthesis will be brought up. The potential research directions in the future and recommendations regarding the perovskite synthesis are proposed. This summary not only offers researchers guidance to synthesize perovskite oxides as needed, but also provide researchers more insights into how to obtain new perovskite-based catalysts with improved bifunctional electrocatalytic properties through rational compositional design.

2. Perovskite oxides as electrocatalysts

The two reactions that the bifunctional catalysts perovskite oxides will stimulate are oxygen evolution/reduction reactions, which are also the respective reaction involved in the charge/discharge process in metal–air batteries [25,30]. Perovskites play important roles as bifunctional catalysts for these two reactions, which are of great importance toward the practical applications of various energy conversion/storage devices, such as fuel cell [1,4,12] and metal–air batteries [25,31]. Thus, researchers have been studying the possible mechanisms of the perovskites electrocatalytic process for a long period. Generally, ORR process involves the oxygen diffusion, the adsorption of oxygen on the catalyst surface followed by the electron transfer process from the anode to the oxygen molecules, leading to the formation of hydroxide ions, which leave the surface of the catalysts to the alkaline electrolyte [25]. Besides, the reaction paths in OER is also very complicated due to multi-step electron-transfer processes involved [32]. In the following section, we will describe the possible mechanisms behind these two reactions, which might help readers to understand the electrocatalytic process of perovskite oxides in both OER/ORR more specifically and thus assist them in rationally designing various perovskites as bifunctional electrocatalysts in OER/ORR. Besides, the parameters/indicators that are used to evaluate the electrocatalytic performance of perovskites, such as the activity and the bifunctionality will also be discussed.

2.1. Mechanisms for ORR and OER

2.1.1. Oxygen reduction reaction

Oxygen reduction reaction in alkaline electrolyte consists of a series of electrochemical reactions, which involves several steps of electron-transfer processes. As has been reported [1,17], in general, the ORR process of perovskites might be divided into two different paths: four-electron pathway or two-electron pathway. The reaction can be described as

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

in a four-electron pathway, while in the two-electron pathway, O_2 can be reduced to peroxide (HO_2^-) ions based on the following reaction:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (2)$$

which is followed by reaction:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (3)$$

or disproportionation:

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

In general, the four-electron transfer process in ORR is favorable since it is more energy efficient.

The ORR mechanisms may vary depending on the composition, crystal structure and electronic structure of the catalysts used [33]. For perovskite oxides, metal cations on the surface can form M-OH complex through coordination with the oxygen in H_2O while H_2O will be reduced to OH^- simultaneously (Eq. (5)). The M-OH can further combine with the surface absorbed O_2 (Eqs. (6) and (7)). As shown in Fig. 2a, the proposed ORR reaction pathway on perovskites is composed of four steps: surface hydroxide displacement, peroxide formation, oxide formation and hydroxide generation [21]. The specific reactions involved in this mechanism are listed below:

$$M^{m+}\text{-}O^{2-} + H_2O + e^- \rightarrow M^{(m-1)+}\text{-}OH^- + OH^- \quad (5)$$

$$O_2 + e^- \rightarrow O_2{}^-{}_{(ads)}. \quad (6)$$

$$M^{(m-1)+}\text{-}OH^- + O_2{}^-{}_{(ads)} \rightarrow M^{m+}\text{-}O\text{-}O^{2-} + OH^- \quad (7)$$

$$M^{m+}\text{-}O\text{-}O^{2-} + H_2O + e^- \rightarrow M^{(m-1)+}\text{-}O\text{-}OH^- + OH^- \quad (8)$$

$$M^{(m-1)+}\text{-}O\text{-}OH^- + e^- \rightarrow M^{m+}\text{-}O^{2-} + OH^- \quad (9)$$

As mentioned above, in addition to the experimental parameters, the ORR mechanisms can also be different due to different chemical composition, crystal structure and the tunable electronic structure of perovskites [25,33–35]. Therefore, the electrocatalytic performance tunablity of perovskites can be achieved through tuning their electronic structures, which can be realized via the optimization of their compositions with A-site doping/deficiency [6,35,36] or B-site doping [4] since the crystal structure of perovskites can also vary with compositions based on the Goldschmidt tolerance factor [37]. This part will be discussed in detail in the following session.

2.1.2. Oxygen evolution reaction

Oxygen evolution reaction is also a complicated process with several steps and the reaction pathways can vary depending on different catalysts utilized as well. While for perovskite oxides, a general OER mechanism in alkaline solution has been proposed [20,25] and the specific reactions [38] involved (Fig. 2b) are listed as follows:

$$M^{m+}\text{-}O^{2-} + OH^- \rightarrow M^{(m-1)+}\text{-}O\text{-}OH^- + e^-$$

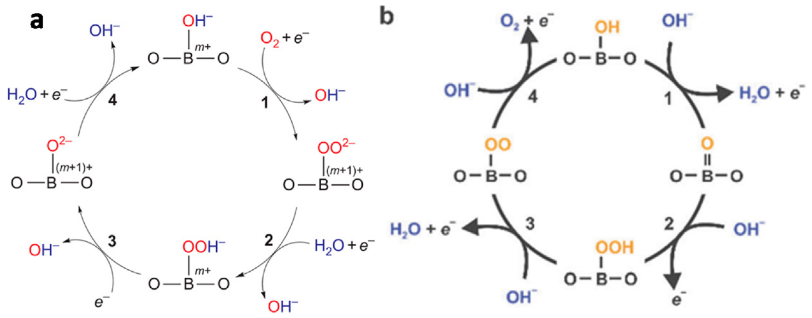

Fig. 2. (a) Proposed ORR mechanism on perovskite oxide catalysts. The ORR process via four steps: 1, surface hydroxide displacement; 2, surface peroxide formation; 3, surface oxide formation; 4, surface hydroxide regeneration. Reprinted with permission from Ref. [21]. Copyright 2015 American Chemical Society. (b) Four-step reaction mechanism proposed by Goodenough et al. for the OER on perovskite surfaces. Reprinted with permission from Ref. [38]. Copyright 1990 American Chemical Society.

$$M^{(m-1)+}\text{-O-OH}^- + OH^- \rightarrow M^{m+}\text{-O-O}^{2-} + H_2O + e^-$$

$$2M^{m+}\text{-O-O}^{2-} \rightarrow 2M^{m+}\text{-O}^{2-} + O_2$$

It is indicated that in the OER process, the bonding strength of M-OH plays an important role in determining the reaction kinetics and even the overall electrocatalytic efficiency [39]. In addition, some researchers have reported that the OER activity of perovskites is related to the number of electrons in the e_g-orbital based on the crystal field theory (CFT) and$e_g = 1$ can be regarded as an indicator of the good OER activities for perovskites [33]. Thus, in order to design a OER catalyst with good electrocatalytic activity, the e_g-electron had better be close to 1 and the bond strength between metal ions and O atoms should be stronger while not too strong according to the Sabatier principle [40].

However, it is still difficult to confirm whether only one single mechanism/pathway can dominate the entire reaction for both OER and ORR. Thus, future research is still impending to be conducted to obtain more insights into the reaction mechanisms of ORR/OER.

2.2. Evaluation of bifunctional electrocatalysts

Before the evaluation of the electrocatalysts, the measured potentials should be corrected due to the existence of Ohmic resistance, mainly referred to the uncompensated resistance of ionic conduction in the electrolyte originated from the large distance between the working electrode and the counter electrode. The real potential of the working electrode can be obtained through the equation: $E_{true} = E_{measured} - iR$, where i is the measured current density and R is the ohmic resistance of the electrolyte solution [4].

Several parameters/indicators, including onset potential, overpotential, Tafel plot, stability and bifunctionality, etc., have been utilized by researchers to evaluate the catalytic performance of the electrocatalyst. The first commonly used notion for electrocatalyst is the onset potential. The definition of onset potential can be very confusing and arbitrary. There are a few ways to define the onset potential. Usually onset potential is defined as the potential at which the reduction/evolution reaction is about to start, when the current starts deviation from the baseline of the linear sweep voltammetry (LSV) [41]. Another more common way to define the onset potential is to get the intersection point of the tangents between the baseline and the rising current in the LSV [42], as shown in Fig. 3. No matter which definition we use to compare the electrocatalytic performance of the catalysts, we have to use the same definition for all samples under study.

Overpotential is another important parameter that is generally used to examine the electrocatalyst performance. Ideally, the applied potential to drive a reaction should be equal to the reaction potential at equilibrium. However, due to the existence of intrinsic kinetic barriers or solution/contact resistances, the potential applied in reality is usually higher than that at equilibrium. Therefore, there is difference between potential at the equilibrium for a specific reaction (the thermodynamic potential) and the real applied potential of the catalyst for the reaction at specific current under certain conditions, which is defined as the overpotential (usually denoted as η) [20]. The definition of overpotential can be interpreted by the equation $\eta = E - E_{equ}$. Usually, the overpotential for OER is reported based on the current density reaching 10 mA cm^{-2} (the current density expected for a solar water-splitting device with an efficiency of 12.3%) [20] since different overpotential can be obtained based on different current density. A lower overpotential indicates the good electrocatalytic activity of a catalyst.

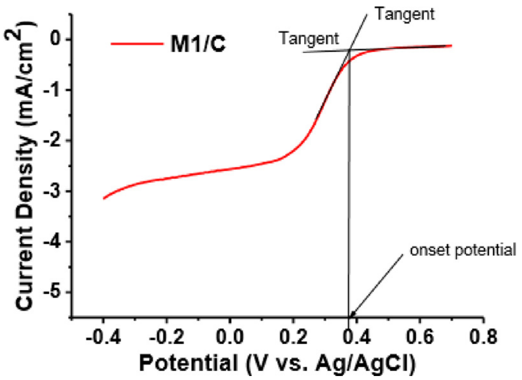

Fig. 3. The determination of the onset potential from the intersection of the tangents between the baseline and the signal current, as shown in the ORR curve of monomer 5,10,15, 20-tetrakis(4′-propynylphenyl) porphyrin Co(II) mixed with carbon black (M1/C) in O_2 saturated 0.1 mol L^{-1} KOH solution at a scan rate of 100 mV s^{-1} with rotation speed of 1600 rpm.

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In order to determine the electrocatalytic activity of the perovskite oxides, the obtained currents are usually normalized to the area of the geometric electrode to get the steady-state current density. Besides, the current for ORR/OER could also be normalized by the catalysts loading or the electrocatalytic surface area to get the mass activity or specific activity. Furthermore, the dependence of current density on the overpotentials can be depicted using Tafel plot, in which the overpotential (η) is logarithmically related to the current density (j). The linear part of the Tafel plot at low currents can be expressed by the equation $\eta = a + b\log(j)$, where a and b are constants. Two parameters, Tafel slop (b) and exchange current density (j_0), can be derived from the Tafel equation. Tafel slope is associated with the electrocatalytic kinetics of the reaction and a smaller Tafel slope indicates faster reaction rate since the current

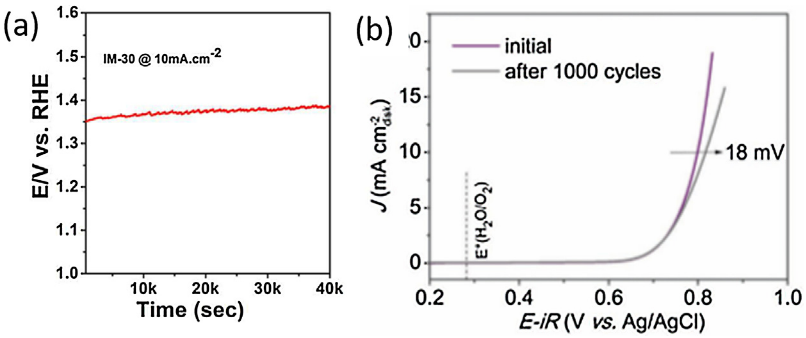

Fig. 4. Two different methods to examine the stability of the electrocatalysts: (a) *I*–*t* curve test of IM-30 (MoO_3–30 mol.% IrO_2 composite) at current density $j = 10\,mA\,cm^{-2}$. (b) LSV curves for the OER at a scan rate of $5\,mV\,s^{-1}$ on the RDE (1600 rpm) for the $SrCoO_{3-\delta}$ before and after accelerated durability test (continuous potential cycling between 0.2 and 1 V vs. Ag/AgCl ($3.5\,mol\,L^{-1}$ KCl) at a scan rate of $100\,mV\,s^{-1}$ of 1000 cycles in O_2-saturated $0.1\,mol\,L^{-1}$ KOH solution.

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density increases faster with a smaller overpotential change based on the Tafel equation. Besides, when $\eta = 0$, the current density obtained is called exchange current density (j_0), which can represent the intrinsic catalytic activity of the material under equilibrium conditions. For a good bifunctional catalyst for both ORR/OER, a small Tafel slope and high exchange current density are desired.

Stability is another indicator that is widely used to examine the practical application of the catalysts. In general, two methods have been employed to investigate the stability of an electrocatalyst. One method is through the measurement of the current variation with time (the *I*–*t* curve) [43], as shown in Fig. 4a. Usually the current density is set to be larger than $10\,mA\,cm^{-2}$ for OER while the reaction time is extended to a long period of time (even up to a few hundred hours). Besides, the cycling experiment by performing cyclic voltammetry (CV) or linear sweep voltammetry (LSV) could also be conducted to elucidate the stability of the catalysts by comparing the potential changes to achieve a specific current density for OER/ORR [4,6,44], as demonstrated in Fig. 4b. The number of cycles should be at least 1000 times or above in order to testify the stability of a material as the electrocatalyst.

A good bifunctional electrocatalyst for both OER/ORR should be simultaneously active for both reactions at the same electrolyte with low-lost and high stability. In order to evaluate the bifunctional electrocatalytic performance of the catalysts, the potential difference (ΔE) between the potential to achieve a current density of $10\,mA\,cm^{-2}$ for OER and the potential to obtain a current density of -1 (or -3) $mA\,cm^{-2}$ for ORR [4,6] is usually used as the indicator. In fact, ΔE is also the sum of the overpotentials for OER and ORR [45]. In general, smaller potential difference (ΔE) indicates smaller total overpotential for the two reactions, which further shows that less extra energy is needed to initiate the reactions and thus better bifunctional catalytic activity of the electrocatalysts.

3. Synthesis of perovskites

Several approaches have been developed to synthesize perovskite oxides, including the conventional solid-state method [46–48], combustion synthesis [49,50], co-precipitation [51], hydrothermal/solvothermal methods [12,17], sol–gel [52] and polymer-assisted approach [53,54]. Among these methods, the solid-sate reaction, combustion and co-precipitation method require high reaction temperature as well as other harsh reaction conditions such as high pressure and special apparatus. Besides, the materials synthesized usually have comparatively large particle size (can be up to micron-size) and low surface area, which is not favorable to improve their electrocatalytic activities. While the hydrothermal/solvothermal method can be used to prepare perovskites with various unique morphologies, their productivity is relatively low due to the limitation of the reactor (autoclave) size. Therefore, sol–gel and polymer-assisted method has been employed in order to obtain perovskites with large-scale production. While sol–gel process consists of more than one step, which first transforms the sol into gel with subsequent calcination process, polymer-assisted method only involves the heat treatment of the metal-polymer complex solution to get the desired product, which is also applicable for large-scale production. Therefore, in our lab, we have applied this method to prepare perovskite oxides.

In addition, some other kinds of methods also have been developed to synthesize perovskites. For instance, mechanical alloying has been employed to synthesize $La_{0.6}Ca_{0.4}CoIr_{0.25}O_{3.5-\delta}$ perovskites as bifunctional electrocatalyst [55]. This process was conducted with a high-energy ball mill in air. Moreover, citric acid-assisted Pechini method was also used to prepare $LaCo_{1-x}Ni_xO_3$ and $LaCo_{1-x}Fe_xO_3$ perovskites [56], which requires the freeze-dyer to dry the metal precursors. In addition, electro-spinning with subsequent calcination method was also applied to synthesize $LaNi_{0.85}Mg_{0.15}O_3$ perovskite nanofibers [57] as efficient bifunctional catalysts toward OER and ORR for zinc-air batteries. All those methods involve complex process as well as special equipment, which will increase the difficulty of material synthesis and the price of the products [4]. Therefore, proper approach needs to be selected based on specific applications of perovskites. The common approaches that researchers are currently used to synthesize perovskites, which are summarized in Table 1, will be discussed in detail in the following sessions.

3.1. Conventional solid-state method

Perovskites can be regarded as a compound consisting of two metal oxides. Therefore, traditionally, perovskites can be synthesized using the solid-state method, in which two metal oxides are mixed and integrated through calcination at high temperature. For example, perovskite $LaCo_{1-x}Ni_xO_3$ [46] has been synthesized using the conventional solid-state reaction by mixing stoichiometric amounts of La_2O_3, Co_2O_3 and NiO with subsequent heat treatment in air at 900 °C and further at 1200 °C for certain time. Although this method is environmentally friendly and does not release any toxic gases during synthesis. However, this method not only requires harsh reaction conditions (very high temperature), also the obtained perovskite particle size is comparatively quite large with low surface area, which might lead to poor electrocatalytic performance. Besides, impurities might exist in the products due to the incomplete mixing of the metal oxide reactants, which might influence the catalytic performance of perovskites. Therefore, most of perovskites synthesized using conventional solid-state approaches are generally used for electronic structure,

Table 1

Summary of ORR and OER activities of the reported bifunctional oxygen electrocatalysts synthesized using different methods listed in this paper. All the electrochemical measurements were carried out in 0.1 M KOH solution, except those from the combustion method, which were measured in 1 M KOH solution.

Catalysts	Methods	E_{onset} ORR (V)	E_{onset} OER (V)	Tafel slope OER	Tafel slope ORR	Ref.
$LaNi_{0.85}Mg_{0.15}O_3$	Electro-spinning	–	0.82 V vs. RHE	95 mV dec^{-1}	105 mV dec^{-1}	[57]
$Ba_{0.9}Co_{0.5}Fe_{0.4}Nb_{0.1}O_{3-\delta}$	Solid-state	−0.2 V vs. Ag/AgCl	0.59 V vs. Ag/AgCl	–	–	[58]
$LaMnO_3$	Combustion	–	–	86 mV dec^{-1}	217 mV dec^{-1}	[59]
$LaNiO_3$	Combustion	–	–	58 mV dec^{-1}	192 mV dec^{-1}	[59]
$La_{0.8}Sr_{0.2}MnO_3$	Co-precipitation	−0.2 V vs. Ag/AgCl	0.60 V vs. Ag/AgCl	–	–	[17]
$La_{0.9}Sr_{0.1}CoO_3$	Hydrothermal	0.806 V vs. RHE	1.612 V vs. RHE	–	–	[12]
$LaCo_{0.8}Mn_{0.2}O_3$	Hydrothermal	−0.21 V vs. Ag/AgCl	0.64 V vs. Ag/AgCl	–	–	[60]
$BaMnO_3$	Hydrothermal	−0.19 V vs. Ag/AgCl	0.60 V vs. Ag/AgCl	–	–	[61]
$BaTiO_{3-x}$	Sol–gel	0.88 V vs. RHE	1.3 V vs. RHE	–	–	[11]
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$	Sol–gel	−0.18 V vs. Ag/AgCl	0.50 V vs. Ag/AgCl	–	–	[62]
$LaMnO_3$	Sol–gel	0.78 V vs. RHE		154 mV dec^{-1}	110.2 mV dec^{-1}	[57]
$(La_{0.8}Sr_{0.2})_{0.95}Mn_{0.95}Ir_{0.05}O_3$	Polymer-assisted	−0.05 V vs. Ag/AgCl	0.48 V vs. Ag/AgCl	–	–	[36]
$LaCo_{0.5}Ni_{0.5}O_3$	Polymer-assisted	–	–	73.9 mV dec^{-1}	112 mV dec^{-1}	[4]
$(La_{0.8}Sr_{0.2})_{0.9}Mn_{0.9}Co_{0.1}O_3$	Polymer-assisted	−0.09 V vs. Ag/AgCl	0.67 V vs. Ag/AgCl	–	–	[6]

electrical transport property or magnetism studies in the early period of perovskites research [46,56].

3.2. Combustion synthesis

In order to explore the application of perovskites as electrocatalysts, perovskite oxides with small particle size and large surface area are desirable in order to expose more active sites to the reactants. Thus, more synthetic approaches need to be developed. To achieve this goal, great efforts have been made to search for alternative methods to prepare perovskites. For instance, redox reactions between a fuel and oxidant can be utilized in combustion method to prepare perovskites [63]. The metal oxides in conventional solid-state method have been replaced by the soluble metal salts, which are used as metal precursors and citric acid is usually applied as the complexing agent. The resultant solution will be under calcination at a high temperature for certain time to obtain perovskites. Compared with the conventional solid-state method, the combustion synthesis can take place at a relatively lower temperature. Several perovskite oxides, including $Sr_{0.85}Ce_{0.15}FeO_{3-x}$, $La_{0.6}Sr_{0.4}Co_{0.95}Fe_{0.05}O_{3-x}$ and $LaMO_3$ (M = Mn, Ni, etc.) [59] have been synthesized using the combustion method [64], in which metal nitrates with stoichiometric ratio were dissolved in deionized water, with citric acid as the complexing agent. Then the pH was adjusted to be 11 and the resultant solution was heated to 1000 °C, which was maintained at this temperature for 5 h. Besides, the particle size can be adjusted by changing the pH value and the citric acid/metal precursor ratio. Therefore, it is much more possible to obtain perovskites with smaller particles and higher surface area using combustion method in comparison with the conventional solid-state approach. However, this method still requires special reaction conditions, such as high reaction temperature or the utilization of combustion reactor, which needs extra energy/finance input, and thus increase the fabrication cost of catalysts.

3.3. Co-precipitation

Co-precipitation is also an effective approach that researchers usually use to synthesize perovskite oxide materials. In this method, metal precursors are first dissolved in deionized water and mixed homogenously to form an aqueous solution. Then the solutions react with an organic base to from precipitates with subsequent filtration and dying process. The dried precipitates are further under heat treatment to go through the crystallization process to form crystallized material. Co-precipitation method with urea as the precipitator has been applied to synthesize urchin-like $La_{0.8}Sr_{0.2}MnO_3$ perovskite oxide [17]. The unique morphology of $La_{0.8}Sr_{0.2}MnO_3$ renders it to exhibit a comparatively high surface area of 48 m^2 g^{-1}, which further showed an encouraging electrocatalytic performance toward both ORR and OER to make $La_{0.8}Sr_{0.2}MnO_3$ a good candidate as bifunctional electrocatalyst for these reactions. Even if co-precipitation method is an easy way to prepare perovskites, however, it is difficult to get materials with pure phase due to the different hydrolysis rate of multi-metal ions [65], which thus shows low mass activities [66,67].

3.4. Hydrothermal/solvothermal method

Hydrothermal/solvothermal method refers to the synthesis of materials through chemical reactions in solution (aqueous or organic) above the ambient temperature and pressure under a sealed environment [68]. The concept of ‘hydrothermal’ was originated from earth science in 19th century [69]. In the lab scale hydrothermal reaction, the crystal growth can be achieved in a steel pressure reactor autoclave. Compared with the previously discussed methods, hydrothermal synthesis shows several advantages. First, the reaction takes place at relatively mild conditions (temperature usually below 300 °C) and the procedure involves one-step reaction, which is environmentally friendly. Furthermore, this method allows for the precise control over the size, shape and crystallinity of metal oxide nanoparticles through changing the experimental parameters, such as the reaction temperature/time, solvents, surfactants or metal precursors. Thus, this method has been widely used for synthesis of materials with various unique morphologies [70], which might exhibit high surface area, beneficial to the electrocatalytic activities of electrochemical reactions.

Therefore, researchers use hydrothermal/solvothermal method with certain additives, such as surfactants to controllably synthesize perovskite oxides with different morphologies. For instance, $La_{0.9}Sr_{0.1}CoO_3$ perovskites with yolk-shell structures [12] have been synthesized using one-pot hydrothermal method. The specific surface area of the material is higher than the regular $La_{0.9}Sr_{0.1}CoO_3$ particles, which leads to better catalytic activities toward ORR and OER as well as good durability. However, the autoclaves are relatively expensive compared with the commonly used apparatus in lab, such as beakers or crucibles. Thus, researchers are still searching for new methods to synthesize perovskite oxides.

3.5. Sol–gel method

To reduce the reaction temperature for material synthesis, researchers have adopted another approach, sol–gel technique, which is a colloidal chemistry technology. Sol–gel technique has become well known since the late 1800s [71,72]. Sol–gel process involves transforming a liquid (sol) to gel with subsequent post-treatment to obtain the solid material. The main attraction of sol–gel method is that the materials with high purity and uniform nanostructures can be achieved. Therefore, sol–gel method has been widely applied in various fields, including the catalysts preparation, especially perovskite oxides [73,74]. Normally citric acid and ethylenediaminetetraacetic acid (EDTA) are used as the complexing agents and metal alkoxides are precursors, which combine together to form the metal-oxo or metal-hydroxo precursors in solution. After removing the liquid from the gel through drying to get the precipitates, thermal treatment in air will be conducted subsequently to form perovskites oxides. Oxygen-deficient $BaTiO_{3-x}$ perovskites with hexagonal phase have been prepared using sol–gel method [11] with a following thermal treatment at 1300 °C in vacuum. The electrochemical measurements of this material indicated that the oxygen-deficient hexagonal $BaTiO_{3-x}$ showed excellent OER/ORR electrocatalytic activities [11], in which the OER activity is even better than the state-of-the-art IrO_2 catalyst. The improved activities may be attributed to the oxygen vacancies in perovskites, which can facilitate the charge transfer during the reaction.

3.6. Polymer-assisted approach

In addition to the above methods that researchers usually use, in our group, a facile polymer-assisted approach, an aqueous solution route, also has been developed to synthesize perovskite oxides. This method was first introduced to prepare metal oxide films in 2004 [53,75,76], which was further extended to other films, including metal nitrides [77,78], metal carbides [79], etc. In our group, we have further applied this technique to metal oxide nanoparticles, including perovskites in view of the advantages of this method. This method employs the advantages of metal ions coordinated with polymers, usually ethylenediaminetetraacetic acid (EDTA) and polyethyleneimine (PEI) as the complexing agents, to form metal-polymer precursors [54]. Since PEI and EDTA can almost combine with any metal ions, resulting in formation of metal precursors, which are soluble in water. Thus, this method can be used to nearly any metal oxides synthesis. Besides, this method is environmentally friendly since no toxic or corrosive chemical are involved in the preparation process. Finally, this method is applicable for large scale synthesis. All these properties render this method to be suitable for metal oxides preparation. Furthermore, it has been reported that there is a thin layer of carbon coating remaining on the surface of the perovskites due to the incomplete decomposition of polymer when the metal-polymer precursor solution is heated at relative lower temperature [36,80,81]. The existence of the carbon layer leads to good conductivity of the samples, resulting in good electron transfer rate. Therefore, extra conductive carbon does not need to be added into the materials to avoid more complicated procedure, which is also another advantage of the polymer-assisted approach in synthesizing perovskites as electrocatalysts. For example, Yan et al. have synthesized $(La_{0.8}Sr_{0.2})_{1-x}Mn_{1-x}Ir_xO_3$ ($x=0$ and 0.05) perovskites nanoparticles [36] as bifunctional oxygen electrocatalysts (Fig. 5) with a comparatively high surface area of $26\,m^2\,g^{-1}$. This material exhibited high ORR and OER catalytic performance, which are comparable or even better than the reported perovskites and other state-of-the-art catalysts. Besides, this method also has been applied to prepare $LaCo_{1-x}Ni_xO_3$ network structures [4], which showed enhanced electrocatalytic activities compared with the pure $LaCoO_3$.

4. Strategies to improve electrocatalytic performance

Perovskite oxides have showed promising intrinsic activities for ORR/OER. However, the perovskites prepared using the conventional methods still exhibit small active surface area and thus less active sites to contact with the reactants, resulting in poor electrocatalytic performance, which further impedes their practical application. Therefore, in order to further promote the electrocatalytic activities of the perovskites, several strategies have been proposed and investigated by researchers recently, which includes oxygen vacancy creation, introduction of extra active sites as well as incorporation with conductive agents (carbon) or co-catalysts (metal oxides) and morphology or size tuning.

4.1. A-site/B-site cation tuning

It has been reported that A or B site cation partial substitution with other cations is an effective way to enhance the OER/ORR performance of perovskites since the electrocatalytic activities of perovskites can change remarkably with different A/B cations due to the variation of the structures and the electronic conductivities [82]. The A or B site cation substitution renders perovskites to possess a new chemical formula of $A_{1-x}A'_xB_{1-y}B'_yO_{3-\delta}$ with different crystal structures, which aims at increasing/creation oxygen vacancy sites or maintaining/increasing the redox couples.

A-site cations do not function as the active sites in the metal oxides but still play an important role in tailoring the valence state of metal ions in B-site and thus tuning the bond strength of B-O bond for ORR and OER while B-site cations determine the catalytic behavior of perovskites [1]. In perovskites, B-sites serve as the active sites, thus have influence on their electrocatalytic activities. Substitution of B-site cation in perovskites with other metal ions can not only introduce extra active sites, but also change the valence state of B-site cation, favoring the formation of B-OH and the electrical conductivities and oxygen mobility increase [83]. Besides, B-site substitution also can cause synergistic effects among the mixed metal cations, leading to favorable electronic structure of the B-site element [63,84]. For instance, Mg-doped perovskites $LaNi_{1-x}Mg_xO_3$ ($x=0$, 0.08 and 0.15) have been synthesized using sol–gel method (Fig. 6) with citric acid as the complexing agent [30]. The performance improvement for both ORR and OER can be attributed to the increased Ni^{3+}/Ni^{2+} ratio, leading to different B–O covalent bond strength as well as the decreased Ni/La ratio on the catalyst surface due to elimination of the inactive NiO material on the catalyst surface, resulting in more accessible active sites to reactants. Furthermore, in our group, polymer-assisted approach has been employed to synthesize $LaCoO_3$-based perovskites with B-site Ni-doping [4]. The electrocatalytic reactions showed that both the ORR and OER performance can be enhanced, resulting in the improved bifunctionality of the perovskites. The enhanced electrolytic activities may be attributed to the synergistic effect between the two metal ions in the B-sites as well as the increased Co^{3+}/Co^{2+} ratio, resulting in higher Co–O bond strength with the enhanced oxygen adsorption on the catalytic surface.

The catalytic performance of perovskites can be improved through selective removal of A-site cations from the ABO_3 framework under acid treatment due to the longer length of the A–O bonds compared to the B–O bonds [72–75]. The enhanced catalytic activity may be due to the termination with B-site elements in ABO_3, which are the active sites for perovskites. This strategy was first introduced to perovskites as catalyst for CO oxidation [85], NO_x storage and reduction [86] and later extended as electrocatalysts for OER/ORR. For instance, $IrO_x/SrIrO_x$ material has been obtained during the electrochemical testing of $SrIrO_x$ thin films in acidic solution due to the Sr leaching from $SrIrO_x$, resulting in improved OER activity, which is superior to that of both IrO_x and RuO_x [87]. Besides, the ORR performance of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ has been enhanced via the nitric acid (HNO_3) treatment [88], which could be attributed to the selective removal of La and Sr cations as well as the increased surface area due to the creation of mesoporous

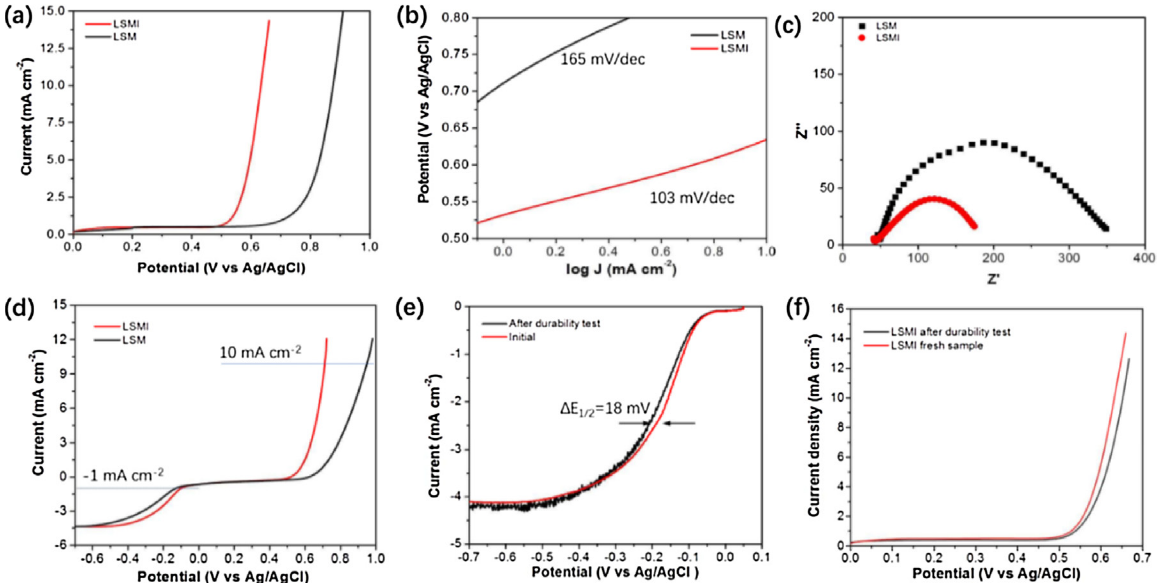

Fig. 5. (a) OER linear sweep voltammetry (LSVs), (b) Tafel plots, (c) the electrochemical impedance spectra, (d) OER and ORR polarization curves for $La_{0.8}Sr_{0.2}MnO_3$ (LSM) and $(La_{0.8}Sr_{0.2})_{0.95}Mn_{0.95}Ir_{0.05}O_3$ (LSMI) as bifunctional electrocatalysts in 0.1 mol L^{-1} KOH with a scan rate of 5 mV s^{-1}; (e) ORR and (f) OER performances for initial and after durability test for $(La_{0.8}Sr_{0.2})_{0.95}Mn_{0.95}Ir_{0.05}O_3$ (LSMI).

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structure in $MnO_x/La0._8Sr_{0.2}MnO_{3-\delta}$, high Mn^{4+}/Mn^{3+} ratio and high oxidative oxygen species concentration.

4.2. Oxygen vacancy creation

Besides A/B site cation tuning, several other methods to create or increase the oxygen vacancies in perovskites, including quenching approach [89], post-annealing [90] and thermal reduction [91] also have been proposed and explored. Through altering the oxygen vacancies and the related crystal structure as well as the surface properties, the electrocatalyst activities can be adjusted. A simple quenching method has been applied to $LaNiO_{3-\delta}$ catalysts from 400, 600, 800 °C to room temperature, the crystal structure of $LaNiO_{3-\delta}$ can be tuned from rhombohedral to cubic (Fig. 7), which caused the ORR/OER activities to increase dramatically due to the difference in Ni–O bond strength [89]. Post-annealing process is another approach that can lead to difference in oxygen vacancies and the oxidation states of transition metals. For example, the annealing temperature influence on the ORR/OER performance of $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ has been investigated, when the annealing temperature is below 300 °C, ORR/OER activities can be enhanced due to the increased OH groups on the surface [90]. Furthermore, other researchers also proposed the thermal reduction method to create nonstoichiometric $CaMnO_{3-\delta}$ [91] and studied the relationship between the oxygen vacancy content and the electrocatalytic activities of the perovskite. The results indicated that $CaMnO_{3-\delta}$ with oxygen vacancy exhibited higher electrocatalytic activity than the stoichiometric $CaMnO_3$ owing to the boosted electronic conductivity of perovskite and the oxygen vacancies inside it.

4.3. Carbon-perovskite composites

Even though pure perovskites have showed good ORR/OER performance, their poor intrinsic electrical conductivity [1,92] still limits their electrocatalytic activities. Thus, surface coating/intermixing of the perovskites with electrically conductive layer, such as carbon-based materials, is an efficient way to increase their conductivity, which has been proved to be able to further improve the electrocatalytic activity and stability.

Even with low oxygen evolution reaction catalytic activity, carbon black, carbon nanotubes and nitrogen-doped carbon materials [93] are widely known to possess high conductivity with low-cost and high oxygen reduction activity, which can be easily implemented and thus used as an additive to the perovskite inks to improve the conductivity of the formed catalyst. The enhanced OER/ORR activity and the metal–air battery performance might be due to the improved conductivity of the catalyst resulted from the strong chemical and electrical coupling [23] between the metal oxides and carbon-based material. For example, carbon layer with a thickness of around 10 nm has been successfully coated on the surface of $BaMnO_3$ perovskite nanorods [61] to investigate their electrocatalytic properties for both ORR/OER (Fig. 8). The results indicated that the carbon-coated materials showed enhanced OER/ORR performance and dramatically improved activity compared with the bare perovskites due to the increased conductivity. Besides, intertwined core-corona structured catalyst, in which $LaNiO_3$ nanoparticles are encapsulated by nitrogen-doped carbon nanotubes [18] also have been produced to serve as bifunctional electrocatalysts for metal–air batteries. The new composite material showed improved catalytic activities as well as enhanced electrochemical stability toward ORR/OER, which is even superior to the state-of-the-art commercial Pt/C and Ir/C catalysts. The boosted electrochemical performance might be attributed to the synergistic effect among the unique structure of the carbon-perovskite composite, which can not only improve the charge transport due to the increased conductivity, but also facilitate the reactants diffusion through the pores. The practical application of this catalyst also has been tested in a zinc-air battery under ambient condition, which delivered better charge/discharge performance and cyclability compared with Pt/C and Ir/C, further suggesting the fast charge transfer and reactant diffusion during the oxygen related reactions.

4.4. Incorporation with other co-catalysts

Recently, the researchers have developed a new approach to improve the electrocatalytic performance of perovskites through integration of other metal oxides. The interfaces between the

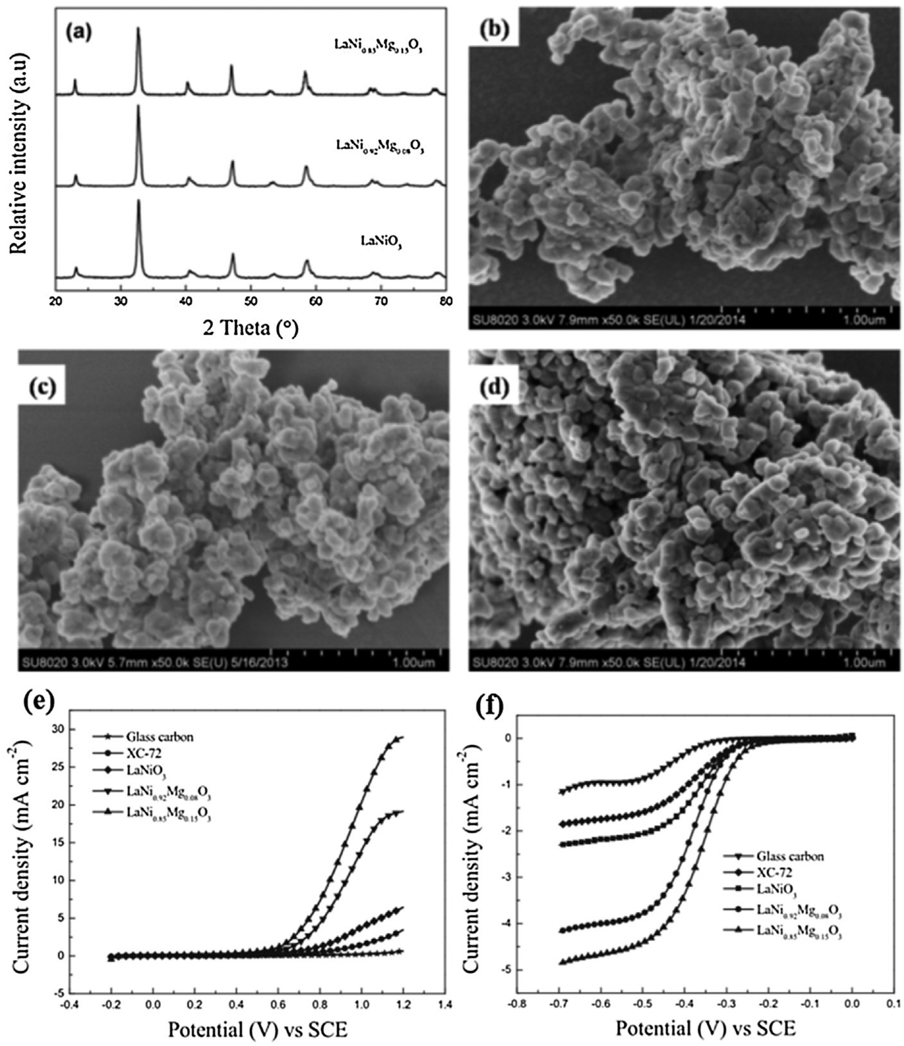

Fig. 6. (a) XRD patterns of $LaNi_{1-x}Mg_xO_3$ ($x = 0$, 0.08, 0.15) perovskite oxides. SEM images of (b) $LaNiO_3$, (c) $LaNi_{0.92}Mg_{0.08}O_3$, (d) $LaNi_{0.85}Mg_{0.15}O_3$; (e) OER and (f) ORR polarization curves of glass carbon electrode, Vulcan XC-72 carbon black, $LaNiO_3$, $LaNi_{0.92}Mg_{0.08}O_3$, $LaNi_{0.85}Mg_{0.15}O_3$ in O_2 saturated 0.1 mol L^{-1} KOH with a sweep rate of 10 mV s^{-1} at 1600 rpm.

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two compounds can expose more active sites to reactants, which can strengthen the charge transfer and reactant diffusion during the catalytic process. In addition, the synergistic effect among perovskites and other metal oxides also can promote the electrocatalytic activities.

For instance, in order to reduce the contents of the expensive noble metal catalysts, noble metal oxides can be doped or assisted with other metal oxides with low price to form the mixed metal oxides, which is viable approach that researchers recently use. IrO_2/MoO_3 hybrid material, in which IrO_2 nanoparticles are adhered on the surface of MoO_3 large particles [43], has been synthesized using hydrothermal method. Their electrocatalytic activity toward OER has been investigated, suggesting that the IrO_2/MoO_3 hybrid (Fig. 9) exhibit better activity compared to the pure IrO_2 and MoO_3 catalysts. This enhanced electrochemical catalytic performance might be due to the synergistic effect between the two metal oxides in the interface caused by the formation of noble metal rich regions on the surface of non-noble metal oxides, which facilitates the electron transport in the channels and improves the conductivity of the material. Even if the content of noble metal oxides is reduced, the cost of the catalyst is still high comparatively. Thus, researchers start using non-noble metal oxides as the co-catalysts. Atomic layer deposition (ALD) has been employed to deposit iron oxide layer with a thickness of 6 nm on the surface of $LaNiO_3$ perovskites (Fig. 10) to be bifunctional catalysts for lithium oxygen batteries [94]. First, $LaNiO_3$ was prepared using a microwave-assisted combustion method with EDTA-citrate as chelators. Then Fe_2O_3 was coated on the surface of $LaNiO_3$ using ALD. Fe_2O_3 was selected due to its earth-abundant properties with low-price. The hybrid of $Fe_2O_3/LaNiO_3$ delivered higher electrocatalytic activities toward ORR/OER compared with the pure $LaNiO_3$ due to the synergistic effect between the two metal oxides owning to the unique structure. Furthermore, the hybrid material showed high battery capacity (10,419 mAh g^{-1} at a current density of 100 mA g^{-1}) and comparable cycling stability (90 cycles without fading), and thus superior lithium-air battery performance, which indicates that the unique structure of the hybrid material favors more active sites exposure to the reactant and the reactant transport inside the structure, leading to higher charge/discharge efficiency and thus the superior lithium-oxygen battery performance.

4.5. Particle size/morphology engineering

It is widely known that smaller particle size with higher surface area might lead to better electrocatalytic performance for both OER and ORR. Thus, researchers also started to synthesize perovskites

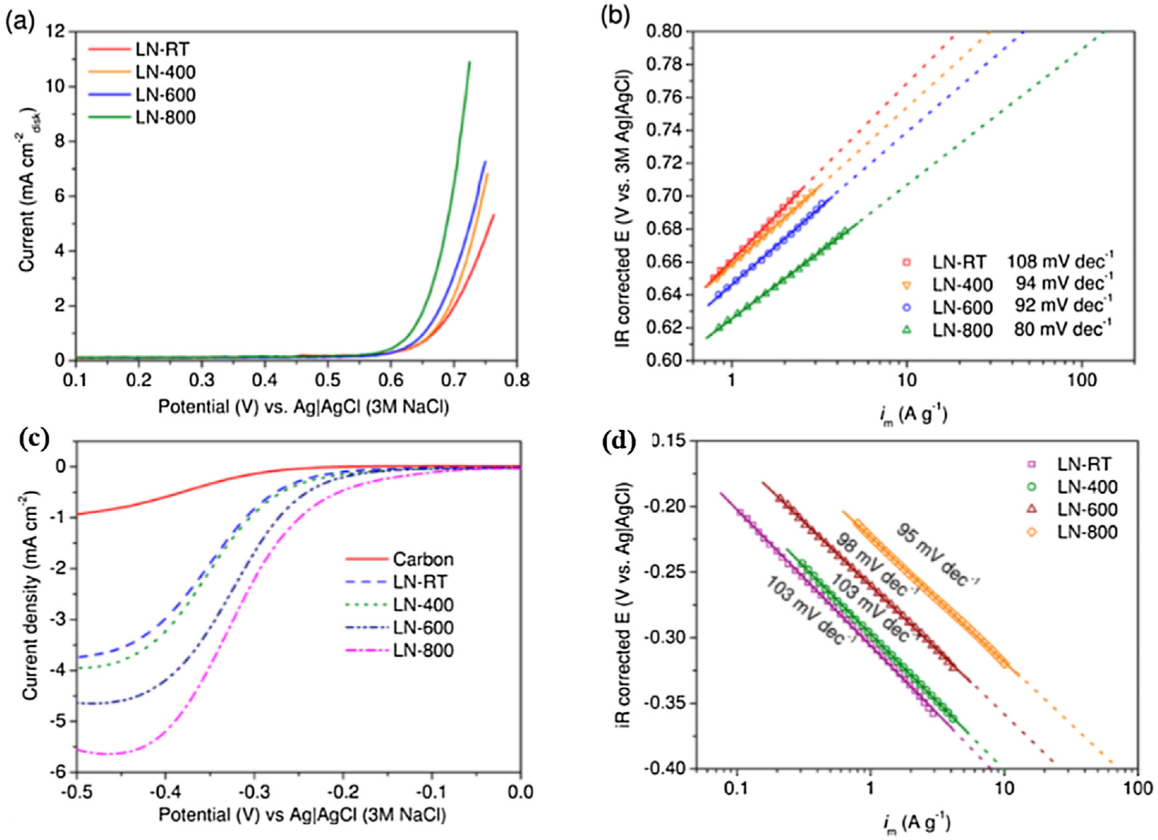

Fig. 7. (a) OER and (c) ORR current densities of glassy carbon (GC)-supported thin film LaNiO$_{3-\delta}$-RT (room temperature), LaNiO$_{3-\delta}$-400, LaNiO$_{3-\delta}$-600, and LaNiO$_{3-\delta}$-800 electrocatalysts at 1600 rpm in O$_2$-saturated 0.1 M KOH at 5 mV s^{-1} (400, 600, 800 °C refer to the synthetic reaction temperature for LaNiO$_{3-\delta}$); (b) OER and (d) ORR mass activities for thin film LaNiO$_{3-\delta}$-RT, LaNiO$_{3-\delta}$-400, LaNiO$_{3-\delta}$-600, and LaNiO$_{3-\delta}$-800 electrocatalysts. Background ORR activity of thin-film Nafion-bonded carbon thin-film electrode is shown for reference (red line). The current i_m value is based on/divided by the total mass of catalysts (LaNiO$_{3-\delta}$ and carbon). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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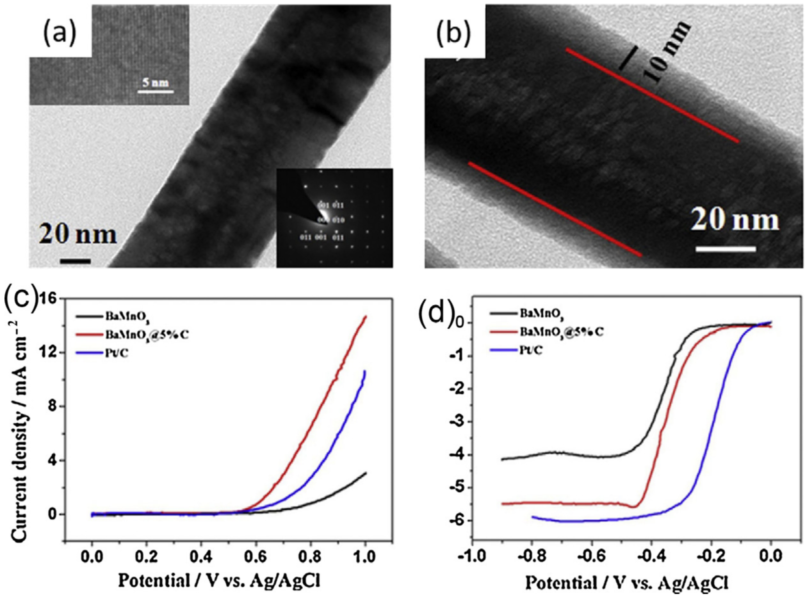

Fig. 8. TEM images of the (a) BaMnO$_3$ and (b) BaMnO$_3$@5% C nanorods; (c) OER and (d) ORR comparison of the BaMnO$_3$ and BaMnO$_3$@5% C nanorods with commercial Pt/C catalyst.

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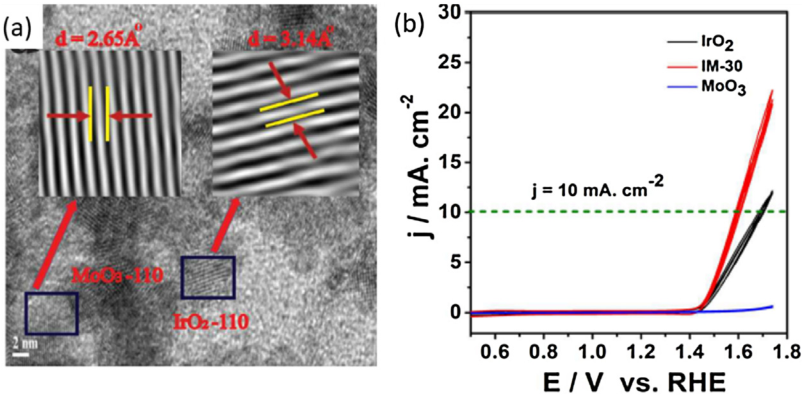

Fig. 9. TEM images of IM-30 (MoO_3–30 mol.% IrO_2). The *d*-spacing of (110) phases of IrO_2 and MoO_3 in IM-30 composite has been indicated. (b) Polarization curves with iR correction for OER activity of three as-prepared composites in 0.1 M NaOH solution with catalyst loading of 0.2 mg cm^{-2}. Horizontal green dash line represents the value of current density j = 10 mA cm^{-2}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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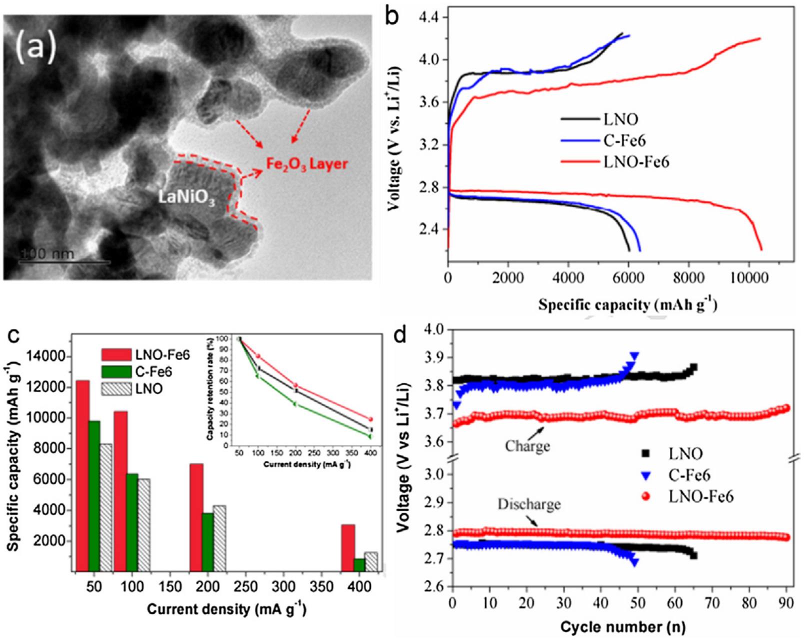

Fig. 10. (a) TEM images of atomic layer deposition (ALD)-Fe_2O_3/$LaNiO_3$ catalyst, (b) fully discharge and charge profiles of Li-O_2 batteries with three kinds of electrodes at 100 mA g^{-1}, (c) discharge capacities of $LaNiO_3$ (LNO), 6 nm thick ALD-Fe_2O_3 coated conductive carbon (C-Fe6) and 6 nm thick Fe_2O_3/$LaNiO_3$ (LNO-Fe6) electrodes at current densities of 50 mA g^{-1}, 100 mA g^{-1}, 200 mA g^{-1}, and 400 mA g^{-1}, and (d) terminal discharge/charge voltages of three electrodes versus cycle number at a current density of 100 mA g^{-1}.

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with various morphologies, especially exhibiting porous structures to improve their electrocatalytic activities and thus the cycle stability performance of metal–oxygen batteries and the efficiency of fuel cells. The porous structure with high surface area can not only provide more active sites, which can contact with the reactants easily for ORR/OER, but also facilitate the electron transport and thus the reaction rate, resulting in superior OER/ORR performance. Liu et al. [95] have synthesized hierarchical mesoporous/microporous $La_{0.5}Sr_{0.5}CoO_{3-x}$ nanotubes using electrospinning method with subsequent calcination process. Excellent ORR/OER activity with a low overvoltage (1.14 V) has been achieved. Besides, the corresponding Li–O_2 batteries also delivered a high specific capacity of 5799 mAh g^{-1} and good rate capability as well as a good cycling life. Besides, urchin-like $La_{0.8}Sr_{0.2}MnO_3$ perovskite oxides [17] also have been prepared through a co-precipitation method (Fig. 11). This material exhibited a high surface area of 48 m^2 g^{-1} and their performance as bifunctional catalyst for both ORR and OER has been investigated, which show better electrocatalytic performance than regular $La_{0.8}Sr_{0.2}MnO_3$ due to the large surface area of the urchin-like $La_{0.8}Sr_{0.2}MnO_3$.

5. Theoretical calculation

In the pursuance of efficient bi-functional oxygen electrocatalysts based on perovskite oxide materials, fundamental theoretical calculations always have an important role to play for the rational design and analysis of electrocatalyst performance for the OER/ORR reactions. In order to understand the ORR/OER reaction mechanism, fundamental theoretical calculations based on first-principles density functional theory (DFT) has become a “standard tool” to analyze the elementary reaction step. In general, electronic structures of the perovskites are critical to the bi-functional reactions. In the

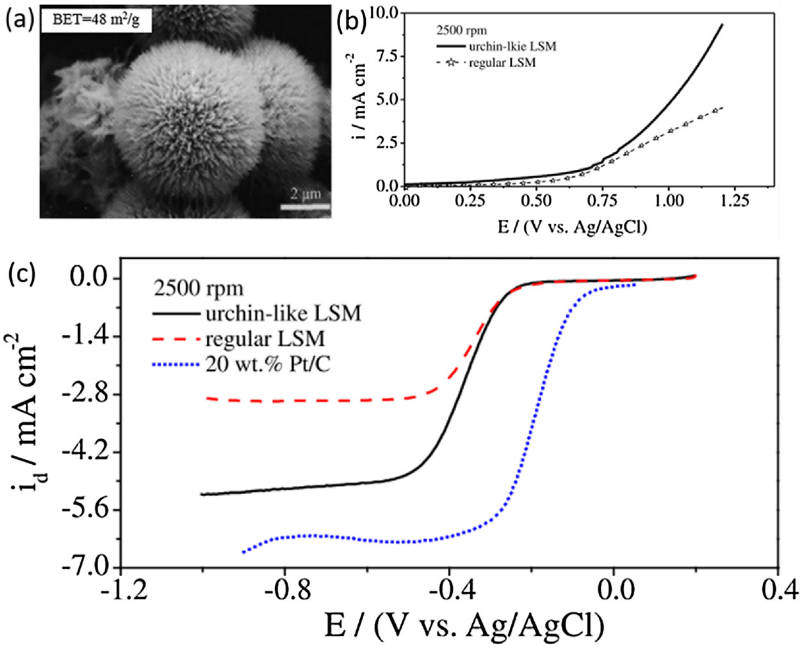

Fig. 11. (a) SEM image of urchin-like $La_{0.8}Sr_{0.2}MnO_3$ (LSM) powders calcined in air at 500 °C for 4 h, (b) the OER catalytic activities comparison for the urchin-like LSM and regular LSM in N_2 saturated 0.1 mol L^{-1} KOH solution at 2500 rpm, and (c) ORR comparison of the urchin-like LSM, regular LSM and Pt/C electrocatalysts in O_2 saturated 0.1 mol L^{-1} KOH at 2500 rpm.

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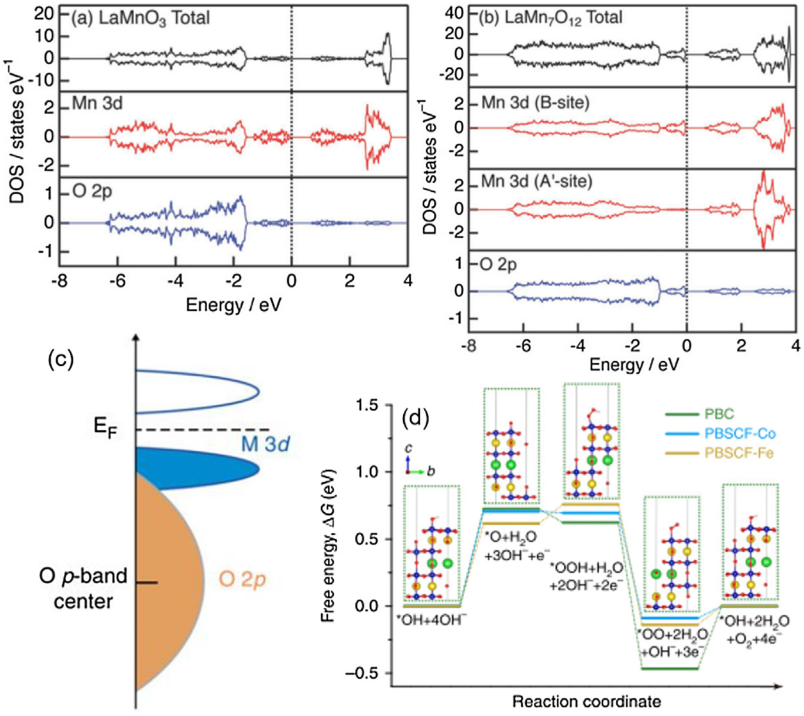

Fig. 12. Total and partial density of states of (a) $LaMnO_3$ and (b) $LaMn_7O_{12}$ obtained from DFT calculations. Reprinted with permission from Ref. [98], Copyright 2016 John Wiley; (c) schematic representation of the O p-band for transition metal oxides. Reprinted with permission from Ref. [100], Copyright 2013 Nature; (d) the computed Gibbs free energy changes for the whole system for the OER at $\eta = 0$ V/298.15 K on a $PrBaCo_2O_{5+\delta}$ (PBC)/$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$ (PBSCF) surface; the B-site in PBC (Co) and PBSCF (Co/Fe) is treated as the catalytically active centers, all adsorbates are bonded to these redox centers; insets are atomic structures of PBC slabs with adsorbates. In all schematics, each deep blue ball is Co or Fe, fluorescent yellow ball is Pr, green ball is Ba or Sr, red ball is O and light pink ball is H. Reprinted with permission from Ref. [101], Copyright 2017 Nature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

perovskite structure, the addition of large cations brings an extra variable as compared to the single metal oxide materials to help optimize the antibonding (e_g) electrons, which is responsible for the electrocatalytic activity [96,97]. Although the general chemical formula of perovskites might look like ABO_3, it can be as close to $AA'BB'O_{(3+\delta)}$, where A′ and B′ are dopant metals and δ represents the oxygen defects. Through the comparison of the electronic structure analysis of various perovskite structures, which can be obtained from DFT calculation, we can determine whether the changing electronic structures can directly influence both the OER/ORR activity and surface stability. For example, the anti-bonding (e_g) electrons can be tuned by adding oxygen (+δ), which can decrease the number of anti-bonding (e_g) electrons, whereas, creating oxygen vacancy ($-\delta$) can lead to increase in the number of anti-bonding (e_g) electrons. On the other hand, creating A-site vacancy ($-\delta$) should increase the oxidation state of cation at the B-site, thereby decreasing the number of anti-bonding (e_g) electrons. Adding A-site cations (+δ) should decrease the oxidation state of cation at the B site, hence increase the anti-bonding (e_g) electrons count. However, adding extra A-site cations is very limited due to the available space in the structure. In contrast, B-site defect can be created with a relative ease. This B-site defect can also influence the anti-bonding (e_g) electrons count. Besides, the other electronic structure information such as the total and partial density of states, obtained from DFT calculations, can be used to get the valence band maximum (VBM) and the conduction band minimum (CBM) and thereby the bandgap (as shown in Fig. 12a and b) of each compound with electrical conductivity property [98], which may have some influence on catalyst turnover rate [99].

As an indicator for the catalyst stability toward OER/ORR, the oxygen 2p band center relative to the Fermi level, can also be evaluated using DFT calculations [100]. It has been proposed that for some Co-based perovskites, the OER catalytic activity increases with the oxygen 2p band center approaching the Fermi level closer while not too close (Fig. 12c) [101]. For some other perovskites, such as Mn-based, oxygen 2p band center is not a good indicator instead the metal–oxygen covalency can be used as an indicator for ORR activity [97,98]. The O p band centers were also found to be related to the rate of oxygen vacancy formation and surface oxygen exchange [102]. Furthermore, the free energy of each elementary reaction step of OER/ORR reactions can also be estimated from DFT calculations through thermodynamic and electric-potential dependent energy corrections with reference to the reversible hydrogen electrode (RHE) [101]. As shown in Fig. 12d, the step 1 from OH^* to O^* and the step 4 from $^*OO$ to $OH^* + O_2$ are uphill, indicating endothermic, which means that an external driving force has to be applied to the drive the reaction. The similar uphill/downhill trend suggests the same mechanism, while different energy profiles indicate the influence of elemental doping (Co, Sr and Fe) on the reaction kinetics. Based on the above discussion, it is clear that DFT can be used to derive various information regarding the electrocatalysis of perovskites, which may provide us guidance into rational design of bifunctional electrocatalysts for OER and ORR.

6. Conclusion and outlook

The recent development of perovskite oxides as bifunctional electrocatalysts for ORR/OER are discussed in this report. The primary goal of this field is to find alternative low-cost non-noble metal based electrocatalysts with high activity and stability to replace the state-of-the-art noble metal/oxides catalysts. Till now many great achievements have been made in looking for new electrocatalysts, which further expedite the practical applications of these catalysts in reality. However, new electrocatalysts with low-cost and better catalytic activities are still in great demand, which brought the perovskite oxides into the center of attention among researchers. Perovskites have been used in many fields due to their tunable properties originated from their flexible crystal structures with the substitution/deficiency of A/B site cations and oxygen non-stoichiometry.

Despite the adjustable properties of perovskites, there are still some challenges that researchers have to face and tackle in order to obtain perovskite oxides with good electrocatalytic performance. First, the conventionally used approaches to prepare perovskites are usually complicated, which either need harsh reaction conditions (e.g. high temperature and high pressure) or extra special equipment such as freeze-dryer or electrospinning. Besides, the particle sizes of the obtained perovskites are usually large with very low surface area which might result in relatively poor electrocatalytic activities. Furthermore, the large-scale synthesis of perovskites is also a great challenge to researchers since most work are still limited to lab scale. Therefore, searching for new facile and environmentally friendly approach to synthesize perovskites is still of great importance in this field. Thus, various approaches to synthesize perovskites have been listed and compared, which can provide researchers more guidance to prepare new perovskite catalysts. In addition to the synthetic routes, finding new techniques to enhance the electrocatalytic activities of perovskites, especially their bifunctionality, is also highly demanded. In this mini-review, different strategies to boost the electrocatalytic performance of perovskites for ORR/OER also have been discussed.

However, there are still more research work to be done regarding both the routes to synthesize perovskites and the strategies to enhance their electrocatalytic activities toward ORR/OER. Therefore, the future research direction in this field would be related to these two aspects as well as the possible mechanisms of ORR/OER in perovskites through DFT calculation, which might provide researchers more insights and guidance into the rational design of perovskites with boosted electrocatalytic activities as demanded. Furthermore, in addition to be good candidates as bifunctional oxygen electrocatalysts, it has been reported that some perovskites, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, also could be used as electrocatalysts for hydrogen evolution reaction (HER) in water-splitting. Therefore, besides the bifunctional activities for OER/ORR, the HER performance of perovskites could also be investigated in the future, which renders them as trifunctional electrocatalysts for OER, ORR and HER, and thus broadens the applications of perovskites as electrocatalysts.

7. Recommendations

As we mentioned above, the traditionally used methods to synthesize perovskite either involves tedious and complicated procedure or needs special equipment, which is very expensive and not applicable for large scale production, even with resulted perovskite oxides with large particle size and thus low electrocatalytic performance. Therefore, in order to obtain perovskites with small particle size, high surface area and better bifunctional electrocatalytic performance for both OER and ORR, suitable synthetic methods should be properly selected or developed, which is a big challenge that researchers face at present. We have listed several synthetic methods that are generally used by researchers now. In fact, researchers can choose the methods to synthesize perovskites based on the strategies they want to apply to enhance the catalytic activities of perovskites. For example, when perovskites with different morphologies are the target materials, hydrothermal/solvothermal methods can be used since this method allows for the precise control over the size, shape and crystallinity of metal oxide nanoparticles through changing the experimental parameters, including the metal precursors, surfactants, solvents and reaction temperature/time. However, due to the limitation of the reactor size, this method can not be used for large scale production while our ultimate goal of developing electrocatalysts is to apply them in real applications. Thus, looking for methods that can be utilized to obtain perovskites with large scale production is really critical. In our group, we have developed the polymer-assisted approach, which was originally used to prepare high-quality metal oxide films and later extended to metal oxide nanoparticle synthesis, including perovskites. This method takes advantages of the coordination of metal ions with polymers, usually ethylenediaminetetraacetic acid (EDTA) and polyethyleneimine (PEI) to form metal-polymer precursors, since these two polymers can almost combine with any metal ions to form metal precursors, which are soluble in water. Therefore, this method can be used to synthesize nearly any metal oxides. In addition, this method is environmentally friendly since no toxic or corrosive chemical are involved in the preparation process, which is especially applicable for large scale synthesis. Furthermore, there is a thin layer of carbon coating remaining on the surface of the perovskites due to the incomplete decomposition of polymers during the heat treatment, which avoids the addition of extra conductive carbon for OER/ORR testing. All these properties render polymer-assisted approach a suitable method to prepare perovskites with applications as bifunctional electrocatalysts for both OER and ORR.

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