In this work, the A-site cation deficient perovskites (La_{0.8}Sr_{0.2})_{1-x}MnO_3 (x=0, 0.02, 0.05) (LSM) and Fe doped perovskite (La_{0.8}Sr_{0.2})_{0.95}Mn_{0.5}Fe_{0.5}O_3 (LSMF) are prepared by sol-gel process assisted with chelating effect of citric acid. The structure, morphology and valence state of the prepared samples were characterized. Their catalytic activities toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) were investigated by rotating-disk electrode (RDE). As expected, appropriate introduction of A-site deficiency can enhance both ORR and OER activities. Among the A-site cation deficient perovskites studied, (La_{0.8}Sr_{0.2})_{0.95}MnO_3 exhibited the highest ORR and OER activities and, hence, the best bifunctionality. After doping with Fe in the B-site, the (La_{0.8}Sr_{0.2})_{0.95}Mn_{0.5}Fe_{0.5}O_3 perovskite exhibits even better electrochemical catalytic activity which is due to the increase of the concentration of oxygen vacancy as compared with (La_{0.8}Sr_{0.2})_{0.95}MnO_3. Furthermore, (La_{0.8}Sr_{0.2})_{0.95}Mn_{0.5}Fe_{0.5}O_3 showed superior durability than commercial 20wt% Pt/C catalyst. This work indicates that introduce of A-site deficiency and B-site Fe doping in perovskite oxides is an effective strategy to enhance ORR and OER activity for the applications in metal-air batteries.

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La_{0.8}Sr_{0.2}MnO_3 based perovskite with A-site deficiencies as high performance bifunctional electrocatalyst for oxygen reduction and evolution reaction in alkaline

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Abstract

In this work, the A-site cation deficient perovskites (La_{0.8}Sr_{0.2})_{1-x}MnO_3 (x=0, 0.02, 0.05) (LSM) and Fe doped perovskite (La_{0.8}Sr_{0.2})_{0.95}Mn_{0.5}Fe_{0.5}O_3 (LSMF) are prepared by sol-gel process assisted with chelating effect of citric acid. The structure, morphology and valence state of the prepared samples were characterized. Their catalytic activities toward oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) were investigated by rotating-disk electrode (RDE). As expected, appropriate introduction of A-site deficiency can enhance both ORR and OER activities. Among the A-site cation deficient perovskites studied, (La_{0.8}Sr_{0.2})_{0.95}MnO_3 exhibited the highest ORR and OER activities and, hence, the best bifunctionality. After doping with Fe in the B-site, the (La_{0.8}Sr_{0.2})_{0.95}Mn_{0.5}Fe_{0.5}O_3 perovskite exhibits even better electrochemical catalytic activity which is due to the increase of the concentration of oxygen vacancy as compared with (La_{0.8}Sr_{0.2})_{0.95}MnO_3. Furthermore, (La_{0.8}Sr_{0.2})_{0.95}Mn_{0.5}Fe_{0.5}O_3 showed superior durability than commercial 20wt% Pt/C catalyst. This work indicates that introduce of A-site deficiency and B-site Fe doping in perovskite oxides is an effective strategy to enhance ORR and OER activity for the applications in metal-air batteries.

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1. Introduction

With the growing demand for secure, clean, and renewable energy, technologies of renewable energy storage have attracted tremendous attentions. Among them, the rechargeable Zinc-air battery has been considered as one of the most promising technologies due to its low cost, high energy conversion efficiency, environmental benignity, and safe operation [1, 2]. However, the intrinsically sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics of electrodes and catalysts has become one of the technical that hinders the commercialization of the rechargeable Zinc–air batteries [3, 4]. Until now, Pt and IrO2 have been regarded as the benchmark catalysts toward ORR and OER, respectively. However, the high cost, unsatisfactory durability, and uni-functionality severely limit their practical applications [5, 6]. Therefore, current research on ORR and OER catalysts in alkaline electrolyte is mainly focused on enhancing the catalytic activities, decreasing the amounts of precious metals, and developing low-cost catalyst materials.

Over the past decades, many types of precious metal-free catalysts for example transition metal oxides in form of perovskites, spinels, and their dopant have been reported [7,8]. Among the various bifunctional electrocatalysts, ABO3-type perovskite oxides with a general formula of ABO3 (A=alkaline-earth or rare-earth metals and B=transition metals) have been applied as cathode electrocatalyst owing to their high catalytic activity for ORR/OER and excellent stability in alkaline solution. Among perovskite oxides, LaMnO3 has been proposed as one of the best ORR catalysts to substitute the noble metal. The factors determined the ORR and OER catalytic activity of the LaMnO3-based perovskites include the intrinsic activity, electronic conductivity, oxygen absorption behavior, conducting additive species, and element vacancy, and most of these factors were investigated in detail [9]. Creating the A-site deficiency in perovskite is an effective approach to induce oxygen vacancy and modify the electronic structure, resulting in the improved electrochemical catalytic properties [10, 11]. For example, it was reported that the La0.95FeO3-d perovskite with A-site cation deficiencies showed high ORR and OER activity due to the creation of surface oxygen vacancies and a small amount of Fe4+ species [12]. The creation of oxygen vacancy is always accompanied by the change of the valence state and electronic structure of transition metal. The A-site deficiencies in the perovskite materials can manipulate the B-site element valence, expose more active sites for ORR, decrease the oxygen migration energy and increase the surface oxygen vacancies [13, 14]. In addition to creating A-deficiency, doping (e.g. cobalt, nickel, and iron) to the B-site of LaMnO3 is also considered as a convincing strategy to easily modify the electronic structure and then subsequently enhance the electrochemical properties [15].

In this report, the A-site deficient perovskite oxides (La0.8Sr0.2)1−xMnO3 (x = 0, 0.02, 0.05) and B-site Fe doped perovskite oxide (La0.8Sr0.2)0.99Mn0.5Fe0.05O3 are prepared by facile sol–gel method. Among them, the (La0.8Sr0.2)0.95Mn0.5Fe0.5O3 perovskite exhibits the best electrochemical catalytic activity in the alkaline electrolyte due to the creating A-deficiency and the B-site Fe doping which is predicted to achieve higher oxygen vacancy concentration and boost both ORR and OER.

2. Experimental

2.1. Material preparation and characterization

The perovskite oxide powders were prepared by a sol–gel method. Appropriate amounts of lanthanum nitrate, strontium nitrate, manganese acetate, iron nitrate were dissolved into deionized water. Then citric acid and glycine were added to the mixed solution at a citric acid: glycine: metal ions mole ratio of 2:1:1. Then, the solution was kept in a water bath at 80°C under continuous stirring to get a gel. Subsequently, heated the gel in an oven at 250°C and calcined at 700°C for 4 h to get the powder. In this paper, the samples of (La0.8Sr0.2)1−xMnO3 (x = 0, 0.02, 0.05) and (La0.8Sr0.2)0.95Mn0.5Fe0.5O3 were abbreviated as LSM1, LSM2, LSM3 and LSMF respectively.

The sample crystallinities and phases were analyzed by X-ray diffraction (XRD) (PANalytical X’Pert3 diffractometer) in the range of 2 theta from 20°C to 80°C. The morphology and structure were observed by scanning electron microscopy (SEM) (EVO-MA10 ZEISS) and Transmission electron microscope (TEM) analysis (FEI Tecnai G2 F30). The surface chemical composition of each sample was analyzed by a X-ray photoelectron spectroscopy (XPS) system (PHI-5000 Versaprobe) with Mg Kα radiation (hv =1253.6 eV).
2.2. Electrochemical Measurements

The ORR and OER activities of perovskite oxides were examined using rotating disk electrode (RDE) technique (Pine Instruments, Inc.). The RDE system was consisted of a platinum foil (2 cm²), a saturated Ag/AgCl electrode, and a glassy carbon substrate (0.196 cm²) as counter, reference, and working electrodes respectively. An aqueous solution of KOH with molar concentration of 0.1 M was used as the electrolyte. Oxides (5 mg) and Vulcan-XC72 carbon (5 mg) were dispersed in 0.9 mL isopropanol solvent mixed with 0.1mL of Nafion (5 wt %, DuPont) solution to prepare a homogeneous ink. After stirring for 3 h, 18μL catalysts ink was coated onto the polished glass carbon substrate and the catalyst loading amount was approximately 458mgcm⁻². In addition, commercial Pt/C (20 wt%, Aladdin Corp.) was used as the reference catalyst with loading amount of 229 mg cm⁻². Before RDE experiments, pure oxygen gas (99.9%) was purged for 30 min to make the electrolyte saturated with oxygen. Polarization curves for the ORR and OER (at a rotation speed of 1600 rpm) were tested in the electrolyte using a CHI electrochemical workstation at scan rate of 10mv/s. Electrochemical impedance measurements were performed in the frequency range from 0.1 Hz to 100 kHz with voltage bias of 5 mV amplitude. The stability of the as prepared catalysts for OER and ORR were executed at 1600 rpm at fixed potentials of -0.4 V (vs. Ag/AgCl) and 0.7 V (vs. Ag/AgCl) for ORR and OER, respectively. All electrochemical experiments were performed in normal atmospheric conditions and room temperature (25°C).

3. Results and discussion

The phase and crystal structure of (LaₐSrₐ)₁₋ₓMnO₃ (x = 0, 0.02, 0.05) and (LaₐSrₐ)₀.₉₅Mn₀.₅Fe₀.₅O₃ perovskites calcined at 700°C were analyzed by XRD as shown in Figure 1a. All samples can become single phase and the main peaks can be well indexed to cubic structure, indicating that neither A-site deficiency nor B-site doping has any influence on the crystalline structure of perovskites. The diffraction profiles of LSM3 and LSMF are analyzed by the Rietveld refinement method as shown in Figure 1b and 1c. Both LSM3 and LSMF powder exhibit a well-formed cubic symmetrical perovskite structure (Pm-3m) with lattice parameters of a=b=c=0.388nm and a=b=c=0.389nm respectively. The slightly expanded lattice parameters are consistent with the negative shift of XRD peaks. The slightly expanded lattice may indicate higher oxygen vacancy in LSMF compared with LSM3, which is the key factor that enhance the ORR and OER activity, as to be discussed below.

SEM and TEM were used to observe the morphology and microstructure of the prepared LSMF sample (Figure 2a and 2b). From the figures we can see that the sample contains irregular and aggregated particles with the average particle size of tens of nanometers. Figure 2c shows high-resolution TEM image of LSMF sample with well-defined lattice fringes. The sample exhibits an interplanar distance of 0.38 nm which is related to (110) lattice plane (Figure 2d and 2e). The result is in conformity with the data above from refined XRD patterns (d110 = 0.389nm).
It is well known that the ORR and OER activity of perovskite oxides is strongly dependent on the valence state of oxygen species on the surface of the catalysts [1, 2]. Therefore, X-ray photoelectron spectroscopy (XPS) was performed and the representative O1s spectrums of LSM3 and LSMF are displayed in Figure 3. The XPS peaks at the binding energies of about 529.2 eV and 530.7 eV are corresponding to the lattice oxygen and the surface absorbed oxygen respectively. The peak at 532.2 eV only in LSM3 can be attributed to the molecular water or carbonates adsorbed on the surface which is largely depended on the atmospheric conditions rather than the materials properties, so adsorbed water is excluded in the calculation. The relative ratios of the O 1s XPS peak intensities are obtained from the deconvolution of the peaks. The counts of adsorbed oxygen on the surface of LSMF (49%) are more than that of LSM3 (36%), indicating more absorbed hydroxyl on the surface of the LSMF catalyst and a stronger covalence of Mn-O bond of the perovskite oxides. It is reported that the ORR kinetics is mainly effected by the rate of O$_2^2/\mathrm{OH}^-$ displacement and OH$^-$ regeneration, as well as the covalent contribution to the Mn-O$_2$ bond of the perovskite oxides [1]. In addition, a high coverage of hydroxyls will accelerate the formation of the OO bond in OOH which also enhanced OER performance. Therefore, LSMF with A-deficiency and Fe-doping has higher concentration of oxygen vacancy may exhibited enhanced electrocatalytic activities.
The ORR activities of the as prepared perovskite samples were evaluated by RDE measurement using a conventional three-electrode system in 0.1 M KOH solution at the rotation speed of 1600 rpm. Figure 4a shows the LSV curves of the perovskite samples. Obviously, the onset potential (the potential at 0.5 mAcm⁻²) of the catalyst slightly increases with the increase of the A-site deficiency. The onset potential of LSM2 with the A-site stoichiometry of 0.98 increases to -0.14 V vs. Ag/AgCl compared with pristine LSM1 (-0.15 V vs. Ag/AgCl) and then it further increases to -0.134 V vs. Ag/AgCl when the A-site stoichiometry is 0.95. To gain more insights into the LSM based catalysts, the Tafel plots calculated by the Tafel equation are shown in Figure 4b. The Tafel slopes for the A-site deficient LSM2 and LSM3 catalysts are smaller than that of the pristine LSM, implying much more rapid ORR rates of the former ones. Clearly, all these data unambiguously suggest that the introduction of A-site deficiency into LSM based catalysts can effectively enhance the ORR activity. In particular, LSM3 exhibited the highest ORR activity among the A-site deficient LSM catalysts. When parts of Mn was substituted by Fe ions for LSM3, the electrocatalytic activity of the perovskite oxide altered and the onset potential shifts more positively to -0.124 V vs. Ag/AgCl. Among the four samples, LSMF showed the highest current density of about 4.5 mA/cm² which is compatible to 20wt% Pt/C (5 mA/cm²). The Tafel slope of the LSMF is -137mV dec⁻¹, which is the lowest among the four samples and close to that of 20wt% Pt/C (132 mV dec⁻¹). The high limiting current density of LSMF indicates that it can better overcome the mass transfer resistance between bulk phase electrolyte and electrode surface.

To evaluate the ORR durability of LSMF and commercial 20wt% Pt/C, chronoamperometric measurements were performed at -0.4 V vs Ag/AgCl at the rotating rate of 1600 rpm for 10000 s. As can be seen in Figure 4c, LSMF shows a slight degradation, and the current retention is as high as 97.1% after 10000s, exhibiting a much better stability than that of commercial 20wt% Pt/C whose retention is 93.5% for 10000s.

OER activities for the as prepared samples were therefore evaluated to explore their application as bifunctional oxygen electrocatalysts. The OER activity was recorded by LSV curves within the OER potential window, as shown in Figure 6a. The onset potential for LSM2 (~0.6V vs Ag/AgCl) and LSM3 (~0.57V vs Ag/AgCl) is much lower and almost 0.1 V negatively shift than that for pristine LSM1 (~0.68 V vs Ag/AgCl), indicating that A-site deficient perovskite with more oxygen vacancy exhibited greater current density under the same potential range and better OER catalytic activity as compared with pristine LSM1. When doped with Fe, onset potential shift more negatively (~0.53 V vs Ag/AgCl), demonstrated higher OER activity than undoped perovskite under the same experimental condition. In addition, the enhanced kinetics of the catalysts toward OER activity was certified by the Tafel plot (Figure 5b) and electrochemical impedance spectroscopy (EIS) analysis (Figure 5c). LSMF has a much smaller Tafel slope, and hence more rapid OER rates and better charge transfer ability among all the catalysts. Electrode polarization resistance, Rₑ indicates charge transfer process. Rₑ for OER measured at 1 V vs Ag/AgCl on LSMF catalysts was ~96Ω, substantially smaller than 289 Ω, 215Ω and 142Ω measured on LSM1, LSM2 and LSM3 respectively. It is worth noting that the order of OER activity for the LSM based catalysts resembles the trend of ORR activity: LSMF>LSM3 >LSM2> LSM1. However, the enhancement effect in OER activity is more pronounced as compared to the ORR activity. Thus, introducing A-site cation deficiency or B-site Fe doping in LSMF perovskite not only improves ORR activity but also enhances OER activity to a great extent.
highest ORR activity among the A-site polarization resistance, $R_P$ indicates charge transfer process. $R_P$ for OER measured at 1 V vs Ag/AgCl on LSMF (Figure 5b) and electrochemical impedance spectroscopy (EIS) analysis (Figure 5c). LSMF has a much smaller

For evaluating the durability, the stability of LSMF and commercial 20 wt% Pt/C was evaluated by the chronoamperometry (CA) measurements at 0.7 V versus Ag/AgCl as shown in Figure 5d. The results clearly indicate that LSMF is a more stable OER catalyst than commercial 20 wt% Pt/C. At the end of a 10000 s continuous test, commercial 20 wt% Pt/C lost as much as 84% of its initial activity, while LSFM shows a much higher stability with an 35% retention. This result further demonstrated the super bifunctionality of introducing A-site cation deficiency and B-site Fe doping in LSMF perovskite.

4. Conclusions

In summary, the A-site cation deficient perovskites ($\text{La}_{0.8}\text{Sr}_{0.2})_{1-x}\text{MnO}_3 (x=0, 0.02, 0.05)$(LSM) and Fe doped perovskite ($\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ (LSMF) are prepared by a simple and cost-effective sol-gel process as highly efficient bifunctional electrocatalysts for ORR and OER in alkaline solutions. Electrochemical investigations reveal that the ORR and OER activity can be tuned by tailoring the A-site cation deficiency in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ perovskite. The enhancement in electrocatalytic activity is especially obvious in the OER process. Among the A-site cation deficient ($\text{La}_{0.8}\text{Sr}_{0.2})_{1-x}\text{MnO}_3$ perovskites studied, the ($\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_3$ showed the highest ORR and OER activity and, hence, the best bifunctional catalyst in alkaline solution. Partial substituted of Mn by Fe in ($\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ can increase the oxygen vacancy which would enhance the electrochemical performance. These results demonstrate that the family of A-site cation deficient and B-site Fe doping in ($\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_3$ perovskite holds promise for applications in metal-air batteries.

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Reference