Rare-earth-regulated Ru–O interaction within the pyrochlore ruthenate for electrocatalytic oxygen evolution in acidic media

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ABSTRACT Ruthenium-based catalyst is one of the most active catalysts for oxygen evolution reaction (OER) in acid media. However, the strong bonding between the Ru sites and oxygen intermediates leads to high overpotential to trigger the OER process. Hence, pyrochlore rare-earth ruthenate ($\text{RE}_2\text{-Ru}_2\text{O}_7$) structures with a series of rare-earth elements (Nd, Sm, Gd, Er, and Yb) were constructed to tune the electronic structure of the Ru sites. Surface structure analysis indicated that the increase of the radius of the rare-earth cations resulted in higher content of defective oxygen (the percentage of the defective oxygen increased from 29.5% to 49.7%) in the $\text{RE}_2\text{Ru}_2\text{O}_7$ structure due to the weakened hybridization of the Ru–O bond. This reduced the valence states of the Ru sites and enlarged the gap between the 4d band center and the Fermi level (E_F) of Ru, resulting in the weakened adsorption of oxygen intermediates and the improved OER performance in acid media. Among the as-prepared ruthenium pyrochlores, $\text{Nd}_2\text{Ru}_2\text{O}_7$ displayed the lowest OER onset overpotential (210 mV) and Tafel slope (58.48 mV dec^{-1}), as well as 30 times higher intrinsic activity and much higher durability than the state-of-art RuO_2 catalyst.

Keywords: oxygen evolution, ruthenium pyrochlore, rare earth elements, defective oxygen, d band center, valence state

INTRODUCTION

The increasing demand of energy and deteriorating environmental crisis call for alternative clean energy to fossil fuel. Electrochemical water splitting, which converts the electricity to chemical energy carrier (H_2), offers a viable strategy [1–6]. At present, proton exchange membrane (PEM) electrolyzers [7–9], operating in acidic media,

have many advantages over alkaline electrolyzers, such as higher efficiency and higher hydrogen purity [10]. However, the sluggish kinetics of the anode reaction (OER) impedes the industrialization of PEM-based electrolysis [11]. Catalysts working in harsh environment especially at low pH are still limited to noble-metal-based materials such as RuO_2 and IrO_2 [12]. Theoretical studies reveal that optimal OER catalysts are supposed to possess neither too strong nor too weak binding strengths to oxygen intermediates [13]. Previous research reports that both RuO_2 and IrO_2 are expected to bind oxygen intermediates too strongly, and thereby hinder the desorption of oxygen intermediates, which restricts the OER performance in acidic media [14]. Compared with iridium dioxide, ruthenium dioxides possess higher activity and lower expense [15]. However, ruthenium dioxide is easily oxidized to RuO_4 at high working potential [16,17], which is expected to result in loss of active sites and instability during the OER process.

Confining Ru in multi-metal oxides has been reported as a promising strategy to enhance the activity and stability of Ru-based catalysts *via* modulating the coordination environment of Ru site [18–20]. For example, Retuerto *et al.* [21] reported $\text{La}_{1.5}\text{Sr}_{0.5}\text{NiMn}_{0.5}\text{Ru}_{0.5}\text{O}_6$ double perovskite with 430 mV overpotential and enhanced durability than RuO_2 . Miao *et al.* [22] reported a quadruple perovskite oxide $\text{CaCu}_3\text{Ru}_4\text{O}_{12}$ as an active catalyst for acidic water oxidation, which exhibits better activity and stability than the state-of-the-art RuO_2 due to optimized binding energy of oxygen intermediates. Recently, pyrochlore-type oxides ($\text{A}_2\text{B}_2\text{O}_7$), which possess stable structure, such as $\text{Y}_2\text{Ru}_2\text{O}_{7-\delta}$ [23], $\text{Bi}_2\text{Ir}_2\text{O}_7$ [24],

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and $\text{PbBiIr}_2\text{O}_{6.5}$ [25] have been reported as a sort of promising catalysts for oxidation reactions [26], in which A atoms close to BO_6 octahedral can efficiently modulate the electron density of B atoms and stabilize the B sites [23].

Given the unique electron configuration of rare earth (RE) elements that the 4f orbits are not fully filled [27,28], which could interact with the electrons of Ru, herein a series of pyrochlore RE ruthenates ($\text{RE}_2\text{Ru}_2\text{O}_7$) electrocatalysts were synthesized by a simple sol-gel approach to explore the correlation between the electronic structure and the catalytic activity. It was noted that as the radius of the RE ions increased, the intrinsic activity of the catalysts displayed a significant improvement. Typically, $\text{Nd}_2\text{Ru}_2\text{O}_7$ exhibited the best OER performance with the lowest onset overpotential (210 mV, which is 170 mV smaller than that of RuO_2) and improved stability compared with RuO_2 . XPS analysis revealed that the relative content of oxygen vacancies increased as the RE radius increases, leading to reduced average valence state of Ru. Density functional theory (DFT) calculation showed that the negative shift of d band center of Ru modulated the adsorption of oxygen intermediate, which promoted the OER kinetics.

EXPERIMENTAL SECTION

Chemicals

$\text{RE}(\text{NO}_3)_3$ (analytical reagent (AR) grade, Beijing HWRK Chem Co., LTD), $\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y$ (AR grade, J&K), citric acid (AR grade, Beijing Chemical Works), and HClO_4 (Beijing Chemical Works) were used.

Synthesis of $\text{RE}_2\text{Ru}_2\text{O}_7$

All the $\text{RE}_2\text{Ru}_2\text{O}_7$ catalysts were prepared by sol-gel approach. $\text{RE}(\text{NO}_3)_3$ (0.25 mmol) and $\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y$ (1684.5 μL) were dissolved in 5 mL deionized (DI) water in a 20-mL vial under ultrasonication. Then, 0.221 g of citric acid was added into the above solution for 30 min. After that the vial was heated in an oil bath at 80°C for 8 h until all the water was vaporized to get the powder precursor. The precursor then was transferred into a tube furnace, and heated at 600°C for 6 h and 1000°C for 12 h at the rate of 5°C min^{-1} .

Material characterization

The crystalline structures of all $\text{RE}(\text{NO}_3)_3$ samples were characterized by X-ray diffraction (XRD) analysis using Shimadzu XRD-6000 diffractometer (Cu K α source, $\lambda = 1.5418 \text{ \AA}$). The morphology was characterized by scan-

ning electron microscope (SEM, Zeiss SUPRA 55, accelerating voltage of 20 kV) and transmission electron microscope (TEM, Hitachi-7700, 100 kV). The X-ray photoelectron spectroscopy (XPS) measurements were carried out with Thermo Electron ESCALAB250 XPS Spectrometer.

Electrochemical measurement

The catalyst ink was prepared by dispersing 5 mg of the synthesized catalyst in the solution containing 1 mL of ethanol and 10 μL of Nafion followed by ultrasonication for 1 h. The catalyst ink (30 μL) was deposited onto a glass carbon electrode (radius of 5 mm). All the electrochemical measurements were performed in a three-electrode system with Pt sheet as the counter electrode and $\text{Hg}/\text{Hg}_2\text{Cl}_2$ as the reference electrode. The HClO_4 solution (0.1 mol L^{-1}) was prepared by diluting the HClO_4 (0.4 mL) with DI water (49.6 mL). All the measured potentials were converted to the reversible hydrogen electrode (RHE) and corrected with *iR*-compensation. OER measurements were performed in 0.1 mol L^{-1} HClO_4 electrolyte with a CHI Electrochemical Workstation (CHI 660e) at a rotating speed of 1600 rpm. The polarization curves (linear sweep voltammetry (LSV)) were recorded with a scan rate of 5 mV s^{-1} after cyclic voltammetry (CV) curves (performed with a scan rate of 50 mV s^{-1}) got stable. The electrochemically active surface area (ECSA) was estimated by measuring the capacitive current related with double-layer charging from the scan-rate dependence of CV [10,22]. In details, the potential window of CV was 0.7–0.75 V vs. RHE, in which no reactions occurred. The scan rates were 2, 3, 4, 5, and 6 mV s^{-1} . The double layer capacitance (C_{dl}) was evaluated by plotting $\Delta J = (J^+ - J^-)/2$ at 0.725 V vs. RHE against the scan rate. The stability tests for $\text{Nd}_2\text{Ru}_2\text{O}_7$ and RuO_2 were carried out at 1 mA cm^{-2} following *iR* correction.

DFT calculation

The density of state (DOS) for Ru 4d and O 2p orbitals were acquired by DFT calculations, which were performed with the projector augmented wave (PAW) method using the Vienna *Ab-initio* Simulation Package (VASP). For all the calculations of $\text{RE}_2\text{Ru}_2\text{O}_7$ and RuO_2 models, the Generalized Gradient Approximation (GGA) of Perdew-Burke-Ernzerh (PBE) was used to describe the exchange and correlation energy density function. For $\text{RE}_2\text{Ru}_2\text{O}_7$ and RuO_2 , the bulk lattice was optimized using the 4 $\times$ 4 $\times$ 4 Monkhorst-Pack type of K-point sampling [23,29]. The models of $\text{RE}_2\text{Ru}_2\text{O}_7$ and RuO_2 bulk were displayed in the Supplementary information. The cutoff

energy was set to be 400 eV in this article. The maximum force and energy change were set as $0.01 \text{ eV } \text{\AA}^{-1}$ and 10–4 eV, respectively. The accuracy of all calculations was further improved by using DFT + U method describing correlation for 3d transition metal systems. The value of U was 4 for Ru and the U value was selected according to the literature [23].

RESULTS AND DISCUSSION

The $\text{RE}_2\text{Ru}_2\text{O}_7$ materials were synthesized by the sol-gel approach followed by thermal treatment in air (Fig. 1a). The precursors were prepared by coordination of rare-earth cations *via* citric acid [23]. The uniformly dispersed precursor solution ensured phase-pure synthesis of pyrochlore rare-earth ruthenate. The XRD patterns (Fig. 1b) of the as-prepared catalysts matched well with the stan-

dard diffraction pattern of pyrochlore-type $\text{RE}_2\text{Ru}_2\text{O}_7$ (PDF#28-0673 for $\text{Nd}_2\text{Ru}_2\text{O}_7$), which indicated that the as-prepared catalysts were phase-pure and well-crystallized. In addition, the (222) crystalline facet at around 30° in the enlarged diffraction patterns showed obvious positive shift from $\text{Nd}_2\text{Ru}_2\text{O}_7$ to $\text{Yb}_2\text{Ru}_2\text{O}_7$ (Fig. 1c), which could be attributed to the decrease of ionic radius from Nd ($0.995 \text{ \AA}$) to Yb ($0.858 \text{ \AA}$) [30]. The SEM images (Fig. 1d and Fig. S1) and TEM images (Fig. S2) indicated that the sizes of $\text{RE}_2\text{Ru}_2\text{O}_7$ were in the range of 100–200 nm. The energy-dispersive spectroscopy (EDS) images (Fig. 1d and Fig. S3) revealed that the RE elements and ruthenium were uniformly distributed throughout the particle, indicating the successful synthesis of pyrochlore oxides. Two kinds of oxygen exist in this $\text{RE}_2\text{Ru}_2\text{O}_7$ pyrochlore: one links RE_2O and Ru_2O_6 to form a network

Figure 1 (a) Illustration of the synthetic route for $\text{RE}_2\text{Ru}_2\text{O}_7$. (b) XRD patterns for $\text{RE}_2\text{Ru}_2\text{O}_7$. (c) Expanded XRD patterns of the as-prepared $\text{RE}_2\text{Ru}_2\text{O}_7$ in the $2\theta = 29^\circ$ – 32° region. (d) SEM image and EDS elemental mappings for $\text{Nd}_2\text{Ru}_2\text{O}_7$.

between the RE- and Ru-site, and the other connects to only the RE-site cations in the form of RE–O'–RE [31].

To investigate the effects caused by different RE elements on the activity of Ru pyrochlore catalysts, the OER performances of the $\text{RE}_2\text{Ru}_2\text{O}_7$ catalysts were compared with commercial RuO_2 in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ electrolyte in a three-electrode configuration. Before the LSV curves were recorded, the CVs were performed until the catalysts exhibited a stable state. The LSV curves normalized to geometric area are shown in Fig. S4. To compare the intrinsic activities, all the current densities were normalized to the ECSA (Figs S5, S6) [32]. As shown in Fig. 2a, the OER activities of the $\text{RE}_2\text{Ru}_2\text{O}_7$ electrocatalysts were closely related to the RE elements used. The RE ionic radii are 0.995, 0.964, 0.938, 0.881 and 0.858 Å for Nd, Sm, Gd, Er and Yb, respectively. The OER activity exhibited a linear dependence on the RE ionic radius. From Yb to Nd used, the current density of the $\text{RE}_2\text{Ru}_2\text{O}_7$ at the same potential increased gradually, and the onset potential decreased from 310 mV (Yb) to 210 mV (Nd). The current densities of $\text{RE}_2\text{Ru}_2\text{O}_7$ and RuO_2 at an applied potential of 1.54 V were compared (Fig. 2b). The $\text{Nd}_2\text{Ru}_2\text{O}_7$ possessed the highest current density of 10 A F^{-1} , which was 4.61, 10.11, 11.14, 39.06 and 30.30

times higher than that of Sm, Gd, Er, Yb and RuO_2 respectively. In addition, the overpotential of $\text{RE}_2\text{Ru}_2\text{O}_7$ and RuO_2 at a current density of 1 A F^{-1} were also compared. As shown in Fig. 2b, $\text{Nd}_2\text{Ru}_2\text{O}_7$ exhibited the lowest overpotential of 220 mV, which was 60, 90, 96, 190 and 160 mV smaller than the others respectively. As shown in Fig. 2c, the as-prepared $\text{Nd}_2\text{Ru}_2\text{O}_7$ exhibited the highest ECSA-normalized intrinsic activity for OER in acid among ruthenium-based and iridium-based catalysts reported recently [33–39]. To better understand the kinetics of the $\text{RE}_2\text{Ru}_2\text{O}_7$, the Tafel plots were measured (Fig. 2d). As reported in multi-electron reactions, different Tafel slope value means different rate determining step (RDS). The Tafel slope for $\text{RE}_2\text{Ru}_2\text{O}_7$ was in the range of 60–80 mV dec^{-1} (58.48, 58.98, 66.9, 79.07, 85.53 mV dec^{-1} for $\text{Nd}_2\text{Ru}_2\text{O}_7$, $\text{Sm}_2\text{Ru}_2\text{O}_7$, $\text{Gd}_2\text{Ru}_2\text{O}_7$, $\text{Er}_2\text{Ru}_2\text{O}_7$ and RuO_2) [40]. $\text{Nd}_2\text{Ru}_2\text{O}_7$ possessed the lowest Tafel slope among the above mentioned catalysts, indicating the fastest OER kinetics [41]. However, $\text{Yb}_2\text{Ru}_2\text{O}_7$ exhibited a much higher Tafel slope, suggesting a limited electron transfer. This indicated that the RE atoms could change the adsorption/desorption behavior of the catalytic active sites with the oxygen intermediates.

The electrochemical impedance spectroscopy (EIS)

Figure 2 Electrocatalytic OER performance of the catalysts in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ solution. (a) OER polarization curves of $\text{RE}_2\text{Ru}_2\text{O}_7$ and commercial RuO_2 with same loading. (b) Current density (left) @1.54 V vs. RHE and overpotential (right) @1 A F^{-1} . (c) Comparison of intrinsic activity@300 mV between the as-prepared catalysts and recently-reported catalysts. (d) The Tafel plots of $\text{RE}_2\text{Ru}_2\text{O}_7$ and commercial RuO_2 .

implemented at 1.5 V vs. RHE was adopted to further explore the OER kinetics. The Nyquist plots of $\text{RE}_2\text{Ru}_2\text{O}_7$ catalysts showed a near-semicircle shape, in which the radius represented the charge transfer resistance. Fig. S7 showed that $\text{Nd}_2\text{Ru}_2\text{O}_7$ and $\text{Sm}_2\text{Ru}_2\text{O}_7$ had relatively smaller charge transfer resistance than $\text{Gd}_2\text{Ru}_2\text{O}_7$, $\text{Er}_2\text{Ru}_2\text{O}_7$ and $\text{Yb}_2\text{Ru}_2\text{O}_7$, which indicated OER was more likely to occur. These results suggested that the intrinsic OER activity of $\text{RE}_2\text{Ru}_2\text{O}_7$ strongly depended on the RE ions used. Especially, Nd, Sm, Gd and Er could improve the OER activity of Ru, while Yb has a negative impact on the activity. The stability of $\text{Nd}_2\text{Ru}_2\text{O}_7$ and RuO_2 was tested under the same current density in 0.1 mol L^{-1}

HClO_4 (Fig. S8). $\text{Nd}_2\text{Ru}_2\text{O}_7$ could maintain its performance for 8 h, while RuO_2 decayed in less than 1 h. The improved stability demonstrated that RE atom could stabilize Ru sites and prevent their oxidation to higher valence state to be dissolved.

The surface chemical states were further investigated by XPS spectra (Fig. S9a). The 4d spectra of RE were consistent with RE^{3+} spectra [42], indicating the RE existed as RE^{3+} on the surface (Fig. S9a). To further elaborate the valence states of Ru on the surface, Ru 3p spectra (Fig. 3a) were analyzed instead of Ru 3d because the spectrum of carbon overlapped with the Ru 3d spectra (Fig. S9c). The small negative shift of the Ru 3p peaks of $\text{RE}_2\text{Ru}_2\text{O}_7$ in-

Figure 3 XPS spectra of $\text{RE}_2\text{Ru}_2\text{O}_7$. (a) Ru 3p. (b) O 1s. (c) Calculated contents of oxygen species and average valence state of Ru for $\text{RE}_2\text{Ru}_2\text{O}_7$.

dedicated decreased valence states of Ru from $\text{Yb}_2\text{Ru}_2\text{O}_7$ to $\text{Nd}_2\text{Ru}_2\text{O}_7$. All the Ru 3p spectra showed two peaks at 462.7 eV and 464.2 eV, which corresponded to Ru^{3+} and Ru^{4+} , respectively [35]. The ratios of Ru^{3+} to Ru^{4+} and the average valence states of Ru in the $\text{RE}_2\text{Ru}_2\text{O}_7$ were calculated and listed in Fig. 3c and Table S1. We found that the average valence state decreased as the RE ionic radius increased, and $\text{Nd}_2\text{Ru}_2\text{O}_7$ showed the lowest valence state of 3.68 in particular, which matched well with the relationship between activity and radius. Lower oxidation state of Ru possessed preferable OER kinetics, which could be attributed to more exposed unsaturated Ru active sites, thus possessing higher intrinsic activity [43,44]. Furthermore, improved stability was observed due to inhibited dissolution of Ru active sites as the valence state of Ru was below +4.

O 1s spectra (Fig. 3b) were also analyzed to understand the valence state change of Ru, peaks at 529.3 eV were ascribed to the lattice oxygen (O_l) of Ru–O. Peaks at 530.5 eV could be assigned to hydroxyl due to longtime exposure to air. The peaks locating at 533.3 eV arise from the adsorbed oxygen (O_ab). In addition, the peaks centered at 531.9 eV corresponding to the defective oxygen (O_d) [45], reflected the oxygen vacancies on the surface, which may account for the reduced valence state of Ru. The percentage of the oxygen species was calculated to quantitatively analyze the difference of the surface oxygen state. As shown in Fig. 3c, the relative content of the defective oxygen for $\text{Nd}_2\text{Ru}_2\text{O}_7$, $\text{Sm}_2\text{Ru}_2\text{O}_7$, $\text{Gd}_2\text{Ru}_2\text{O}_7$, $\text{Er}_2\text{Ru}_2\text{O}_7$ and $\text{Yb}_2\text{Ru}_2\text{O}_7$ were 47.9%, 40%, 38%, 36.3% and 29.5%, showing a decreasing trend. The relative contents of the defective oxygen highly depended on the bonding strength of Ru–O, which was susceptible to the RE. As the ionic radius increased from Yb to Nd, the bond length of Ru–O was elongated, which weakened the bonding strength of Ru–O and resulted in increased defective oxygen concentration. To keep the material electrically neutral, the average valence state of Ru decreased with the increase of defective oxygen [46].

DFT calculations were employed to elucidate the activity difference caused by the RE elements. The band gaps of the $\text{RE}_2\text{Ru}_2\text{O}_7$ were observed around the Fermi level (Fig. 4a), indicating conductive characteristics of the as-prepared materials, which were similar to semiconductor. The band gap showed increasing tendency (0.97, 0.86, 1.09 and 1.23 eV for $\text{Nd}_2\text{Ru}_2\text{O}_7$, $\text{Sm}_2\text{Ru}_2\text{O}_7$, $\text{Gd}_2\text{Ru}_2\text{O}_7$ and $\text{Er}_2\text{Ru}_2\text{O}_7$) with the decrease of the RE ionic radius, corresponding to the increased resistivity (Fig. S7), which was also associated with Ru 4d band center (Table S1) that shifted away from the Fermi level

[22]. The downshift of Ru 4d band center increased the hybridization between Ru 4d band and O 2p band from Nd to Yb (Fig. 4b), resulting in increased bonding strength of Ru–O. The strengthened Ru–O from Nd to Yb impeded the releasing of lattice oxygen atoms during the annealing process, giving a reasonable explanation for the decreased defective oxygen content. In addition, the weakened metal-oxygen bonding allowed adjustment of the electronic structure of Ru that accommodated local charge changes during the OER process [47,48], facilitating the OER kinetics.

Previous theoretical studies demonstrate that the OER intrinsic activity is strongly related to the metal-oxygen binding strength according to adsorbate evolution mechanism theory [1,49]. The optimal OER catalysts ought to have neither too strong nor too weak metal-oxygen binding strengths [17,30]. It is generally accepted that the metal-oxygen binding strength could be regulated by modulating the d band center of the active sites [35,50]. Thus, the correlation between the Ru 4d band center and the intrinsic activity of $\text{RE}_2\text{Ru}_2\text{O}_7$ and RuO_2 was plotted in Fig. 4c, which displayed a volcano shape. The RuO_2 catalyst with Ru 4d band center located at -0.89 eV approaching the Fermi level possessed poor OER performance due to the strong adsorption of oxygen intermediates on the Ru site, which hindered the OER kinetics. A lower d band center yields a weakened metal-oxygen bonding, and thus modulates the Ru 4d band center away from Fermi level favoring OER kinetics [51].

Combining the electrochemical performance (Fig. 2a) and DFT simulation (Fig. 4c), the Ru 4d band center of $\text{Nd}_2\text{Ru}_2\text{O}_7$ was regulated to a moderate value which exhibited an extraordinary OER activity. When Nb was replaced by Sm, Gd and Yb, the Ru 4d band center descended further away from the Fermi level, leading to worse OER activity than Nd because of impeded adsorption of oxygen intermediates, which hampered the OER kinetics. The Ru 4d band center of $\text{Yb}_2\text{Ru}_2\text{O}_7$ was about -2.6 eV, which was too far from the Fermi level, resulting in further decreased ability to adsorb oxygen intermediates on Ru sites [52].

CONCLUSIONS

In summary, we developed a class of pyrochlore RE ruthenates with regulated electronic structure of Ru sites, affording highly active and stable OER in acidic media that surpassed the state-of-art RuO_2 catalyst. The ionic radius of the RE ion in this material was found related to the electronic state and the adsorption behavior of the active Ru center. The increase of RE ionic radius in-

Figure 4 (a) Calculated densities of the state of Ru 4d and O 2p for RE₂Ru₂O₇. (b) Schematic rigid band diagram for RuO₂, Nd₂Ru₂O₇ and Yb₂Ru₂O₇. (c) Correlation between Ru 4d band center and OER activity.

roduced defective oxygen and reduced the valence state of Ru by weakening the hybridization of Ru–O bond within the material. This coordination environment regulation and electronic structure tuning strategy might also be applicable in other ABO_x or multi-metallic oxide materials for higher OER performances in neutral or acid media.

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Supplementary information Supporting data are available in the online version of the paper.

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稀土调控烧绿石钌酸盐中钌氧相互作用用于酸性析氧反应

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摘要 钌(Ru)基催化剂是酸性介质中析氧反应(OER)最为活泼的催化剂之一。然而, Ru活性位点与含氧中间产物之间的强键合导致析氧反应过电势较高。本文, 利用一系列稀土元素(Nd、Sm、Gd、Er和Yb)构建了烧绿石型稀土钌酸盐($\text{RE}_2\text{Ru}_2\text{O}_7$)结构来调整Ru位点的电子结构。表面结构分析表明, 由于Ru–O键杂化减弱, 随着稀土离子半径的增大, $\text{RE}_2\text{Ru}_2\text{O}_7$ 结构中缺陷氧含量增加(缺陷氧的比例从29.5%增加到49.7%)。降低了的Ru的价态, 扩大了Ru的4d能带中心与费米能级(E_F)之间的间隙, 从而削弱了对氧中间体的吸附, 提高了酸性介质中的OER性能。在所制备的钌烧绿石中, $\text{Nd}_2\text{Ru}_2\text{O}_7$ 表现出最低的OER起始过电势(210 mV)和Tafel斜率(58.48 mV dec^{-1}), 并且比最先进的 RuO_2 催化剂具有高30倍的固有活性和更好的耐久性。