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Research article

Mixed B-site ruddlesden-popper phase $Sr_2(Ru_xIr_{1-x})O_4$ enables enhanced activity for oxygen evolution reaction

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ABSTRACT

Development of high performance electrocatalysts for oxygen evolution reaction (OER) in acidic media remains a challenge for direct water splitting using an electrolyzer. Recently, Ruddlesden-Popper phase Sr_2IrO_4 was discovered to be an efficient OER catalyst because of its unique structure, which consists of layers of both rock salt and perovskite phases simultaneously. In this study, we prepared a series of B-site mixed, Ruddlesden-Popper phase of $Sr_2(Ru_xIr_{1-x})O_4$ and examined their electrocatalytic properties for OER in acidic media. Through partial substitution of Ru in the B-site of Ruddlesden-Popper phase materials, we achieved much enhanced OER performance for this series of $Sr_2(Ru_xIr_{1-x})O_4$ electrocatalysts, among which $Sr_2(Ru_0.5Ir_{0.5})O_4$ exhibited the best catalytic activity with a current density of 8.06 mA/ cm² at 1.55 V and a Tafel slope of 47 mV/dec. This current density is three times higher than that of Sr_2IrO_4 . The B-site mixed $Sr_2(Ru_0.5Ir_{0.5})O_4$ retained good stability in acidic conditions for > 24 h at 10 mA/cm². A range of techniques were used to characterize the crystal and electronic structures of the $Sr_2(Ru_xIr_{1-x})O_4$ samples. Our data indicate that the improved OER performance can be correlated to the formation of high level of hydroxyl groups and the enhanced overlap between Ir/Ru 4d and O 2p orbitals, revealing a new way for the design of efficient OER electrocatalysts by regulating their composition and electronic structures.

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1. Introduction

Hydrogen production through water splitting is an energy conversion and storage technology that could be significant for the energy transition to a carbon-neutral society [1-3]. In a water electrolyzer, the rate of oxygen evolution reaction (OER) at anode is usually slow, because of the sluggish kinetics of the fourelectron (4e⁻) transfer process [4–8]. Acidic media are preferred in cases over the alkaline systems because of the high ionic (proton) conductivity, low ohmic loss, and fewer side reactions at low temperature. Currently, there is no alkaline membrane that can be compared with Nafion in ion transport properties. Thus, acidic electrolyzers have been actively studied for the intermittent energy supply from renewables and for the store of electric energy in the form of chemical energy in hydrogen [9–14]. Iridium- and ruthenium-based oxides are considered as state-of-the-art OER electrocatalysts in acidic media because of their good stability

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and performance [15,16]. The scarcity of iridium in Earth crust may limit its potential for large-scale applications, whereas Rubased electrocatalysts are relatively more earth-abundant [17,18]. Therefore, it is important to develop new OER electrocatalysts in acidic media with both high activity and stability at the reduced use of Ir.

Recently, Ruddlesden-Popper phase Sr_2IrO_4 has attracted increasing interests as an OER electrocatalyst because of its unique layered structure, which is consisted of both rock salt and perovskite layers, where IrO_6 octahedrons are considered as the catalytically active sub-units [7,19–21]. Substitution of metal cation is an effective strategy to regulate the lattice structures of the octahedrons which may change the catalytic performance [22–24]. Crystal structure, oxidation state, concentration of surface binding groups and electronic structure are a few important structural parameters that could be controlled through the substitution of alterative elements. For these OER oxide electrocatalysts, lattice oxygen-mediated mechanism (LOM) was recently identified, which suggests the activity of these systems could overcome the kinetic limitations based on the conventional adsorbate evolution mechanism (AEM) [25–27]. In LOM, water reacts with lattice oxy-

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gen instead of metal sites, and oxygen vacancies are formed while O₂ is generated:

O_{lat} + $H_2O \rightarrow V_0$ + O_2 + $2H^+$ + $2e^-$.

In the LOM, energy barrier is lowered than that based on AEM, resulting in a higher OER activity [23,27,28]. The involvement of lattice oxygen in reaction and the formation of oxygen vacancies and soluble high-valence intermediates often lead to the change of structures of the catalysts [29–33]. The adsorption of hydroxyl groups on the active sites of the catalysts is a crucial step in both AEM and LOM mechanisms, these hydroxyl groups either adsorb on the metal elements in AEM, or fill the oxygen vacancies when participate a LOM process. In addition, the hydroxyl adsorption is identified as the rate determining step in LOM. Thus the surface coverage of hydroxyl groups was determined as an activity descriptor for OER catalysts [34–38]. Metal substitution usually helps creation of the hydroxyl groups on the surface.

Herewith, we describe the use of this strategy to develop Ruddlesden-Popper phase-derived electrocatalysts [10.22]. Specifically, a series of mixed B-site, Ruddlesden-Popper $Sr_2(Ru_xIr_{1-x})O_4$ (denoted as SRIO-x) oxides were created for OER electrocatalysts in acidic media. Porous, mixed B-site pyrochlore was previously showed to possess much improved OER activities due to the high surface area and likely also the disordered nature of lattice [11]. Thus, we hypothesize that introducing Ru into the B site of Sr₂IrO₄ (denoted as SIO) may increase the disordering of the lattice structures and enhance the OER activity, while retaining the stability. Our findings showed that the mixed B-site Ruddlesden-Popper phase $Sr_2(Ru_xIr_{1-x})O_4$ indeed exhibited much higher current density and smaller overpotential than SIO, among which Sr₂(Ru_{0.5}-Ir_{0.5})O₄ showed the highest OER current density. Our structureproperty relationship study suggests that the formation of hydroxyl groups and distortion of IrO₆ octahedrons play important roles in the enhanced OER performance, providing a new way for the design of electrocatalysts.

2. Experimental section

2.1. Chemicals

Strontium carbonate (SrCO₃, 99.9%), ruthenium (IV) oxide (RuO₂, 99.9%), Nafion[®] 117 solution (~5%) were purchased from Sigma-Aldrich. Iridium (IV) oxide (IrO₂, 99.9%) was purchased from Alfa Aesar. Citric acid monohydrate (C₆H₈O₇ · H₂O, 99%) and sodium hydroxide (NaOH, 99.4%) were from Fisher Chemical. Veritas[®] double distilled perchloric acid (HClO₄, 70%) was obtained from GFS Chemicals. Tetrahydrofuran (THF) was obtained from Macron Fine Chemicals. Vulcan carbon XC-72 was purchased from Cabot Corporation. Hydrogen (H₂, 99.999%) and oxygen (O₂, 99.999%) were supplied by Airgas, Inc. Carbon paper (Sigracet 29 BC) was purchased from Fuel Cell Store. All chemicals and gases were used without further purification. Deionized water was obtained after passing through Barnstead E-pure water purification system (18.2 MΩ cm, Thermo Fisher Scientific).

2.2. Preparation of $Sr_2(Ru_xIr_{1-x})O_4$ compounds

Samples were prepared by the solid-state method. In a standard procedure, 147.6 mg of SrCO₃ was mixed with predetermined amounts of IrO₂ and RuO₂ powders. The IrO₂/RuO₂ ratios used in the synthesis were 89.7 mg/13.3 mg for making Sr₂(Ru_{0.2}Ir_{0.8})O₄, 67.3 mg/26.6 mg for Sr₂(Ru_{0.4}Ir_{0.6})O₄, 56.1 mg/33.3 mg for Sr₂(-Ru_{0.5}Ir_{0.5})O₄, 44.8 mg/39.9 mg for Sr₂(Ru_{0.6}Ir_{0.4})O₄, and 22.4 mg/53.2 mg for Sr₂(Ru_{0.8}Ir_{0.2})O₄. This mixture was then ball-milled for 2 h in a rotary ball mill (Fritsch Planetary Micro-Mill) using a

12-mL crucible equipped with five 12-mm agate balls. The wellmixed powders were collected and placed in an alumina boat (Sigma-Aldrich, 5 mL) and then transferred to a tube furnace (MTI GSL-1500X). The temperature of the furnace was raised at a heating rate of 3 °C/min to 1200 °C and kept for 15 min before it was cooled to room temperature also at a rate of 3 °C/min in air. The powder sample was then grounded using pestle and mortar for 20 min. A disposable spatula was used to mix the sample several times during the grinding process. Finally, the sample was transferred to a tube furnace and heated again, following the same procedure mentioned in the above. The as-prepared samples were black in color.

Preparation of Sr₂IrO₄

The preparation method was the same as those for making the $Sr_2(Ru_xIr_{1-x})O_4$ series, except the amounts of the precursors used were 147.6 mg of SrCO₃ and 112.1 mg of IrO₂.

Preparation of Sr₂RuO₄

The preparation method was the same as those for making the $Sr_2(Ru_x Ir_{1-x})O_4$ series, except the amounts of the precursors used were 147.6 mg of SrCO₃ and 66.5 mg of RuO₂.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were measured between 10° and 80° 2 θ at a scan rate of 0.02° 2 θ per second using a Rigaku Miniflex 600 diffractometer with Cu K_{α} X-ray source (λ = 0.154056 nm). X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos Axis ULTRA with Al K_{α} X-ray source to determine the binding energy. All samples were directly measured on copper tape. The data processing and peak fitting were performed using the CasaXPS software.

Scanning electron microscopy (SEM) images were obtained on a Hitachi S4700 microscope at an acceleration voltage of 15 kV. The SEM specimen was prepared by depositing the catalyst powder on a carbon tape on an SEM stub. Transmission electron microscopy (TEM) micrographs were obtained using JEOL 2100 Cryo TEM with a LaB₆ emitter at 200 kV. For the preparation of TEM samples, electrocatalyst materials were scratched off from the electrodes using a plastic spatula. The obtained powder sample was sonicated in ethanol for 30 min to form a uniform dispersion. One drop of dispersion was deposited on a TEM grid (CF400-CU, carbon film, 400 mesh copper) and dried at room temperature for about 10 min to make a specimen. Energy dispersive X-ray fluorescence (EDXRF) analysis was performed on a Shimadzu EDX-700 spectrometer with Rh X-ray source. The specimens of electrodes were directly loaded on the sample holder for testing.

2.4. Study of electrocatalytic performance

Preparation of catalyst inks

Vulcan carbon XC-72 was used as the support for these catalysts. The Nafion solution with pH of 7 was prepared using Nafion 117 aqueous solution mixed with 0.1 M NaOH solution. To prepare an ink, 2 mg of catalysts, 2 mg of carbon black, and 3 μ L of neutralized Nafion solution were added in 2 mL of THF in a 16-mL vial with Teflon cap, followed by placing it in an ice bath to sonicate for 30 min.

Preparation of electrodes

In a typical procedure, 5 μ L of the prepared ink was dropped onto a glassy carbon rotating disk electrode (RDE). After the ink dried for about 5 min, 5 μ L of a Nafion-THF solution (3 μ L neutralized Nafion solution in 2 mL of THF) was dropped twice onto the RDE (0.196 cm²) in about 2 min.

Preparation of electrodes for chronopotentiometry test

Carbon paper was used as the substrate for the chronopotentiometry test. The dimension of the carbon paper was 1 cm wide and 3 cm long, with a working area of 1 cm \times 1 cm, which was covered by the ink. In a typical procedure, 0.75 mL of the prepared ink was dropped onto the carbon paper several times using a 100-µL pipette, followed by adding 0.3 mL of a Nafion-THF solution (15 µL neutralized Nafion solution in a 2 mL of THF) dropwise onto the same carbon paper.

Electrochemical study

Electrochemical measurements were performed in a threeelectrode cell using a CHI 760B potentiostat (CH Instruments, Inc.). The catalyst-loaded RDE was used as the working electrode, a platinum wire connected with platinum foil as the counter, and a hydrogen electrode (HydroFlex) as the reference. The reference electrode was calibrated in H₂-saturated 0.1-M HClO₄ solution before the tests. OER measurements (i.e., polarization) were performed after purging with O₂ in this HClO₄ solution for at least 30 min. Cyclic voltammetry (CV) curves were recorded from 1.1 to 1.6 V versus RHE at a rate of 10 mV/s under a rotating speed of 1600 r/min after the completion of the conditioning step, namely, the initial cycle.

Electrochemical impedance spectroscopy (EIS) measurements were performed at three different potential values, with a frequency range from 1×10^4 to 0.1 Hz. For each test, 10 µL of ink was deposited onto the RDE. The impedance spectra were presented in the form of Nyquist plot and fit using ZView software. The equivalent electrical circuit of EIS data is consisted of three components: solution resistance (R_{sol}), charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}). The double layer capacitance was used to describe the surface roughness of the electrocatalysts, and it is regarded as a constant phase element (CPE), which is composed of CPE-P (n, the semicircle in the Nyquist plot) and CPE-T (Q, pseudo capacitance).

3. Result and discussion

Fig. 1(a and b) show the powder XRD patterns of the powder samples. When no Ru element was added (x = 0), the XRD peaks could be fitted to the tetragonal phase of Sr₂IrO₄ (I41/acd, JCPDS 01-070-4305) (Fig. 1c). Similarly, when no Ir element was used (x = 1), the tetragonal phase of Sr₂RuO₄ (I4/mmm, JCPDS 01-081-1977) formed. Noticeably, Sr₂IrO₄ structure is composed of SrO rock salt and SrIrO₃ perovskite layers along *c*-axis. The cornershared IrO₆ octahedrons can be subjective to large degrees of distortion and identified as the active structures of OER catalysts [39,40]. This structure could result in controls over the lattice oxygen structures and the corresponding electronic configures of octahedral building units, which are important for OER performance [41–43].

For the mixed B-site compounds, all XRD peaks could be fitted to the Ruddlesden-Popper tetragonal phase. No extra peak was detected, suggesting these compounds were phase pure across the entire composition range. Fig. 1(b) shows the shift in 2θ for (116) and (200) diffractions of SIO as a function of metal composition. The XRD peaks shifted to higher angles and closer to the pure phase of Sr₂RuO₄ (denoted as SRO) when more Ru was added, indicating the change of crystal structure when Ru was incorporated into the B site. Rietveld refinement was used to analyze this change in crystal structure and the results were summarized in Table S1. When x value is equal to 0 and 1, the space group is I41/acd and I41/mmm, respectively (Fig. 1c and d) [44–47]. The substitution of Ru⁴⁺ cation greatly changes the lattice geometry and subsequently the electronic environment, affecting the catalytic activity through modulating the crystal structures.

Fig. 1(e) shows the SEM image of SRIO-0.6. The powder samples are uniform with a typical particle size of around 1 μ m or less. All of the other SRIO-*x* samples had similar morphologies and sizes, as shown in SEM images (Fig. S1). Representative TEM micrograph shows the lattice structure of the SRIO-0.6 sample (Fig. 1f). The as-made catalyst powder shown in the TEM micrograph has a *d*spacing of around 0.280 nm, which corresponds to the (103) plane of Ruddlesden-Popper in I4/mmm space group. The atomic ratio of the samples was characterized by X-ray fluorescence (XRF) technique, which is fairly consistent with the feeding ratio of the metal precursors within the errors of measurements (Table S2).

The OER performances of SRIO-*x* series and the reference RuO₂ electrocatalysts were evaluated in 0.1 M HClO₄ aqueous solution using a three-electrode system and the rotating disc electrode (RDE) technique. Fig. 2(a) shows the polarization curves after the iR correction The SIO sample exhibited a current density of around 7.8 mA/cm² at 1.6 V, which almost doubles the performance of RuO₂. On the other hand, SRO showed negligible activity, likely due to its poor stability in acidic media [48,49]. In comparison, all the mixed B-site samples exhibit higher current density and lower overpotential than SIO. Among the samples tested, SRIO-0.5 shows the highest performance with a current density of 8.06 mA/cm² at 1.55 V, which is about three and six times higher than that of Sr_2IrO_4 (2.88 mA/cm²) and RuO_2 (1.34 mA/cm²), respectively. The OER mass activity was found to be 0.55 A/mg measured at 1.6 V vs. RHE for SRIO-0.5 and 0.3 A/mg for SIO (Fig. 2b). The OER mass activity of SRIO-0.5 was 3.7 times of that for the reference RuO₂ (0.15 A/mg). This result indicates Ru substitution in SIO resulted in the high OER performance.

Fig. 2(c) shows the Tafel plots of these SRIO-x catalysts, which show all the mixed B-site samples exhibit smaller slopes than that of SIO. The SRIO-0.5 electrocatalyst exhibits the smallest Tafel slope of 47.6 mV/dec, much lower than the value of 59.3 mV/dec for SIO. According to Butler-Volmer equation [50], the Tafel slope is inversely proportional to the charge transfer coefficient, thereby B-site substitution with Ru effectively accelerates OER kinetics. The stability was tested using the chronopotentiometry technique at a current density of 10 mA/cm² for 24 h, as shown in Fig. 2(d). We found that the SIO and SRIO-x were quite stable, retaining the low overpotentials, among which SRIO-0.5 exhibited the lowest overpotential of ~280 mV after 24-h test. Our stability study shows when the Ir/Ru ratio is close the unity, the catalysts have both high activity and high stability. The pure SRO catalyst however appeared to dissolve rapidly and lost its activity within the first 2 min. In comparison, the potential for RuO₂ jumped after about 6 h. Thus, a balanced metal composition between Ir and Ru is crucial for the high stability. Table S3 lists the catalytic performance of some Ru and Ir-based catalysts for OER in acidic media. Compared with other catalysts, SRIO-0.5 is most stable in acid with a smallest Tafel slope, indicating that B-site substitution is an effective strategy for the design of OER catalysts with balanced high stability and performance in acidic media.

To gain a better understanding of the electrochemical properties of the SRIO-*x* series, EIS measurements were performed at three different potentials: 0 V, onset potential (1.42 V for x = 0.4-0.8, 1.45 V for x = 0.2, 1.47 V for x = 0 and 1), and 1.50 V. The Nyquist plots are shown in Fig. 3 and Fig. S2. When no potential was applied (0 V) (Fig. S2a and Table S4), the charge transfer resistance (R_{ct}), which reflects the intrinsic conductivity, was 6.1 k Ω for SIO, lower than all the samples expect SRIO-0.2, indicating majority of the SRIO-*x* samples were electrically more resistive than SIO (Table S4). When measured at their corresponding onset potentials, the resistance SRIO-0.5 was the lowest among all the samples, and the resistance of SIO and SRIO-0.2 became the highest



Fig. 1. (a and b) XRD patterns of as-made Sr₂(Ru_xIr_{1-x})O₄ compounds in two different 20 ranges; crystal structures of Ruddlesden-Popper phase of (c) Sr₂IrO₄ (tetragonal, I41/ acd) and (d) Sr₂RuO₄ (tetragonal, I4/mmm); and (e) SEM image and (f) TEM micrograph of the mixed-B site Sr₂(Ru_{0.6}Ir_{0.4})O₄ compound.

(Table S5). At a higher potential of 1.50 V, the charge transfer resistances (R_{ct}) of all the SRIO-x electrocatalysts decreased dramatically to facilitate interfacial electron transfer, and became much lower than that of SIO (Table S6). The EIS study indicates that all the SRIO-x samples exhibit faster kinetics than SIO and SRO under the same operating potentials for OER.

X-ray photoelectron spectroscopy was carried out to study the surface properties of SRIO-*x* samples (Fig. 4, and Tables S7–S9). Fig. 4(a and b) show the XPS scans and fits of Ir 4*f* and Ru 3*d* regions, respectively. No obvious peak shift was detected in these two regions with the substitution of Ru, indicating that the oxidation state of Ru and Ir did not have detectable changes and retained their valence in these SRIO-*x* electrocatalysts, and the valence states of Ir and Ru are both + 4 (Tables S7 and S8) [43,51,52]. The density of hydroxyl group of these catalysts were probed by XPS in O 1s region [53,54]. Fig. 4(c) shows the O 1s region of these SRIO-*x* catalysts, which can be fitted into three peaks: surface lattice oxygen (O_{lat}) centered at 529.2 eV, hydroxyl groups at

531.1 eV, and adsorbed water at 532.8 eV. The surface hydroxyl groups act as active sites of the catalytic process, so the concentration of hydroxyl groups is regarded as a suitable descriptor for the activity of OER [53,54]. Among these samples, SRIO-0.4 shows highest population of hydroxyl groups, followed by SRIO-0.6 and SRIO-0.5, indicating that the samples with higher hydroxyl density usually exhibit higher OER activity (Fig. 2a). This result strongly suggests the correlation between the surface hydroxyl groups with the OER performances of SRIO-*x* series [53,54].

The performance trend of the enhanced OER catalytic activity for this SRIO-*x* series was further analyzed based on the lattice structures, which affect the electronic configurations. Fig. 5(a and b) show the crystal structures of SIO (x = 0) and SRO (x = 1) catalysts. The crystal structures indicate the Ir/Ru-O-Ir/Ru bond angle increases from 152.7° when *x* is equal to 0 to 180° when *x* is equal to 1, corresponding to the space group change from I41/acd to I41/ mmm. With the increased amount of Ir being replaced by Ru, the distortion of the RuO₆/IrO₆ octahedron along *z*-axis decreases.



Fig. 2. OER performance of SRIO-x series and reference RuO₂ electrocatalysts. (a) CV curves in 0.1 M HClO₄, (b) mass activities at 1.6 V, and (c) Tafel and (d) chronopotentiometry plots.



Fig. 3. Nyquist plots of SRIO-x, SIO, and SRO electrocatalysts at (a) onset potential, and (b) 1.50 V, respectively.

When Ir^{4+} is partially replaced by Ru^{4+} , the coordination is modulated and the corresponding electronic structures are affected. For SRIO-*x*, the enlarged Ru/Ir-O-Ru/Ir bond angle and alleviated Ru/ IrO₆ distortion could promote B-site metal cation 4d/5d-O 2*p* orbital overlap spatially to broaden the bandwidth near the Fermi level (*E*_F) [22,55]. Such change in bond structure and the corresponding change in electron structure facilitate the enhancement of catalytic activity [56,57]. When Ru cation further substitutes Ir after *x* reaches 0.5, the phase of the mixed B-site compounds gradually dominates by the SRO structure. The OER performance decreases with the increase of *x* value, which may be due to the unfavored crystal phase of 141/mmm for OER [10,42,58]. Our results of the lattice characterizations and the corresponding electronic structure analysis suggest the crystal and electronic structures play the key roles for the observed high performance of the mixed B-site electrocatalysts.

4. Conclusions

In summary, we developed the mixed B-site Ruddlesden-Popper $Sr_2(Ru_xIr_{1-x})O_4$ compounds and showed the superior OER activity and stability in acidic media. At the Ru/Ir ratio of 0.5/0.5, the electrocatalyst exhibits the best performance with a current density of 8.06 mA/cm² at 1.55 V and the Tafel slope around 47 mV/dec. The catalyst also retained a low overpotential of 280 mV in acid for 24 h at a current density of 10 mA/cm². XPS analysis reveals abundant hydroxyl groups on the surface for $Sr_2(Ru_xIr_{1-x})O_4$



Fig. 4. XPS scans of (a) Ir 4f, (b) Ru 3d and (c) O 1 s regions of SRIO-x, SIO, and SRO electrocatalysts, respectively.



Fig. 5. Illustration of crystal structures of (a) SIO, (b) SRO, and (c) IrO₆/RuO₆ octahedral building blocks of SIO (left), SRIO (middle), and SRO (right), respectively.

(x = 0.4, 0.5, 0.6), which could form from rich oxygen species through the metal substitution. The studies on the electronic structures of SRIO-*x* also suggests that large Ru-O-Ru bond angle leads to a broadened Ru 4*d* band, which is beneficial to the fast OER kinetics. This work provides new evident to support the idea of surface hydroxyl groups favoring the OER, and provides an approach to the design of highly active oxygen electrocatalysts in acidic media.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jechem.2022.02.051.

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