Highly Efficient Oxygen Evolution Activity of Ca$_2$IrO$_4$ in an Acidic Environment due to Its Crystal Configuration

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**ABSTRACT:** We systematically characterized the perovskite-like oxides Ca$_2$IrO$_4$ and CaIrO$_3$ as the oxygen evolution reaction (OER) catalysts. Compared with IrO$_2$, universally accepted as the current state-of-the-art OER catalyst, Ca$_2$IrO$_4$ showed an excellent OER catalytic activity in an acidic environment, whereas CaIrO$_3$ did not. X-ray photoelectron spectroscopy (XPS) spectra showed that the oxidation of iridium in Ca$_2$IrO$_4$ and CaIrO$_3$ was slightly beyond +4. X-ray absorption near-edge structure (XANES) spectra illustrated that the IrO$_6$ octahedral geometric structure in Ca$_2$IrO$_4$ and CaIrO$_3$ showed differences. The IrO$_6$ octahedral is asymmetrically distorted and uniformly compressed in Ca$_2$IrO$_4$ and CaIrO$_3$. Therefore, we propose that the IrO$_6$ octahedral distortion plays an important role in the OER activities.

1. INTRODUCTION

Global concerns about increasing energy demands have stimulated extensive studies on the production of renewable energy sources and energy storage, including processes such as water splitting, direct solar, and rechargeable fuel cells. The oxygen evolution reaction (OER), in particular, is often a critical step in these energy production/storage options. Although precious metal-based catalysts with high OER activity are efficient and durable, their cost and scarcity limit their application. Perovskites are a large family with a general formula ABO$_3$, in which the transition metal is iridium. Thus, we put efforts to design the perovskite-like octahedral distortion activity of La$_{1-x}$Fe$_x$O$_3$ compared to that of LaFeO$_3$ is due to the increasing Fe$^{4+}$ population through oxygen vacancies in La$_{1-x}$Fe$_x$O$_3$. However, perovskites are mostly utilized as catalysts for OER in an alkaline environment. Given that Ir$^{4+}$ has been proven to be the active site of the OER catalyst in an acidic environment, we, herein, attempt to design the perovskite-like oxides, in which the transition metal is iridium. Thus, we put insights into calcium iridium oxides, Ca$_2$IrO$_4$ and CaIrO$_3$, which are the members of the perovskite family. They are often prepared at conditions of high pressure and temperature. Niwa et al. prepared the perovskite and postperovskite phases of CaIrO$_3$ by a high-pressure synthesis method using a multianvil apparatus. Keawprak et al. pressed the powders into pellets after mixing with a small amount of ethanol and calcined at 1273 to 1473 K in air. Ohgushi et al. mixed the starting materials with the molar ratio CaO/IrO$_2$ = 1:1 and heated them at 1 GPa and 1450 °C for 30 min.

To simplify the synthesis process, we prepared Ca$_2$IrO$_4$ and CaIrO$_3$ by the hydrothermal synthesis and sol–gel method. Conclusively, Ca$_2$IrO$_4$ and CaIrO$_3$ can be prepared successfully by sol–gel method so that the highly associated preparatory costs of other processes can be minimized. In addition, the internal structures of Ca$_2$IrO$_4$ and CaIrO$_3$ have been analyzed to reveal the reason, why these kinds of perovskites show an OER activity. The X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) have been tested for getting insights into the electronic structure and the surface

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chemical states of perovskites. We found that the IrO$_6$ octahedral coordination be the decisive factor of the OER activity.

2. EXPERIMENTAL SECTION

2.1. Hydrothermal Reaction. For preparing the composition of Ca$_2$IrO$_4$ and CaIrO$_3$, CaCl$_2$ at 180 mmol/L and IrCl$_3$·3H$_2$O at 56.7 mmol/L in variable stoichiometric amounts were mixed into a 40 mL Teflon-lined pressure vessel with 10 mL of deionized water and 5 mL of 0.5 M aqueous NaOH. The mixture was loaded into an oven to heat the solution to 250 °C for 720 min; then, the vessels were cooled naturally at room temperature. The precipitates were suction filtered and washed with deionized water twice to remove other unwanted ions. The remaining retentate on the filter was dried to dehydration in an oven at 80 °C for 1 h. After filtration and evaporation, the samples were transferred into crucibles and calcined at 700 °C for 360 min. The annealing step was required for converting the amorphous hydrothermal precipitate to a fine crystalline product (Table 1).

2.2. Sol–Gel Method. First, CaCl$_2$ and IrCl$_3$ were mixed according to the above mixing ratio, and both of the samples were added into 8 mL of citric acid. Then, they were transferred to the COD thermostatic heater heated at 150 °C for 60 min. After cooling, they were transferred to a beaker heated at 110 °C, which resulted in the state transition from liquid to solid powder.

Then, the samples were transferred to crucibles and heated at 700 °C for 360 min. After cooling, the samples were mixed with HCl under an ultrasonic environment for 30 min. Finally, the samples were turned into their final form after filtration and evaporation.

2.3. Characterization. The morphologies of the catalysts were observed using scanning electron microscopy (SEM) equipped with a Nova Nano S. Transmission electron microscopy (TEM) was performed using a JEOL model 2100 LaB$_6$ instrument, operating at 200 kV. The specimens were dispersed ultrasonically in ethanol and then deposited dropwise onto 3 mm lacey carbon grids supplied by Agar. Powder X-ray diffraction (XRD) data were collected using a Bruker D8 ADVANCE X-ray diffractometer operating with Cu K$_\alpha$ radiation and equipped with a VÂNTEC-1 solid-state detector. Energy dispersive spectrometer (EDS) was utilized to confirm the composition using a TEAMApollo system. XPS was performed using a Thermo ESCALAB 250 system. The radiation used was monochromatized using Al K$_\alpha$ radiation with a 650 μm spot size. The XAS data at the Ir L$_{III}$-edge of the samples, which were mixed with LiF to reach 50 mg, were recorded at room temperature in transmission mode using ion chambers using the BL14W1 beam line of the Shanghai Synchrotron Radiation Facility, China.

Table 1. Atomic Percent of All Elements in Perovskite Compositions

| Catalysts  | C (at. %) | O (at. %) | Ca (at. %) | Ir (at. %) |
|------------|-----------|-----------|------------|------------|
| CaIrO$_3$  | 12.37     | 40.21     | 20.30      | 27.11      |
| Ca$_2$IrO$_4$ | 14.21     | 38.79     | 27.02      | 19.98      |

Figure 1. (a) XRD pattern of Ca$_2$IrO$_4$ prepared via hydrothermal reaction (Ca$_2$IrO$_4$-hyd), Ca$_2$IrO$_4$ prepared via sol–gel method (Ca$_2$IrO$_4$-sol-700), CaIrO$_3$ prepared via sol–gel method (CaIrO$_3$-sol-700), and CaIrO$_3$ prepared via new sol–gel method (CaIrO$_3$-sol-1200). (b) EDS for the CaIrO$_3$ and (c) Ca$_2$IrO$_4$ sample.
2.4. Electrochemistry. To fabricate electrodes, a typical ink preparation was done as follows: 6 mg of the prepared sample, 1.0 mL of isopropanol, and 0.5 mL of deionized water were added. The entire mixture was homogenized by a high-power sonication probe for 10 min. Fifteen microliters (15 μL) of the ink prepared as described above was dispensed onto the titanium (Ti) plate and heated in a muffle furnace for 10 min. The step above was repeated 5 times. This gave a catalyst loading of 0.20 mg/cm² geometric on the Ti plate. For each electrochemical experiment, a fresh electrode with similar catalyst loading was fabricated in the same way. A conventional three-electrode electrochemical cell was used for all the electrochemical measurements. The working electrode was a thin layer of the catalyst prepared on the Ti plate as described above; the reference electrode was a saturated calomel electrode, and the counter electrode was a Pt plate. The electrochemical measurements were all performed at room temperature (25 °C).

3. RESULTS & DISCUSSION

3.1. Structure and Morphology. The prepared catalyst (Ca₃IrO₄ and CaIrO₃) samples are analyzed by XRD measurements.

Given the XRD pattern of Ca₃IrO₄-hyd (see in Figure 1a), we can see six peaks of high intensity at the position of 19°, 33°, 34°, 28°, 34.5°, and 54°. These characteristic peaks correspond to Ca₃IrO₄ and IrO₂, as reported in the literature.²² Because Ca₃IrO₄-hyd is prepared via hydrothermal synthesis, we come to the conclusion that we can synthesize the mixture of Ca₂IrO₄ and IrO₂ instead of pure Ca₂IrO₄ by this method. The second and third line shows the XRD patterns of CaIrO₃-sol-700 and CaIrO₃-sol-1200, respectively, whose preparation method is by sol–gel method. The characteristic peaks corresponding to IrO₂ do not appear in the pattern of CaIrO₃-sol-700 but appear in that of CaIrO₃-sol-700. This fact demonstrates that Ca₂IrO₄ can be synthesized via sol–gel method, whereas CaIrO₃ cannot. On the basis of the results above, we raise the calcination temperature from 700 to 1200 °C when other procedures remain the same. The last line in Figure 1a illustrates the XRD pattern of CaIrO₃-sol-1200. Obviously, the low intensity of characteristic peaks of IrO₂ elucidates the purity of CaIrO₃-sol-1200. Given that the XRD patterns of perovskites are similar, we use EDS to have an insight into the chemical composition of Ca₂IrO₄-sol-700 and CaIrO₃-sol-1200. The ratio of the amount of calcium and iridium is 0.749 in CaIrO₃-sol-1200 and 1.35 in Ca₂IrO₄-sol-700, depicting that the latter is twice as the former. Therefore, Ca₂IrO₄-sol-700 and CaIrO₃-sol-1200 can be confirmed to be the pure Ca₂IrO₄ and CaIrO₃.

Figure 2a–d shows SEM of calcium iridium oxides, which illustrated molar ratios of Ir to Ca (R_{Ir/Ca}) dependence of the crystal morphology. At R_{Ir/Ca} = 0.5, Ca₂IrO₄ had a granular microstructure with a grain size of about 0.8 μm. At R_{Ir/Ca} = 1, elongated grains about 10 μm in length and 2 μm in width were observed in the CaIrO₃ bulk phase. This result is consistent with the research of Keawprak et al. In their research work, TEM of CaIrO₃ has also been tested. They confirmed that the rodlike CaIrO₃ crystal grows in the [100] direction. The TEM of Ca₂IrO₄ and CaIrO₃ samples, showed in Figure 2e–h, illustrated that two types of crystalline planes, respectively, exist in these samples, in which (110) and (111) correspond to Ca₂IrO₄-sol-700 and CaIrO₃-sol-1200, depicting that the latter is twice as the former.

3.2. Electrochemical Studies. To determine the OER activity of Ca₂IrO₄ and CaIrO₃, we coated the prepared catalyst samples on the surface of titanium plates as the working electrode in the three-electrode system. The polarization curve is shown in Figure 3a. The curve illustrates that the onset OER potential of Ca₂IrO₄ is approximately 1.50 V. According to the study of Bernicke et al., the theoretical potential of the OER amounts to 1.23 V under standard conditions and the lowest onset OER potential of IrO₂ is 1.48 V. The discrepancy between the onset OER potential of IrO₂ and Ca₂IrO₄ is 0.20 V, which is smaller than being compared with 1.44 V.

Besides, we can see that the current density amounts to 22 mA/cm² when the potential is 1.66 V. Under the same conditions, the current density of IrO₂ amounts to about 15 mA/cm², which is significantly lower than that of Ca₂IrO₄. Then, normalized CV curve with different scan rates for Ca₂IrO₄ is shown in the Figure 3b. We can see that two obvious pairs of reduction/oxidation peaks are seen in the CV curve at about 0.80 and 1.20 V. As the scan rate becomes faster, the difference between anodic and cathodic currents increases. The position of redox peaks changes with the increasing scan rate as well. The absolute value of anodic and cathodic currents of every pair of redox peaks is not the same. This result is similar...
to the CV curve of the IrO$_2$ electrode, which is in accordance with the result of Lee et al.\textsuperscript{25} To further investigate the redox reaction, the relationship of the anodic peak current $I_p$ and the scan rate $\nu$ is shown in Figure 3c. The peak current varies linearly with scan rate, which is consistent with a surface couple.\textsuperscript{26} We deduce that capacitance charging current is not obvious in the scan range, the redox peak at 0.80 V corresponds to the proton transfer and that 1.20 V corresponds to the Ir$^{3+}$/Ir$^{4+}$ couple.

The durability is another important factor to evaluate the performance of OER catalysts. Therefore, we take the stability measurement of the Ca$_2$IrO$_4$ catalyst at 1.6 V for 5 h, as shown in the Figure 4a. During the OER process, the normalized current slightly decreases because of the subtle change on the electrode surface. As shown in Figure 4b,c, the catalyst formed as islands separated by cracks is more evenly distributed after the stability measurement.

In summary, the OER reaction rate on the surface of the Ca$_2$IrO$_4$-coated electrode is higher than that on the surface of the IrO$_2$-coated electrode in an acidic environment. The onset OER potential of the Ca$_2$IrO$_4$- or IrO$_2$-coated electrode is
approximately equal. The chronoamperometric experiment confirms that Ca$_2$IrO$_4$ remains stable during the OER.

3.3. XPS Analysis. As an additional assignment of metal oxidation states, we measured XPS spectra for Ca$_2$IrO$_4$ and CaIrO$_3$ (see in Figure 5). The samples were sputter-coated with carbon, and the spectra were calibrated with respect to C 1s at a binding energy (BE) of 284.8 eV. The major feature peak locates at 284.4 eV; therefore, the $\Delta$Eb value is 0.4 eV. In Figure 5, two peaks at Eb = 529.5 and 531.4 eV and a weakly intense peak at Eb = 533.2 eV are identified in the spectra of O 1s in both Ca$_2$IrO$_4$ and CaIrO$_3$. Literature analysis shows that the oxygen states in perovskite-like systems are rather complex and ambiguous to interpret. However, the O 1s peak at Eb = 529.3 eV may be assigned to the lattice oxygen O$_2^-$, and the peak at Eb = 531.2 eV is the characteristics of oxygen vacancy, whereas the peak at the highest binding energy is assigned to water molecules adsorbed on the surface. In the Ir 4f region of Figure 5f, the 4f$_{7/2}$ peak shows a major feature at 62.8 eV and a smaller component at 64.1 eV. The former may be attributed to the presence of Ir$^{4+}$, as in IrO$_2$, whereas the higher energy feature may indicate the presence of some iridium oxidized beyond $+4$. In the Ir 4f region of Figure 5e, the proportion of the peak at 64.1 eV increases, which means the proportion of higher valence iridium increases. Therefore, we get the result that there is no relationship between the iridium valence state and the OER catalytic activity of perovskites.

3.4. XAS Spectroscopy and Related Analysis. Figure 6a shows Ir L$_{III}$-edge X-ray absorption near-edge structure (XANES) spectra of Ca$_3$IrO$_4$, CaIrO$_3$, and IrO$_2$ compositions, (a) normalized Ir L$_{III}$-edge XANES spectra, (b) second derivative of Ir L$_{III}$-edge XANES, and (c) Fourier transforms of the $k^3$-normalized Ir L$_{III}$-edge EXAFS are shown; crystal structures of (d) CaIrO$_3$ and (e) Ca$_2$IrO$_4$. The dotted rectangles are corresponded to different coordination bonds.

Figure 5. High-resolution XPS spectra of (a) O 1s, (b) Ca 2p, and (c) Ir 4f in Ca$_2$IrO$_4$ and (d) O 1s, (e) Ca 2p, and (f) Ir 4f in CaIrO$_3$. The dashed lines show the binding energy position of Ir 4f in IrO$_2$. Figure 6. For Ca$_3$IrO$_4$, CaIrO$_3$, and IrO$_2$ compositions, (a) normalized Ir L$_{III}$-edge XANES spectra, (b) second derivative of Ir L$_{III}$-edge XANES, and (c) Fourier transforms of the $k^3$-normalized Ir L$_{III}$-edge EXAFS are shown; crystal structures of (d) CaIrO$_3$ and (e) Ca$_2$IrO$_4$. The dotted rectangles are corresponded to different coordination bonds.
consistent with the result acquired in XPS. Because the Ir L_{III} edge in these three samples are almost overlapped, the second derivative (see in Figure 6b) gives the change in the oxidation state, and the same conclusion is given. The higher valence of Ir promises a shorter bond of Ir–O in Ca$_2$IrO$_4$ than in IrO$_2$.

Fourier transforms of the k$^2$-normalized Ir L$_{III}$-edge extended X-ray absorption fine structure (EXAFS) for Ca$_2$IrO$_4$ and IrO$_2$ compositions are shown in Figure 6c, and the k-range is 3–12.5 Å. The first peak is mainly formed by the Ir–O bond from IrO$_6$ coordination.$^9$ As a result, it can be clearly found that Ca$_2$IrO$_4$ has a smaller R value than IrO$_2$ implying that the Ir–O bond in Ca$_2$IrO$_4$ is a little bit shorter. The Ir–O bonds in IrO$_2$ are four long plane bonds of 1.99 Å and two short apical bonds of 1.96 Å, whereas three different pairs of bonds in Ca$_2$IrO$_4$, whose lengths are 2.01, 2.04, and 1.98 Å, give rise to a distorted octahedral configuration.

The second peak arises mainly from Ir–Ir, which corresponds to the c axis length of 3.16 Å for IrO$_2$. For Ca$_2$IrO$_4$, the Ir–Ir bond length is 3.19 Å, which is obvious that the Ir–Ir distance of Ca$_2$IrO$_4$ is almost the same as that of IrO$_2$. It comes to the same conclusion that Ir–Ir peaks correspond to similar resultant values. Therefore, we can deduce from the XPS and XAS data that less electrons occupy the 5d states, and similar resultant values. Therefore, we can deduce from the XPS and XAS data that less electrons occupy the 5d states, and thus exhibits a high OER activity.

In Ca$_2$IrO$_4$, the IrO$_6$ octahedron has an obviously compressed character (see in Figure 6d), in which the Ir–Ir bond length is 3.19 Å, which is obvious that the Ir–Ir distance of Ca$_2$IrO$_4$ is almost the same as that of IrO$_2$. In Ca$_2$IrO$_4$, three pairs of Ir–O bonds with different lengths (2.01, 2.04, and 1.98 Å), as shown in Figure 6e, clarifies the fact that the octahedral coordination is intensively distorted, where the unequal length bonds not only exist in an apical direction, but also in the four planar Ir–O bonds. The properties associated to Ir–O bonds in Ca$_2$IrO$_4$ present asymmetric and uneven distribution of charge density, whereas it is symmetric and uniform in the case of CaIrO$_3$ in their 4-coordination plane.

As the investigation of our laboratory on the Cu-doped IrO$_2$, the Cu replacement of the Ir site in IrO$_2$ gives rise to a distortion of the IrO$_6$ coordination due to a strong Jahn-Teller effect of CuO$_{6}$ and results in higher OER activity compared with pure IrO$_2$. $^6$ K$_{\text{Cu}}$IrO$_2$ contains distorted IrO$_6$ octahedron, which changes its electronic structure, and thus exhibits a high OER activity. Reier et al. reported that Ir–Ni oxides offer an excellent OER activity, and the O K-edge XANES also showed the changes in electron distributions of Ir–O bonds.$^3$

In summary, the enhancement in the OER activity results from the IrO$_6$ coordination transformation. The Ca$_2$IrO$_4$ has a strong distorted IrO$_6$ geometry because of different Ir–O bond lengths, whereas the CaIrO$_3$ gives a $D_{2h}$ symmetry IrO$_6$ octahedron. The distorted IrO$_6$ octahedron promotes the OER activity, whereas the symmetry one does not. Therefore, Ca$_2$IrO$_4$ exhibits an outstanding catalytic performance in water splitting.

4. CONCLUSIONS

In our current conducted research work, we provide a new method synthesizing the Ca$_2$IrO$_4$ and CaIrO$_3$ at atmospheric pressure. In the electrochemical experiments, we prove that the OER activity of Ca$_2$IrO$_4$ is higher than that of IrO$_2$, whereas CaIrO$_3$ shows no OER activity. The XPS and XAS data show that a higher valence of the Ir site in Ca$_2$IrO$_4$ and CaIrO$_3$. The distorted octahedral symmetry leads to a strong interaction between Ir 5d states and oxygen intermediates. Therefore, we come to the conclusion that the key factor affecting the OER activity of the perovskite is the IrO$_6$ octahedral distortion.

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