Sr, Fe Co-doped Perovskite Oxides With High Performance for Oxygen Evolution Reaction

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INTRODUCTION

Oxygen electrocatalyst plays a very important role in oxy-renewable energy technologies (Zhu et al., 2015a), such as rechargeable metal-air batteries, regenerative fuel cells and water splitting. Recently, the development of highly active oxygen evolution reaction (OER) catalysts in alkaline solutions has become a hot topic of electrocatalytic water splitting technology (Gupta et al., 2016; Zhao et al., 2017). However, the OER at the anode of the water electrolyzer is hindered by the kinetics of the complex four-electron oxidation process, which requires a considerable overpotential ($\eta$), leading to a significant decrease in the overall efficiency of water splitting (Jiao et al., 2015). In order to acquire high reaction kinetic and low overpotential in practical applications, noble metal oxides are usually used as catalysts (such as IrO$_2$ and RuO$_2$), but the high cost and scarcity of noble metals restrict their large-scale commercialization.

More recently, non-noble metal perovskite oxide (ABO$_3$) have been extensively investigated as OER catalysts for their electronic adjustability and flexibility in physical and chemical properties (Jin et al., 2011; Grimaud et al., 2013; Hong et al., 2015; Hwang et al., 2017). For instance, Suntivich et al. reported the rational design of a descriptor with a high OER perovskite electrocatalyst, that is the intrinsic activity of ORR (oxygen reduction reaction)/OER (Jin et al., 2011; Suntivich et al., 2011) in alkaline solutions can be enhanced when the high energy anti-bonding orbital $e_g$ of the B-site transition metal in the perovskite oxides is occupied close to unity. This is because the number of the electrons in the $e_g$ orbit of B-site transition metal can greatly influence the bonding of oxygen-containing intermediate, especially for OH$^-$, during OER process, and thus
optimizing the OER performance (Suntivich et al., 2011). Based on this theory, they obtained a highly efficient dual-function perovskite electrocatalyst $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\cdot\text{Fe}_2\text{O}_3 \cdot \delta$. Its performance surpasses that of the most active IrO$_2$ catalyst in alkaline media (Suntivich et al., 2011). After these two pioneering works, many high efficient perovskite catalysts were obtained when the $\varepsilon_f$ filling of the B-site transition metal was adjusted to 1.2, which is served as the optimal value for high performance (Petrie et al., 2016; Zhou et al., 2016; Retuerto et al., 2017; Tong et al., 2017), through the regulating the grain size (Zhou et al., 2016; Retuerto et al., 2017), the lattice mismatch at the interface (Petrie et al., 2016; Tong et al., 2017) and co-doping of cations (Tiwari et al., 1996; Ge et al., 2016; Raabe et al., 2016; Chen et al., 2017). Among these methods, co-doping of cations is the most efficient way for adjusting the $\varepsilon_f$ filling to enhance the electrochemical performance of perovskite. Especially based on the Shao-Horn’s researches, the doping of B-site metal can effectively adjust the $\varepsilon_f$ filling of perovskite oxides. Recently, Zhu et al. (2015b) achieved high OER activity by using Nb partial substitution of the B-site Co ions in SrCo$_{0.5}$Fe$_{2.5}$O$_3$ to adjust the $\varepsilon_f$ filling to $\sim$1.2. However, only B-site metal doping usually deviate from the optimal $\varepsilon_f$ filling (Guo et al., 2015; Tong et al., 2017). The partial substitution of A-site metal ion with a valence state of +2 or +1 is an effective way for amending the deviation (Mefford et al., 2016). Furthermore, the doping of A-site can also enhance the electrical conductivity of the catalyst (Mefford et al., 2016; Yan et al., 2017).

Herein, we designed a series of La$_{1-x}$Sr$_x$Ni$_{1-z}$Fe$_z$O$_3$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 1$; $y = 0.2, 0.4, 0.6$) by co-doping LaNiO$_3$ parent oxide with Fe and Sr to optimize $\varepsilon_f$ filling and enhance conductivity. By tuning the ratio of La/Sr and Ni/Fe, we can maximize the LaNiO$_3$ OER performance. The particle size of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ obtained in this paper is about 25 nm, which is more favorable for the OER reaction in alkaline solution (Zhou et al., 2016; Retuerto et al., 2017). The La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ exhibits an overpotential of 320 mV at 10mA cm$^{-2}$, a tafel slope of 52.77 mV dec$^{-1}$ and a high stability, i.e., the current density of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ decreased only 9.3% after 10 h of continuous polarization, which is comparable with commercial RuO$_2$. These electrochemical results proved that La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ is a promising OER reaction electrocatalyst that can be applied in fuel cell, rechargeable metal-air batteries and so on.

**Experimental Section**

**Material**

All chemicals (analytical reagent grade) used in this work, including La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$·4H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, ethylene glycol (HOCH$_2$CH$_2$OH), KOH, Citric acid (HOC(COOH)(CH$_2$COOH)$_2$, ≥99.5%), and ethanol (CH$_3$CH$_2$OH), were purchased from Sigma-Aldrich and used without further purification. Deionized water was used in all experiments.

**Material Synthesis**

A series of LaNi$_{1-x}$Fe$_x$O$_3$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 1$), La$_{1-y}$Sr$_y$Ni$_{0.5}$Fe$_{0.5}$O$_3$ ($y = 0.2, 0.4, 0.6$), and La$_{1-z}$Sr$_z$NiO$_3$ ($z = 0.2, 0.4, 0.6, 0.8$) perovskite nanoparticles were prepared by sol-gel method and solid-state method reported previously (Yuasa et al., 2012; Xu et al., 2016a). Briefly, La(NO$_3$)$_3$·6H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and Sr(NO$_3$)$_2$·4H$_2$O, were dissolved in deionized water to form a 5 mL solution. Subsequently, the above metal nitrate solution was gradually added to citric acid (HOC(COOH)(CH$_2$COOH)$_2$, ≥99.5%) and ethylene glycol (HOCH$_2$CH$_2$OH, ≥99.8%) under vigorous stirring conditions at room temperature. The mixture was then heated at 80°C with water bath to form a viscous gel, and then it was heated at 200°C in oven until a xerogel formed. The obtained xerogel was sintered in a muffle furnace at 750°C for 10 h to form a perovskite oxide powder with well-crystallized structure. All the powders after heat treatment were finely ground using mortar and pestle prior to further characterization.

**Material Characterization**

All the obtain perovskite oxides were characterized by X-ray diffraction (XRD, Siemens-Bruker D5000) with Cu Kα radiation. Transmission electron microscope (TEM) images, energy dispersive spectrometer, EDS mapping, were carried out on FEI Tecnai G2 F20 transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analyses were performed using a PHI Quantum 2000 scanning ESCA Microprobe spectrometer, and scanning electron microscope (SEM) images were performed by a field emission scanning electron microscope model S-4800. Brunauer-Emmett-Teller (BET) surface area and pore size distribution was measured by N$_2$ adsorption-desorption analysis using Quantachrome Autosorb-IQ.

**Electrode Calibration**

The relation: E (RHE) = E (SCE) + 1.041 V is come from E (RHE) = E (SCE) + 0.0591pH + 0.244 V. Before the electrochemical test, we have calibrated the reference electrode of the saturated calomel electrode.

The calibration of saturated calomel electrode:

- Calibration is performed in a three-electrode system in which a platinum electrode as a counter electrode, and a saturated calomel electrode as a reference electrode. And the calibration is also performed in a H$_2$ saturated 1 M KOH electrolyte.
- Cyclic voltammetry scanning was repeated at a sweep rate of 1 mV s$^{-1}$ until the cycle curves were completely coincident.
- Draw the CV curve of the last lap as shown in Figure S5. When the current value is 0, there are two corresponding potentials. The average value of the two potentials is taken as the thermodynamic potential. Therefore, in a 1 M KOH electrolyte, the calibration formula is E (RHE) = E (SCE) + 1.041 V.

**Electrochemical Measurement**

Electrochemical measurements were performed in a three-electrode electrochemical cell configuration with O$_2$-saturated 1.0 M KOH at pH = 14 controlled by a CHI 750E
RESULTS AND DISCUSSION

As shown in the inset of Figure 1a, the crystal structure of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ has a cubic structure with an average size of 25 nm. The high resolution TEM (HRTEM) image (Figure 1b) of a nanoparticle exhibits lattice fringes with spacings of 0.272 nm and 0.191 nm, corresponding to the (110) and (202) crystal planes of LaNiO$_3$ (PDF#34-1028), respectively, indicating the structure retained after Sr and Fe co-doping. High angle angular dark field (HAADF) image (Figure 1c) and energy dispersive spectrometer (EDS) mapping (Figure S2a) reveals that the La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ nanoparticles are composed of La, Sr, Ni, Fe, and O elements, which are distributed evenly throughout the particle, suggesting that Sr and Fe successfully doping into LaNiO$_3$ crystal structure (Klaus et al., 2015). The X-ray diffraction (XRD) pattern shown in Figure 1d further prove the cubic structure of the La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$. Moreover, a small amount of NiO occurs during the synthesis of perovskite, and the presence of NiO does not affect the catalytic performance (Retuerto et al., 2017). Compared with LaNi$_{1−x}$Fe$_x$O$_3$ and La$_{1−y}$Sr$_y$Ni$_{0.5}$Fe$_{0.5}$O$_3$ (Figures S2b,c), the La$_{1−y}$Sr$_y$NiO$_3$ (Figure S2d) cannot maintain the cubic structure. Thus, we did not discuss the electrochemical performance of La$_{1−y}$Sr$_y$NiO$_3$ in subsequent electrochemical performance tests. The scanning electron microscope (SEM) showed that the morphology of LaNiO$_3$ was unchanged after Fe and Sr co-doping (Figures S3, S4).

The electrochemical performance of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ was studied by a standard three-electrode system calibrated with a reversible hydrogen electrode (RHE) (Figure S5) in an O$_2$-saturated 1 M KOH solution. For comparison, the electrochemical performance of LaNiO$_3$, LaFeO$_3$, LaNi$_{0.5}$Fe$_{0.5}$O$_3$, and commercial RuO$_2$ were also examined. From the linear scanning voltammogram (LSV) profile (Figure 2A, Figure S6), it can be seen that the OER overpotential of LaNi$_{0.5}$Fe$_{0.5}$O$_3$ is 340 and 133 mV lower than the overpotentials of LaNiO$_3$ (473 mV @ 10 mA cm$^{-2}$). The overpotential further decreased to 320 mV for La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$, almost the same to that of commercial RuO$_2$. These results demonstrate the B-site Fe doping is the main reason for the overpotential decrease, and the A-site Sr doping could further optimize the performance. The OER kinetics of the catalyst were also evaluated by the tafel curves. La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$ possesses a small tafel slope (52.77 mV dec$^{-1}$) (Figure 2B), even lower than that of RuO$_2$ (54.25 mV dec$^{-1}$). Then the electrochemical active surface area (ECSA) was measured to provide information on the density of active sites (Chen et al., 2016) (Figures S7, S8). As shown in Figure 2C, the ECSA value of La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$ (12.13 mF/cm$^2$) was smaller than that of RuO$_2$ (17.4 mF/cm$^2$), which represented that the exposed high active sites of La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$ is less than RuO$_2$ in the OER progress. While the specific activity of La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$ was calculated by normalizing the OER current at 1.6 V vs. RHE related to the corresponding ECSA, is much superior than that of LaNi$_{0.5}$Fe$_{0.5}$O$_3$ and RuO$_2$ (Figure 2D and Table S2), indicating the intrinsic catalytic activity of La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$ is higher than RuO$_2$. In addition, La$_{0.4}$Sr$_{0.6}$LaNi$_{0.5}$Fe$_{0.5}$O$_3$ exhibits...
an exceedingly high turnover frequency (TOF), (0.0378 s⁻¹), 2.4 times larger than that of RuO₂ (0.016 s⁻¹) (Gao et al., 2018) (Figure 2D) further proving its excellent intrinsic activity (see detailed calculations in the Supporting Information).

It can be seen from cyclic voltammetry curves (Figure S9) that the peak current density of the oxidation peak [within a certain margin of error, Ni²⁺/Ni³⁺ (1.39–1.45 V vs. RHE)] of La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ is higher than LaNiO₃, LaFeO₃ and LaNi₀.₅Fe₀.₅O₃, indicating that La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ has the highest OER intrinsic catalytic activity (Vij et al., 2017). The ring test results (Figure S10) show that the FE of the OER is determined by the rotating ring disk electrode (RRDE), and the high FE value of perovskite La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ (97.1%) indicates that the observed oxidation current is completely originates from water oxidation rather than other side reactions.

It is well-known that the conductivity of catalyst is another key factor in the improvement of OER performance (Zhang et al., 2018). The carrier concentration (Na) of LaNiO₃, LaNi₀.₅Fe₀.₅O₃, La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃, and LaFeO₃ were estimated from the slope MS plots (Figure 2E, see detailed calculations in the Supporting Information). The calculated results show that the Na of La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ (8.34×10⁹ cm⁻³) (Figure S11) is higher than LaNiO₃ (6.73×10⁹ cm⁻³), LaNi₀.₅Fe₀.₅O₃ (9.35×10⁸ cm⁻³), and LaFeO₃ (1.75×10⁸ cm⁻³), indicating that La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ has the highest electronic conductivity, which was also proved by the EIS test (Figure 2F).

To originate the high OER activity, X-ray photoelectron spectroscopy (XPS) of La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ was performed as shown in Figure S12. For comparison, XPS spectrum of LaNiO₃, LaNi₀.₅Fe₀.₅O₃ and LaFeO₃ were also studied. In order to accurately obtain the valence and content of Ni on the perovskite catalyst surface, we then fitted the La₃d₃/₂ XPS spectrum at high binding energy and subtracted it (La: 3d₃/₂ and Ni: 2p₃/₂ XPS spectra overlap under high binding energy). The peaks at 854 and 856 eV in spectrum of Figure 3A are typical peaks of Ni²⁺ and Ni³⁺ (Yin et al., 2017), respectively. Based on the calculation of XPS peak area intensity (Table S1a), the ratio of Ni³⁺/Ni²⁺ for LaNiO₃ is 4.559. After Fe doping, the ratio dramatically decreased to 2.123. While the ratio returned to 2.891 after Sr and Fe co-doping. Therefore, we can conclude that the ratio change of Ni³⁺/Ni²⁺ is mainly induced by the doping of Fe element, and the reason could be attributed to the existence of both Fe²⁺ and Fe³⁺ in LaNi₀.₅Fe₀.₅O₃, and La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃ (Figure 3B and Table S1b). In addition, the Sr doping could compensate the ratio decrease of Ni³⁺/Ni²⁺ induced by Fe doping. These different ratios of Ni³⁺/Ni²⁺ lead to various average valences of Ni in different samples, i.e., 2.89, 2.65, and 2.77 for LaNiO₃, LaNi₀.₅Fe₀.₅O₃, and La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃, respectively (Zhu et al., 2015b; Ge et al., 2016). It has been proved that the valence state of B-site metal ions on the catalyst surface are conducive to optimize the eᵢ (Seitz et al., 2016; Li et al., 2017; Vij et al., 2017), due to the electron number of M³⁺ (M = Ni, Co) in anti-bonding orbital (eᵢ) is different (for Ni ions, Ni³⁺ (ᵢ) Ni²⁺ (ᵢ) Ni²⁺ (ᵢ) Ni²⁺) (Figure 3D) (Jin et al., 2011; Suntivich et al., 2011; Hwang et al., 2017). Therefore, the eᵢ of Fe filling is 1.1, 1.35, and 1.23 for LaNiO₃, LaNi₀.₅Fe₀.₅O₃, and La₀.₄Sr₀.₆Ni₀.₅Fe₀.₅O₃, respectively, indicating that the eᵢ filling of Ni in LaNiO₃ can be effectively optimized to an ideal value of 1.2 (green dot) by adjusting the ratio of Ni³⁺ and Ni²⁺ through the Sr and Fe co-doping (Figure 3C) (Hong et al., 2015). The M-T (Magnetizations Temperature-dependent) test also shows that La's eᵢ filling is close to 1.25 (Figure S13).
FIGURE 2 | (A) Linear sweeping voltammogram curves of various catalysts (LaNiO$_3$, LaNi$_0.5$Fe$_0.5$O$_3$, La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$, LaFeO$_3$, and commercial RuO$_2$) in 1.0 M KOH at a scan rate of 5 mV s$^{-1}$; Inset compare the OER overpotential for the corresponding catalyst in (A) at $J = 10$ mA cm$^{-2}$; (B) Tafel plots for the corresponding catalysts; (C) Plots of the current density vs. the scan rate to determine the double layer capacitance ($C_{dl}$) of various catalysts; (D) Specific activity of various catalysts (OER current density @ 1.6 V vs. RHE normalized by electrochemical surface area) and TOF calculated at overpotential $\eta = 400$ mV; (E) Mott-Schottky plots for the corresponding various catalysts; (F) Electrochemical impedance spectra of various catalysts recorded at 1.58 V vs. RHE under the influence of an AC voltage of 5 mV.

The optimal $e_g$ filling resulted in a moderate adsorption of OH$^-$ on the B-site metal atoms of the perovskite catalyst to form OH$^*$ (Xu et al., 2016b), which is seen as the rate limiting step for OER of perovskite in alkaline solution, and thus leading to a high OER performance (Jin et al., 2011; Suntivich et al., 2011). As shown in Figure 3D, the exposed Ni sites have the coordination environment NiO$_5$, with the apical (vertical) oxygen removed, which is benefit for the adsorption of OH$^-$ (Zhang et al., 2015; Ge et al., 2016). Compared with other perovskite, the peaks strength of Ni-OH in La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ are moderate, indicating the appropriate OH$^-$ adsorption on the surface of the catalyst (Suntivich et al., 2011; Hwang et al., 2017). Based on the above analysis results, La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ is a promising catalyst for OER in alkaline solution due to its appropriate OH$^-$ adsorption.

In addition to the excellent electrochemical activity, it is also required for catalysts to exhibit high stability in 1 M KOH in various engineering applications (Zhou et al., 2015). In the chronoamperometry test, compared with the LaNi$_{0.5}$Fe$_{0.5}$O$_3$, LaNiO$_3$, and commercial RuO$_2$, the current density of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ decreased only 9.3% after 10 h of continuous polarization (Figure 4A), which is comparable with the electrochemical performance of commercial RuO$_2$. Moreover, the overpotential (@10 mA cm$^{-2}$) increases only 13 mV, demonstrating the high durability of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ (illustration of Figure 4A). Compared with the original La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$, no heterogenic peak in XRD spectrum emerged after 10 h electrochemistry testing, demonstrating the high stability of the structure of the La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ (Figure 4B).

CONCLUSION

In summary, the perovskite oxide La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ with an average size around 25 nm is obtained by a simple co-doping method, which exhibits a high OER performance in an alkaline
solution (Table S3). Electrochemical test results indicate that the OER activity can be enhanced by changing the ratio of Ni$^{3+}$/Ni$^{2+}$ and optimizing its $e_g$ filling, as well as the OH adsorption. Such significant intrinsic OER activity may result from the synergistic effect of the co-doping of Sr and Fe. Furthermore, the chronoamperometry test of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ also demonstrated 9.3% decay for OER within 10 h. We tested the SEM of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ after OER cycles test. Comparing the morphology of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ before the test, it can be seen that the morphology of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ did

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**Figure 3**  
(A) Ni 2p$_{3/2}$, (B) Fe 2p$_{3/2}$, and (E) O 1s spectra of LaNiO$_3$, LaNi$_0.5$Fe$_0.5$O$_3$, La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$, and LaFeO$_3$ perovskite oxides; The $e_g$ orbital filling of perovskites. (C) $e_g$ filling and OER activity as a function of Ni$^{3+}$/Ni$^{2+}$ rate; The green dot only represents the ideal $e_g$ filling; (D) Electronic configuration and relevant metal orbitals of Ni$^{2+}$ and Ni$^{3+}$ for a NiO$_5$ configuration.

**Figure 4**  
(A) Chronoamperometric response of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$, commercial RuO$_2$, LaNi$_0.5$Fe$_0.5$O$_3$ and LaNiO$_3$, where inset shows the LSV curves of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ before and after 10 h durability test. (B) The XRD patterns of La$_{0.4}$Sr$_{0.6}$Ni$_{0.5}$Fe$_{0.5}$O$_3$ before and after 10 h durability test.
not change much after 10 h durability test while the particles had a certain agglomeration after the test (Figure S14). The electrochemical results indicate that the synthesized perovskite oxide La$_{0.8}$Sr$_{0.4}$Ni$_{0.1}$Fe$_{0.9}$O$_{1.5}$ may become a promising catalyst in metal-air batteries and solar fuel applications.

**DATA AVAILABILITY**

The raw data supporting the conclusions of this manuscript will be made available by the authors, without undue reservation, to any qualified researcher.

**AUTHOR CONTRIBUTIONS**

HL and ZL designed the project. QG performed the experiment under the direction of ZL. QG and XL performed the experimental data analysis. QG, HL, XL, ZL, XY, LL, YL, HW, and XZ developed the formation mechanism. QG, HL, and XL wrote the paper. All authors contributed to discussion of the results.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2019.00224/full#supplementary-material

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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