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High efficiency electrocatalyst of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ nanoparticles on oxygen-evolution reaction

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Due to the multistep proton-coupled electron transfer, it remains a huge challenge to accelerate the kinetics of oxygen evolution reaction (OER). Here, we demonstrate that perovskite-type $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ nanoparticles can be used as highly active and stable OER electrocatalysts, where it shows a low overpotential of 390 mV at 10 mA/cm², a small Tafel slope of 114.4 mV/dec and excellent stability with slight current decrease after 20 h, superior than that of their individual counterparts (LaFeO_3 and LaCrO_3). This finding confirms that the present hybrid material would be an effective means to electrocatalyst for catalyzing OER.

It is very urgent that develop low cost, high stability and efficient energy convert and storage system (eg. metal-air batteries¹, fuel cells² and super capacitors³) for clean energy. Oxygen evolution reaction (OER) is the important step for many energy storage systems^{4–6}, where noble metal-based (eg. $\text{IrO}_2/\text{RuO}_2$) catalysts are generally used as the most active catalysts to accelerate the kinetics of OER. However, it is difficult to meet the needs of commercialization, due to its scarcity and expensive of these precious metals⁷. Therefore, it is inevitable and great interest to explore the efficient and low-cost alternative non-precious electrocatalysts.

Recently, the stable structural, controllable electronic states⁸ and relatively high ionic/electronic conductivity make oxide perovskite electrocatalysts popular. In particular, as the most important parent oxides in the family of perovskite, LaFeO_3 has been widely reported as efficient electrocatalyst. Unfortunately, calculations^{9,10} and experimental measurements¹¹ results proved that individual LaFeO_3 perovskite has poor oxygen reduction reactions (ORR) and oxygen evolution reaction (OER) activity in alkaline electrolyte. As a consequence, many attempts have been used to optimize the electronic structure and further optimize the ORR/OER activity of LaFeO_3 . For instance, Wang et al. used phosphorus doping strategy to optimize the OER and ORR electrocatalytic activity of $\text{LaFeO}_{3-\delta}$ perovskite¹². Copper and zinc co-doped LaFeO_3 perovskite oxides with enhanced electrocatalytic activity were also reported by Mahmoud Omari¹³. Schon et al. reported the highest catalytic activity for CO oxidation in $\text{LaFe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ ¹⁴. Furthermore, the OER activity of LaFeO_3 was enhanced through coating an amorphous cobalt-phosphate¹⁵. Based on the conclusions reported in the above articles, we can see that the A or B ions in the perovskite oxide (ABO_3) are partially replaced by other ions can cause changes in oxygen vacancies, ion valence and structural distortions. These can also lead to the improvement of its catalytic performance. Generally speaking, the stability and electrocatalytic activity of the perovskite oxide are more affected by the B-site cation¹⁶. Therefore, the method of replacing the B-site cation by incorporating some heteroatoms is an effective strategy to promote the electrocatalytic activity.

Herein, double perovskite $\text{LaCr}_x\text{Fe}_{1-x}\text{O}_3$ with enhanced OER activity is reported, where the optimized sample of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ displays the lowest overpotential of 390 mV at 10 mA/cm², Tafel slope of 114.4 mV/dec and long-term durability (20 h). We also through the electrocatalytic test and the first principle calculations results prove that the excellent performance of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ are raised from the improved conductivity, tailored electronic structure and strong hybridization between oxygen and imetallic atoms.

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Figure 1. The DOS diagram of (a) LaFeO_3 , (c) LaCrO_3 and (e) $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$. The atomic structure optimization diagram of (b) LaFeO_3 , (d) LaCrO_3 and (f) $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$.

Results and discussion

Since the OER electrocatalytic activity of the catalyst is highly correlated with its electronic structure, we therefore first verify this relationship through first principle calculation. Figure 1 shows the calculated the density of states (DOS) results of LaFeO_3 , $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ and LaCrO_3 models. They all exhibit the full electron occupied states at the Fermi level, revealing the metal-like state of LaFeO_3 , $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ and LaCrO_3 . For $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ case, there are more electron occupied states at the Fermi level, ascribing the strong hybridization of Fe d/Cr d/O-p orbitals. Furthermore, it is well-known that the adsorbate-metal interactions can be predicted by the energy difference between d-band center and Fermi level (ΔE_O)^{17,18}. Based on the d-band center model, the smaller value of ΔE_O , the stronger bond between the metal atom and the adsorbed oxygen-containing substance, which means the higher intrinsic OER activity^{19,20}. Apparently, our calculation results indicate that the $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ exhibits the smallest ΔE_O value [O(-3.33 eV), Fe(-1.64 eV), Cr(-1.55 eV)] compared with LaFeO_3 [O(-3.79 eV), Fe(-2.02 eV)] and LaCrO_3 [O(-4.70 eV), Cr(-1.49 eV)], revealing the OER activity and electron can be significantly promoted through the strongest binding between surface Cr/Fe atoms and the adsorbed oxygenated species upon electrolysis.

Figure 2a and Figure S1 (Supporting Information) show the X-ray diffraction (XRD) patterns of as-synthesized $\text{LaCr}_x\text{Fe}_{1-x}\text{O}_3$ ($x = 0, 0.2, 0.5, 0.7, 0.9, 1$, respectively) perovskite oxides. The diffraction peak of LaFeO_3 ($x = 0$) corresponds to the standard cubic spinel LaFeO_3 (PDF# 75-0541). Nevertheless, as the concentration of Cr increased, the characteristic peaks gradually shifts to the body-centered tetragonal spinel structure of LaCrO_3 (PDF #75-0441)²¹. The morphology of the as-prepared $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ was examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as presented in Figure S2 (Supporting Information) and Fig. 2b, respectively. The morphology of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ displays some pore structures formed by aggregated or randomly stacked irregularly shaped particles. Noting that all the samples show the same particles morphology

Figure 2. (a) XRD patterns of LaFeO_3 , $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$ and LaCrO_3 . (b) TEM images of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$. (c) HRTEM image of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$. (d) Corresponding EDX element mapping images of $\text{LaCr}_{0.5}\text{Fe}_{0.5}\text{O}_3$.

Figure 3. XPS spectrum of (a) La 3d, (b) Cr 2p, (c) Fe 2p and (d) O 1s.

Figure 4. (a) The polarization curves, (b) overpotential at 10 mA/cm² and (c) Tafel plots of LaFeO₃, LaCr_{0.5}Fe_{0.5}O₃ and LaCrO₃ for OER. (d) The CV-curcalculated Cdl of all samples (e) EIS Nyquist plots of all samples. (f) Overpotential (η) of previously reported material for OER at 10 mA/cm².

as revealed in Figures S2, S3 (Supporting Information). The high-resolution TEM (HRTEM) was carried out to further characterize the structures of LaCr_{0.5}Fe_{0.5}O₃. As shown in Fig. 2c, the obvious lattice fringe of 0.388 nm matched with the (100) plane. Further, as revealed by the high-angle annular dark-field scanning TEM-EDS mapping (Fig. 2d), the element distributions are highly even in LaCr_{0.5}Fe_{0.5}O₃.

The oxidation state and composition of the electrocatalysts were detected via X-ray photoelectron spectroscopy (XPS). Figure 3a exhibits La 3d spectra of LaFeO₃, LaCr_{0.5}Fe_{0.5}O₃ and LaCrO₃, which are deconvoluted into two different characteristic peaks of La 3d_{3/2} (850.4 and 854.7 eV) and La 3d_{5/2} (833.5 and 837.5 eV)²². Noting that the peak positions of LaCr_{0.5}Fe_{0.5}O₃ have a slight shift to low energy compared with LaFeO₃ and LaCrO₃, revealing that there are valence change or electron transfer in LaCr_{0.5}Fe_{0.5}O₃. The high resolution spectrums of Cr 2p_{1/2} and Cr 2p_{3/2} peaks are consistent with 586.2 and 577.0 eV, respectively²³. As can be seen in Fig. 3b, the peak at 577 eV of Cr 2p_{3/2} can be assigned to Cr³⁺, and as the literature reports that the catalytic activity will be promoted by Cr³⁺ of the high-valence Cr species²⁴. As shown in Fig. 3c, the peaks at 709.9 and 723.6 eV were assigned to Fe 2p_{3/2} and Fe 2p_{1/2} respectively²⁵. Compared to the LaFeO₃, the Fe 2p_{3/2} peaks of LaCr_{0.5}Fe_{0.5}O₃ shift from 709.9 eV to 710.2 eV. The O 1s spectrum illustrated in Fig. 3d shows three peaks that are matched with lattice oxygen (O₁, 529.8 eV), defect oxygen (O₂, 531.5 eV) and surface absorbed oxygen (O₃, 533.0 eV), respectively²⁶. Furthermore, the result indicates that LaCr_{0.5}Fe_{0.5}O₃ possesses higher ratio of oxygen defects (48.4%) than other samples (LaCrO₃-31.3%, LaFeO₃-40.7%), indicating that Cr doping can introduce more oxygen defects, which will enhance the interaction of hybrids and absorbed oxygen-containing species²⁷.

As displayed in Table S1 and Figures S4, S6 (Supporting Information), the ration of x in LaCr_xFe_{1-x}O₃ (x = 0, 0.2, 0.5, 0.7, 0.9, 1, respectively) can tune the electrocatalytic activity of the electrocatalysts and the optimized x is about 0.5. Thus, the linear sweep voltammetry (LSV) of LaCr_{0.5}Fe_{0.5}O₃ reveals an OER overpotential at 10 mA/

Figure 5. (a) LSV curves of LaCr_{0.4}Fe_{0.6}O₃ catalyst before and after 1000 cycles. (b) The chronoamperometry test of LaCr_{0.5}Fe_{0.5}O₃. (c) The XRD pattern of LaCr_{0.5}Fe_{0.5}O₃ after OER test. (d) The SEM image of LaCr_{0.5}Fe_{0.5}O₃ after OER test.

cm² of 390 mV, which is smaller than 510 mV of LaFeO₃ and 550 mV of LaCrO₃ (Fig. 4a,b). Besides, as shown in Fig. 4c, LaCr_{0.5}Fe_{0.5}O₃ owns the lowest Tafel slope (114.4 mV/dec) among LaFeO₃ (142.4 mV/dec) and LaCrO₃ (192.6 mV/dec), respectively. In addition, the cyclic voltammetry (CV) curve (Figure S5, Supporting Information) illustrates that *C_{dl}* (Fig. 4d) of LaCr_{0.5}Fe_{0.5}O₃ is about 21.6 mF/cm², larger than LaFeO₃ (11.1 mF/cm²) and LaCrO₃ (5.7 mF/cm²). To our knowledge, *C_{dl}* is proportional to electrocatalytically active surface areas (ECSA) of electrocatalysts²⁸, and the largest *C_{dl}* of LaCr_{0.5}Fe_{0.5}O₃ indicates it possesses the largest ECSA. In addition, we also can get the Charge transfer resistance by electrochemical impedance spectra (EIS)²⁹ in Fig. 4e. It can be seen that the charge transfer resistance of LaCr_{0.5}Fe_{0.5}O₃ is smaller than that of LaFeO₃ and LaCrO₃, demonstrating that LaCr_{0.5}Fe_{0.5}O₃ owns fastest OER rates and the optimal charge transfer capability. Further, as summarized in Fig. 4f, the LaCr_{0.5}Fe_{0.5}O₃ shows better electrocatalytic activity than some recent reported electrocatalysts, such as LFP-5¹², La_{0.95}FeO_{3-δ}³⁰, SrCo_{0.9}Ti_{0.1}O_{3-δ}³¹, La_{0.7}(Ba_{0.5}Sr_{0.5})_{0.3}Co_{0.8}Fe_{0.2}O₃³², and SrFe_{0.9}Ti_{0.1}O_{3-δ}³¹.

At the same time, the excellent stability of the electrocatalyst can also be proved by the following tests. Figure 5a exhibits that the change of the overpotential (η) for LaCr_{0.5}Fe_{0.5}O₃ is about 13 mV after 8,000 cycles under 35 mA/cm². Moreover, the chronoamperometry test also can be carried out to prove the excellent stability of the LaCr_{0.5}Fe_{0.5}O₃. It can be acquired from Fig. 5b and Figure S7 (Supporting Information) that the initial activity of LaCr_{0.5}Fe_{0.5}O₃ remains almost unchanged after 20 h, demonstrating the outstanding stability of LaCr_{0.5}Fe_{0.5}O₃ for OER. In addition, the XRD pattern (Fig. 5c), SEM image (Fig. 5d), TEM image (Figure S6a, Supporting Information) and HRTEM image (Figure S6b, Supporting Information) show that the structure is basically consistent with that before the OER test, confirming the LaCr_{0.5}Fe_{0.5}O₃ has good structural stability. In light of all these findings, it is corroborated that LaCr_{0.5}Fe_{0.5}O₃ possesses excellent electrocatalytic stability.

Conclusions

In summary, theoretical calculations demonstrate that LaCr_{0.5}Fe_{0.5}O₃ possesses the stronger bond between the metal atom and the adsorbed oxygen-containing substance, and greater electrical conductivity for electron transport, thus having better OER electrocatalysis active. Experimentally, electrocatalytic activity of LaCr_xFe_{1-x}O₃ (*x* = 0, 0.2, 0.5, 0.7, 0.9, 1, respectively) perovskites are studied, where the sample LaCr_{0.5}Fe_{0.5}O₃ shows highly active (lower overpotential and larger ECSA) and excellent stability (structural and test stability). These results prove that doping the B-site perovskite oxide is an effective strategy to conceive more efficient and stable OER electrocatalysts.

Experimental section

Preparation of LaCr_xFe_{1-x}O₃. The catalysts of LaCr_xFe_{1-x}O₃ (*x* represent the amount of Cr incorporated ration in the sample, *x* = 0, 0.2, 0.5, 0.7, 0.9, 1) nanostructures were prepared by conventional sol-gel method. First of all, (0.005 mol) La(NO₃)₃·6H₂O, (0.005·1-*x* mol) Fe(NO₃)₃·9H₂O, (0.005·*x* mol) Cr(NO₃)₃·9H₂O and

(0.01 mol) $C_6H_8O_7$ were added in 30 mL solution ($V_{H_2O}:V_{C_2H_6O} = 1:2$) with 10 min stirring. Next, the uniform mixture was dried in an oven (90 °C for 24 h). Subsequently, the precursor was annealed under air atmosphere at 600 °C for 5 h with a 2 °C min⁻¹ rate of heating. When the value of x is 0.5, we name it $LaCr_{0.5}Fe_{0.5}O_3$. By analogy we have prepared $LaFeO_3$, $LaCr_{0.2}Fe_{0.8}O_3$, $LaCr_{0.7}Fe_{0.3}O_3$, $LaCr_{0.9}Fe_{0.1}O_3$, $LaCrO_3$, respectively.

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Author contributions

X.G., J.R. and D.G. wrote the main manuscript text. J.L. prepared Fig. 1, J.Z. prepared transmission test and data processing. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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