Study on the Effect of A/B Site Co-Doping on the Oxygen Evolution Reaction Performance of Strontium Cobaltite

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Abstract: The perovskite oxide SrCoO$_{3-x}$ is a promising oxygen electrocatalyst for renewable energy storage and conversion technologies. Here, A, B-site Co-doped perovskite Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ nanoparticles were rationally designed and synthesized by the sol-gel method with an average size of 30–40 nm. It has a remarkable intrinsic activity and stability in 1 M KOH solution. Compared with other A-site (Sr$_{x}$A$_{1-x}$CoO$_{3-x}$ A=Ba, Ca) and B-site doped perovskite (SrCo$_{0.6}$R$_{1-x}$O$_{3-x}$ R=Mn, Fe, Ni, B) catalysts, Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ exhibits superior oxygen evolution reaction (OER) performance, smaller Tafel slope, and lower overpotential. The high electrochemical performance of Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ is attributed to its optimized crystal structure and the increase in the content of Co$^{3+}$. This study demonstrates that highly symmetrical cubic perovskite structure catalytic displays better OER performance.

Keywords: perovskite; OER; lattice oxygen; electronic structure

1. Introduction

With the gradual depletion of fossil fuels, various sustainable energy conversion and storage systems have been researched [1]. Electrochemical water splitting for hydrogen production is one of the most promising systems among them, which can convert solar and wind energies into chemical fuel form, i.e., hydrogen [2]. However, the oxygen evolution reaction (OER)–half reactions during water splitting–has sluggish kinetics because of the complex four-electron oxidation process [3–5]. To achieve the ideal electrochemical reaction efficiency in practical applications, it must rely on the corresponding catalyst. At present, the best performance of the OER is mostly the noble metal Ir/Ru-based catalyst. Its low reserve and high price have created great obstacles to its wide application in actual production [6].

Over the past few years, perovskite has attracted widespread attention due to its unique ABO$_3$ (A = alkaline-earth or rare-earth metals and B = transition metals) structure [7–11]. Recently, it was reported that perovskites exhibit high OER activity in an alkaline solution. The F substituted BSCF (F-BSCF) catalyst exhibits outstanding electrocatalytic activity, with an overpotential of only 280 mV to deliver 10 mA cm$^{-2}$ OER, which is among the results for state-of-the-art metal oxide-based catalysts [12]. Moreover, the Rossmeisl group and Koper group theoretically calculated that SrCoO$_3$ parent oxide performs better OER activity among LaMO$_3$ and SrMO$_3$ (M = transition metals) parent oxides via density functional theory calculations [13]. Yumin Da et al. also showed that the OER performance of SrCoO$_3$ is significantly enhanced after a small amount of Fe is doped; its overpotential at 10 mA/cm$^2$ is 370 mV [14]. Due to its unique reversible oxygen storage and oxygen release capabilities, SrCoO$_{3-x}$ is a bifunctional material used as an oxygen electrode for medium temperature reversible solid oxide fuel cells (RSOFC) [15,16]. As shown in Figure 1a, the ideal cubic perovskite structure SrCoO$_3$ (P-SCO) has excellent ORR (oxygen reduction reaction) and OER (oxygen evolution reaction) activities. However, this kind of material...
is only stable at high oxygen partial pressure (>15 MPa) [17–19]. Under the working conditions of RSOFC, it is easy for P-SCO to lose one sixth of its lattice oxygen due to insufficient environmental pressure, decomposing into a more stable limonite phase BM-SCO (Figure 1b). Compared with P-SCO, BM-SCO has poor ORR or OER catalytic activity due to the ordered arrangement of oxygen vacancies at lower temperatures [20]. To obtain better performance, it is necessary to regulate the structure of BM-SCO.

Figure 1. (a) P-SCO and (b) BM-SCO structures of strontium cobaltite.

In this work, a combination of sol-gel and solid-phase sintering was used to prepare the perovskite (ABO₃) material SrCoO₃₋ₓ. Then, the crystal and internal electronic structure of SrCoO₃₋ₓ were optimized by co-doping of Ba and Mn at A, B sites, respectively, which increased the OER performance. It is found that the introduction of Ba²⁺ with larger ion radius can make the tolerance factor (t) closer to 1, which means a better crystal structure that is beneficial for the OER. In addition, the introduction of Mn further enhances the OER performance of the catalyst. On one hand, the introduction of Mn increases the content of lattice oxygen and further optimizes the crystal structure of the catalyst. On the other hand, after Mn was doped, the ratio of Co³⁺/Co²⁺ was adjusted and the content of Co³⁺ was increased, which contributed to the OER performance. The combination of the two makes the OER performance of the catalyst further enhanced after the introduction of Mn. The experimental results showed that the Sr₀.₅Ba₀.₅Co₀.₉₅Mn₀.₀₅O₃₋ₓ exhibits a better OER performance and stability, which fully proved that Sr₀.₅Ba₀.₅Co₀.₉₅Mn₀.₀₅O₃₋ₓ is a promising OER electrocatalyst.

2. Experimental

2.1. Materials

All chemicals (analytical reagent grade) used in this work, including Co(NO₃)₂·6H₂O, Sr(NO₃)₂·4H₂O, Fe(NO₃)₂·6H₂O, (CH₃COO)₂Mn·4H₂O, H₃BO₃, Ba(NO₃)₂, CaCO₃, Ni(NO₃)₂·6H₂O, ethylene glycol(HOCH₂CH₂OH, ≥99.8%), ethanol (CH₃CH₂OH), KOH, Citric acid [HOC(COOH)(CH₂COOH)]₂, ≥99.5%, and Nafion (15 wt%) were purchased from Sigma-Aldrich and used without further purification. Deionized water was used in all experiments.

2.2. Material Synthesis

The perovskite nanoparticles SrCoO₃₋ₓ were prepared by sol-gel method and solid-state method previously reported [21,22]. Strontium nitrate and cobalt nitrate were dissolved in 5 mL deionized water with equal molar ratio. The aqueous solution of the above metal ions was mixed and dissolved in the aqueous solution of citric acid, and ethylene
glycol was added to the water bath at 70–90 °C to make the dissolved solution grow into a gel skeleton. The formed gel was then placed in an oven at 130 °C for 2 h to obtain a dry gel. The dry rubber was ground into powder, calcined in muffle furnace at 550 °C for 4 h to remove carbon, then calcined at high temperature for 4–10 h, cooled, and ground many times to obtain the required sample. The doped samples were produced in the same way.

2.3. Material Characterization

All the obtain perovskite samples were characterized by X-ray diffraction (XRD, D8/max 2500PC, Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation. Scanning Electron Microscope (SEM, S-4800, Hitachi Limited, Tokyo, Japan) was used to analyze the topography of the samples. Transmission electron microscopy (TEM, TECNAI 20, Royal Philips, Amsterdam, The Netherlands) was used to analyze the morphology and size of the nanoparticles operated at 200 kV. X-Ray photoelectron spectroscopy (XPS) analyses were performed using a PHI 1600 (PerkinElmer, Waltham, MA, USA) to analyze the element valence.

2.4. Electrochemical Measurement

The OER performance was measured in a three-electrode electrochemical cell configuration with O$_2$-saturated 1.0 M KOH at pH = 14 controlled by a CHI 750E electrochemistry workstation. All potentials were converted to reversible hydrogen electrode (RHE) via the Nernst equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.244 + 0.059 \times \text{pH}$. During the electrochemical test, our perovskite catalysts were loaded on a glass carbon electrode (GC) as a working electrode—an Hg/Hg$_2$Cl$_2$ saturated calomel electrode (SCE) in saturated KCl solution—was used as a reference electrode, and a carbon rod was used as a counter electrode. Before testing, the GC electrode was pre-polished with 50 nm α-Al$_2$O$_3$ slurries on a polishing cloth and rinsed with deionized water. The catalyst ink was a composite of 5 mg perovskite oxide power and 5 mg carbon black (XC-72, which was treated by nitric acid for 5 h). Then, 1 mL mixture of water and ethanol and 30 µL Nafion solution (5 wt%) was added for 2h ultrasonication to form a homogeneous ink. Subsequently, 3.3 µL of the catalyst ink was transferred onto the surface of the GC electrode, which was used as a working electrode with a load capacity of 0.25 mg cm$^{-2}$ catalyst. During the electrochemical test, a flow of ultra-pure O$_2$ was maintained over the system to ensure the O$_2$/H$_2$O equilibrium at 1.23 V vs. reversible hydrogen electrode (RHE). All electrochemical measurements were performed in 1M KOH solution. Before the OER recording, the potential of the perovskite catalyst was scanned at 50 mV s$^{-1}$ between 0 and 0.5 V (vs. SCE) until a stable cyclic voltammogram (CV) was obtained. The line scan voltammogram (LSV) polarization curves were tested between 0 to 0.8 V (vs. SCE) with a scan rate 5 mV s$^{-1}$. The Tafel slope was obtained by plotting log(J) from LSV curves. The electrochemical impedance spectroscopy was measured at 0.55 V (vs. SCE) with a frequency from 0.1 to 10$^6$ Hz. The electrochemical workstation (CHI 750E) and three electrode systems were also used in EIS test.

3. Result and Discussion

To obtain the best calcination conditions, the samples were calcined at different temperatures and different hours, and the corresponding OER properties were tested. As shown in Figure 2a, the OER performance of the catalyst is the best at 700 °C and 800 °C. However, at 700 °C, the phase of SrCoO$_3$ could not be formed (Figure 2c), so the optimal calcination temperature was determined to be 800 °C. Then, as shown in Figure 2b, the samples were calcined at 800 °C for different periods of time, and the properties of the samples were tested. When the calcination time is 6 h, the sample has the best OER performance, so the calcination time is set as 6 h. Under the same conditions, a series of perovskite samples were prepared. The diffraction peaks of the synthesized SrCoO$_3$–x particles (Figure 3a) at the (100), (101), (110), (201), (211), (300) crystal planes all coincide with the 2θ position of the theoretical diffraction peak (PDF#48-0875), which belongs to the hexagon crystal system; the unit cell parameters are $a = 5.471, c = 4.235; \alpha = \beta = 90^\circ, \gamma = 120^\circ$. The crystal structure
of the sample doped with Mn (Figure 3a) and other doped samples (Figure 3c–f) have the same diffraction peak as the SrCoO$_{3-x}$ standard card PDF#48-0875. It shows that the joint introduction of Mn, Ni, B, and Ba, Ca did not destroy the crystal structure of SrCoO$_{3-x}$.

Figure 2. OER polarization curves of SrCoO$_{3-x}$ calcined at (a) different temperatures (700–900 °C) for 6 h and (b) 800 °C for different times (4–10 h) and corresponding XRD patterns (c,d).

Figure 3. XRD patterns of Sr$_{1-v}$A$_v$CoO$_{3-x}$ and SrCo$_{1-v}$R$_v$O$_{3-x}$ [R = (a) Mn; (b) Fe; (c) Ni; (d) B; A = (e) Ba; (f) Ca].

While in Figure 3b, with the incorporation of Fe ions, the crystal structure of SrCoO$_{3-x}$ is transformed to P-SCO, which corresponds to the research results in the literature [23].
Since the bond energy of Fe-O (408.8 kJ/mol) is greater than that of Co-O (368 kJ/mol), Fe\(^{2+}/Fe^{3+}\) has a strong ability to bind oxygen, increasing the content of lattice oxygen in the crystal structure. FeO\(_6\) octahedron and CoO\(_6\) octahedron are uniformly distributed, the oxygen vacancy concentration is reduced, and a cubic perovskite structure with high oxygen content is formed [24].

The electrochemical performance of Sr\(_{1-x}\)A\(_{1+x}\)Co\(_3-x\)O\(_x\) (A=Ba, Ca) and SrCo\(_1-x\)R\(_x\)O\(_3-x\) (R=Mn, Fe, Ni, B) were examined as shown in Figure 4. In the A-site doped samples, the Ba doping has a better OER performance compared with Ca because of the better crystal structure. In previous studies [25,26], the formation of the ABO\(_3\) cubic perovskite structure needs to meet the tolerance factor:

\[
t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}
\]

where \(r_A\), \(r_B\), and \(r_O\) are the ionic radius for the A-site cation, B-site cation, and O\(^{-}\) anion, respectively. The closer the tolerance factor gets to \(t = 1\), the more stable the structure is; when \(t = 1\), a stable highly symmetrical cubic perovskite structure is formed, which has the best OER catalytic activity. The A-site ion in the crystal structure does not directly participate in the catalytic reaction but stabilizes the perovskite structure through the A0\(_{12}\) polyhedron [27,28]. When the A-site ion is doped, the lattice distortion is formed, which will affect the catalytic activity of the B-site. \(t = 0.9379\) for incompletely oxidized SrCoO\(_{3-x}\), since the ionic radius of the A-site Ca\(^{2+}\) (112 pm) is smaller than Sr\(^{2+}\) (126 pm), the tolerance factor tends to decrease, and the crystals deviate more from the perovskite structure, resulting in a decrease in catalytic activity after Ca was doped. When the Ba\(^{2+}\) (142 pm) was doped in A-site, the tolerance factor tends to increase with the catalytic activity. When the doping amount of Ba\(^{2+}\) in the A site is Sr: Ba = 1:1 (molar ratio), a better OER performance is obtained (Figure 4e).

Figure 4. LSV patterns of Sr\(_{1-x}\)A\(_{1+x}\)Co\(_3-x\)O\(_x\) and SrCo\(_1-x\)R\(_x\)O\(_3-x\) [R = (a) Mn; (b) Fe; (c) Ni; (d) B; A = (e) Ba; (f) Ca].

In B site-doped samples, the OER performance of Mn, Fe Ni, and B doped samples were evaluated, where Mn doped samples performance best. In Figure 4a, the catalytic activity gradually decreases with the increase in the Mn doping. The sample SrCo\(_{0.95}\)Mn\(_{0.05}\)O\(_{3-x}\) has the lowest overpotential, which is 390 mV. Given all of this, we co-doped Ba and Mn into the A-site and B-site of the perovskite, respectively; the doping amount of Mn was
slightly adjusted, and the amount of Ba was fixed to 0.5, hoping that samples with better OER performance can be obtained.

The XRD and SEM of the co-doped samples are shown in Figure 5. It can be seen that the co-doping of Ba and Mn does not change the crystal structure of SrCoO₃. Figure 5b is the SEM image of the sample. The results show that the particles of the synthetic sample are evenly dispersed without agglomeration. From the comparison of the elemental composition analysis results, Figure 5c shows the EDS spectrum of Sr₀.₅Ba₀.₅Co₀.₉₅Mn₀.₀₅O₃₋ₓ, demonstrating that Ba and Mn are well doped into the SrCoO₃₋ₓ lattice, and the theoretical stoichiometric ratio Sr:Ba:Co:Mn = 1:1:0.95:0.05 is close to the experimental results. EDS energy spectrum shows that the sample contains a small amount of carbon, which may be the trace residue produced during the calcination of the dry gel.

Some obvious changes can be observed in the TEM images (Figure 6a–e) of the perovskite samples. Compared with the undoped SrCoO₃₋ₓ in Figure 6a, the morphology of the sample in Figure 6b is basically unchanged. It shows that the introduction of Mn does not change the morphology of the sample. Figure 6c shows the morphological changes of the sample after the introduction of Ba. It can be seen that the introduction of Ba significantly changes the morphology of the samples: the catalyst is transformed from irregular spherical particles to particles with cubic shapes. Compared with undoped samples, Ba doped samples have lower agglomeration and more exposed surfaces, which is conducive to OER reaction. The TEM images of co-doped samples (Figure 6d–f) illustrate SrCoO₃₋ₓ has particles with a cubic shape and a size of 30–40 nm, dispersed uniformly without agglomeration. With the increasing of Mn, particles grow and agglomerate (Figure 6e). Therefore, the content of Mn should not be too high. The TEM (HRTEM) image (Figure 6f) of the nanoparticle exhibits lattice fringes with spacings of 0.312 nm and 0.274 nm, corresponding to the (101) and (110) crystal planes of SrCoO₃₋ₓ, respectively, indicating the structure retained after
doping with Ba and Mn. In general, the morphology of the Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x} sample is optimized while maintaining the original crystal structure, which contributes to the improved OER performance.

![Figure 6. TEM images of (a) SrCoO_{3−x}; (b) SrCo_{0.95}Mn_{0.05}O_{3−x}; (c) Sr_{0.5}Ba_{0.5}Co_{0.8}O_{3−x}; (d) Sr_{0.5}Ba_{0.5}Co_{0.9}Mn_{0.1}O_{3−x}; (e) Sr_{0.5}Ba_{0.5}Co_{0.9}Mn_{0.10}O_{3−x}; (f) Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x}.](image)

The OER electrocatalytic properties of Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x} and Sr_{0.5}Ba_{0.5}Co_{0.9}Mn_{0.1}O_{3−x} were evaluated by a standard three-electrode system in an O_{2}-saturated 1M KOH solution as shown in Figure 7. With the increase in Mn doping, the oxidation peak tends to weaken gradually, which shows that the OER activity of the catalyst also tends to decline (Figure 7a) [29]. Figure 7b shows that Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x} has a better OER performance with the over potential of 320 mV at 10 mAcm⁻². It has the same performance as the noble metal oxide IrO_{2} (320 mV overpotential at a current density of 10 mA/cm² in 1 M NaOH solution) [30,31]. The EIS (Figure 7c) spectrum of electrochemical impedance shows that the sample Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x} has high charge transfer ability and strong conductivity. Figure 7d shows that the Tafel slope of the sample Sr_{0.5}Ba_{0.5}Co_{0.9}Mn_{0.1}O_{3−x} is 111.1 mV/dec while the Tafel slope of Sr_{0.5}Ba_{0.5}Co_{0.9}Mn_{0.05}O_{3−x} is 97.9 mV/dec. A lower Tafel slope means faster reaction kinetics, which is conducive to OER reaction. Therefore, Tafel test results also show that Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x} has a better OER performance. Above all, as the OER electrocatalytic activity of SrCoO_{3−x} samples with Ba and Mn co-doped at A and B sites has been significantly improved compared to the single-doped samples, the sample Sr_{0.5}Ba_{0.5}Co_{0.95}Mn_{0.05}O_{3−x} has relatively better reaction kinetics during the OER electrocatalytic reaction, and the catalytic reaction is more likely to occur and has a higher intrinsic catalytic activity.
Figure 7. OER test curves of Sr$_{0.5}$Ba$_{0.5}$Co$_{b}$Mn$_{1-b}$O$_{3-x}$ (a) CV, (b) LSV, (c) EIS, (d) Tafel.

As shown in Figure 8, the XPS test was performed on the sample to understand the enhancement in OER electrocatalytic activity of the Sr$_{a}$Ba$_{1-a}$Co$_{b}$Mn$_{1-b}$O$_{3-x}$. Figure 8a is the XPS spectrum of Co 2p3/2 of the Sr$_{a}$Ba$_{1-a}$Co$_{b}$Mn$_{1-b}$O$_{3-x}$ catalyst, showing that Co iron in the sample has two oxidation states: Co$^{3+}$ at 779.4 eV and Co$^{2+}$ at 780.5 eV. Figure 8b shows that the O1s of the four samples is composed of 528.9 eV lattice oxygen (O$_{L}$) and 530.8 eV adsorbed oxygen (O$_{A}$) [32]. The Mn 2p3/2 and Ba 3d spectrum of the Sr$_{a}$Ba$_{1-a}$Co$_{b}$Mn$_{1-b}$O$_{3-x}$ catalyst were also tested (Figure 8c,d); some details are recorded in Table 1. The enhancement of perovskite properties is attributed to two main reasons: on one hand, compared with Co$^{2+}$, the Co$^{3+}$ has easier access to electrons, which is beneficial to the catalytic reaction [33]. When the A, B-site ions are co-doped, the ratio of Co$^{3+}$/Co$^{2+}$ significantly increases, the maximum ratio of the sample Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ is 3.54, and the ratio of the co-doped sample Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ is 2.84. The ratio of co-doping sample is lower than Ba doping of SrCo$_{3-x}$, probably because the high-priced Mn$^{3+}$/Mn$^{4+}$ doped at the B site inhibits the formation of Co$^{3+}$, or it may be because the Mn$^{3+}$ ions replace the Co$^{3+}$ in the CoO$_{6}$ octahedron, while Instead of directly combining with oxygen to form a new MnO$_{6}$ octahedron. However, it is still twice as high as that of undoped SrCo$_{3-x}$. On the other hand, it could be found that the content of the lattice oxygen (O$_{L}$) of perovskites (14% < 21% < 27% < 32%) conforms to the laws of SrCo$_{3-x}$ < SrCo$_{0.95}$Mn$_{0.05}$O$_{3-x}$ < Sr$_{0.5}$Ba$_{0.5}$Co$_{3-x}$ < Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$, which is consistent with the OER performance (450 mV < 390 mV < 370 mV < 320 mV at a current density of 10 mA/cm$^2$ in 1 M NaOH solution) of these samples. All in all, when the A, B sites Ba and Mn are co-doped with SrCo$_{3-x}$, the lattice oxygen content in the catalyst is greatly increased, more Mn$^{3+}$ can combine with oxygen to form BO$_{6}$ octahedron, which increases the number of active sites. Additionally, increased Co$^{3+}$ also contributes to the enhanced OER performance.
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 [34]. The stability of the catalyst was tested by chronoamperometry. Figure 9a shows the I-t curve measured by different catalysts in a 1 M KOH solution for 10 h at a constant potential. The overall current density of Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ is higher than other samples; after 10 h, it only decreased by 8.9%. The illustration in Figure 9a shows that in Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$, the corresponding overpotential at 10 mA/cm$^2$ after 10 h only increased by 23 mV. In the XRD characterization of Sr$_{0.5}$Ba$_{0.5}$Co$_{0.95}$Mn$_{0.05}$O$_{3-x}$ samples before and after the 10 h stability test, as shown in Figure 9b, the diffraction peak intensity of the sample was reduced and the crystallinity was reduced, but no other diffraction peaks appeared, indicating that the co-doped sample has an excellent stability.

Table 1. Proportion of Co, O, Mn elements in the catalyst.

<table>
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<tr>
<th>Catalyst</th>
<th>Co$^{2+}$%</th>
<th>Co$^{3+}$%</th>
<th>Co$^{3+}$/Co$^{2+}$</th>
<th>O$^-$%</th>
<th>Mn$^{3+}$</th>
<th>Mn$^{4+}$</th>
<th>Mn$^{3+}$/Mn$^{4+}$</th>
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<tr>
<td>SrCoO$_{3-x}$</td>
<td>44</td>
<td>56</td>
<td>1.27</td>
<td>14</td>
<td>——</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>SrCo$<em>{0.95}$Mn$</em>{0.05}$O$_{3-x}$</td>
<td>42</td>
<td>58</td>
<td>1.38</td>
<td>21</td>
<td>54</td>
<td>46</td>
<td>1.17</td>
</tr>
<tr>
<td>Sr$<em>{0.5}$Ba$</em>{0.5}$CoO$_{3-x}$</td>
<td>22</td>
<td>78</td>
<td>3.54</td>
<td>27</td>
<td>——</td>
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<td>——</td>
</tr>
<tr>
<td>Sr$<em>{0.5}$Ba$</em>{0.5}$Co$<em>{0.95}$Mn$</em>{0.05}$O$_{3-x}$</td>
<td>26</td>
<td>74</td>
<td>2.84</td>
<td>32</td>
<td>58</td>
<td>42</td>
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4. Conclusions

In summary, perovskite oxide Sr0.5Ba0.5Co0.95Mn0.05O3−x was obtained by a simple co-doping method, which showed high OER performance under alkaline conditions. The test results show that the co-doping of Ba and Mn can optimize the crystal structure of the catalyst and increase the content of lattice oxygen, which is conducive to the OER reaction. In addition, the contents of Co3+ and Co2+ were also optimized to improve the OER activity of the catalyst. Sr0.5Ba0.5Co0.95Mn0.05O3−x exhibits the over potential of 320 mV at 10 mAcm −2, which is the same performance as the noble metal oxide IrO 2. Furthermore, the chronoamperometry test of Sr0.5Ba0.5Co0.95Mn0.05O3−x also demonstrated 8.9% decay for OER within 10 h. The electrochemical results indicate that adjusting the crystal structure of the catalyst is an effective way to enhance the OER performance of the sample and the synthesized perovskite oxide Sr0.5Ba0.5Co0.95Mn0.05O3−x may become a promising catalyst in metal–air batteries and solar fuel applications.

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