Praseodymium iridium oxide as a competitive electrocatalyst for oxygen evolution reaction in acid media

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ABSTRACT Amorphous iridium oxides (IrO_x) are highly active for oxygen evolution reaction (OER) in acid media; however, it is generally unstable compared with commercial IrO_2 . Recently, many non-noble metal-iridium mixed oxides are prepared for catalyzing OER efficiently. Herein, we report a cubic fluorite-type praseodymium iridium oxide with the surface of IrO_x ($\text{IrO}_x/\text{Pr}_3\text{IrO}_7$) that shows the improved activity and stability in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ solution, characterized by an overpotential of 305 mV at the benchmark of 10 mA cm^{-2} and a small Tafel slope of 37 mV dec^{-1} , indicating a fast reaction kinetics and a competitive activity compared with the benchmark IrO_2 and most reported electrocatalysts. The initial potential increases by less than 0.07 V after continuous OER testing over 60,000 s. In contrast, IrO_2 becomes nearly inactive for the OER within 20,000 s. Density functional theory calculations uncover that the optimal energy level path follows lattice oxygen mechanism (LOM). This work enlarges the family of the IrO_x -type OER electrocatalyst in acid media.

Keywords: oxygen evolution reaction, water splitting, electrocatalysts, non-noble metal, energy conversion

INTRODUCTION

Proton exchange membrane (PEM) water electrolysis is regarded as an important clean energy technology in the sustainable energy landscape to produce hydrogen [1–6]. Despite intense research, serious challenges remain because of the lack of low-cost, high-efficiency anodic electrocatalysts for boosting the sluggish oxygen evolution reaction (OER) [7,8]. Currently, iridium oxides are considered the most promising candidates to tackle the

aforementioned challenges, especially the recently reported non-noble metal-iridium mixed oxides, such as Ir-Ni oxides [9–11], SrIrO_3 perovskite [12], $\text{Ba}_2\text{PrIrO}_6$ and Ba_2YIrO_6 double perovskites [13], and $\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ and $\text{Y}_2\text{Ir}_2\text{O}_7$ pyrochlores [14,15], which not only significantly enhance the OER activities, but also reduce the costs, when compared with the state-of-the-art, commercially available IrO_2 . Many IrO_x -type OER catalysts are formed by surface restructuring upon electrochemical leaching of non-noble metal ion under harsh conditions [16–19].

Besides the activity, the stability of an electrocatalyst is also very important. Experimental results combined with density functional theory (DFT) calculations indicate that dynamic surface reconstruction and formation of amorphous iridium oxide structure contribute greatly to high OER activities of the above mentioned electrocatalysts [12,15], but the reconstruction also causes the decrease of the stability. Therefore, more stable IrO_x -type OER catalysts need to be designed and prepared as a fundamental prerequisite to harness the superior catalytic activity of amorphous iridium oxides.

In this work, we demonstrate a competitive electrocatalytic OER activity and stability in acidic medium after Pr ion leaching of a fluorite-type praseodymium iridium oxide (Pr_3IrO_7), which is comparable to the commercial IrO_2 and most reported Ir-based OER electrocatalysts. Especially, the mass activity is approximately 4.8 times higher than that of IrO_2 at 1.58 V (vs. reversible hydrogen electrode (RHE)). Surprisingly, the resulting $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ shows the enhanced stability for the OER compared with IrO_2 using glass carbon as the working electrode. DFT calculations reveal that the surface Ir 5d orbitals of IrO_x /

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Pr_3IrO_7 are at a lower energy level than the O 2p orbitals, which will reduce the charges on oxygen atom, thus making it escape easily from the lattice to participate the OER process.

EXPERIMENTAL SECTION

Chemicals

$\text{C}_6\text{H}_9\text{O}_6\text{Pr}\cdot x\text{H}_2\text{O}$ (M: 318.03, 99.9%), and $\text{IrCl}_4\cdot x\text{H}_2\text{O}$ (M: 334.03, Ir 48.0%–55.0%) were purchased from Aladdin. The commercial IrO_2 (99.9%) was purchased from Macklin. Other reagents were purchased and directly used without purification.

Synthesis of Pr_3IrO_7 catalyst

In a typical procedure, 33.4 mg of $\text{IrCl}_4\cdot x\text{H}_2\text{O}$ was firstly mixed with 63.6 mg of $\text{C}_6\text{H}_9\text{O}_6\text{Pr}\cdot x\text{H}_2\text{O}$ by fully grinding in an agate mortar. Then, the solid powder was put into a tube furnace using corundum crucible as utensil. After annealing at 1200°C for 4 h under ambient conditions, the obtained products were collected for electrochemical testing. To investigate the influence of reaction temperature on the catalytic performance, a series of temperature-dependent experiments were carried out.

Electrochemical measurements

The electrocatalytic OER performance of the prepared catalysts was investigated in a typical three-electrode system, in which carbon rod and the RHE were used as the counter electrode and reference electrode, respectively. The glass carbon (GC, 3 mm in diameter) with loading of 0.2 mg of catalyst was served as the working electrode. The electrolyte was 0.1 mol L^{-1} HClO_4 solution. The polarization curves were measured in the potential range of 1.0–1.65 V (vs. RHE), with a scanning speed of 5 mV s^{-1} . All data were obtained with iR (95%) compensation. The electrochemical impedance spectroscopy (EIS) measurements were carried out at an open circuit potential within the frequency range of 100 kHz–0.01 Hz. The durability testing was conducted by a chronopotentiometry method at 10 mA cm^{-2} .

RESULTS AND DISCUSSION

The synthesis of Pr_3IrO_7 pre-catalyst was conducted *via* a simple one-step solid-state reaction under air atmosphere. As shown in Fig. 1a, all the X-ray diffraction (XRD) peaks of pre-catalyst match well with orthorhombic Pr_3IrO_7 with unit cell parameters of $a = 10.9782 \text{ \AA}$, $b = 7.4389 \text{ \AA}$, $c = 7.5361 \text{ \AA}$ (PDF No. 97-009-9670), which is one superstructure of typical cubic

fluorite-type iridates Ln_3IrO_7 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$) with the space group Cmcm [20]. The corresponding crystal structure is shown in Fig. S1, featured with chains of tilted and vertex-sharing IrO_6 (Ir^{5+}) octahedra oriented along the c -axis [21]. The representative scanning electron microscopy (SEM) image of the prepared Pr_3IrO_7 in Fig. 1b shows the morphology of three-dimensional (3D) hierarchical nano blocks with the jagged edge. The large pore structure between the blocks is beneficial to the storage of electrolyte and gas diffusion. Meanwhile, the “Steps” and “Defects” originating from the jagged morphology (Fig. S2) could offer more exposed active sites and increase the contact area between the catalyst and electrolyte [22]. Magnified high-resolution transmission electron microscopy (HRTEM) image in Fig. 1d corresponds to the region in Fig. 1c that marked with yellow box. The clear lattice spacing of 0.31 nm is assigned to the (202) plane of orthorhombic Pr_3IrO_7 . The corresponding selected area electron diffraction (SAED) pattern further confirms the prepared Pr_3IrO_7 is single crystal with a Cmcm space group. As displayed in Fig. 1f, the atomic resolution high-angle annular dark field- scanning TEM (HAADF-STEM) image displays a periodic light and dark contrast arrangement. As reported, the atomic number determines the brightness of an atom column in an HAADF-STEM image [23]; thus the brightness level of atoms is $\text{Ir} (77) > \text{Pr} (59)$. Energy dispersive spectroscopy (EDS) mapping (Fig. 1g–j) reveals the even distribution of O, Ir, and Pr elements throughout the entire catalyst.

The evolution of structure, composition, and valence states on the surface of Pr_3IrO_7 under working conditions were investigated using *ex situ* characterization techniques, including HRTEM, X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) spectroscopy, and extended X-ray absorption fine-structure (EXAFS) spectroscopy. XPS survey spectrum of the prepared catalysts is shown in Fig. S3, demonstrating the fundamental components of Ir, Pr and O. The binding energies (BEs) of Ir 4f, Pr 3d and O 1s for Pr_3IrO_7 and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ were measured to detect the changes in chemical environment and electronic state of Ir and O in the structures. As illustrated in Fig. 2a, two sets of doublet peaks in the Ir 4f spectra of Pr_3IrO_7 and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ were fitted. For the Pr_3IrO_7 doublet, the peaks with BEs of 62.6 and 65.8 eV are assigned to $\text{Ir } 4f_{7/2}$ and $\text{Ir } 4f_{5/2}$, and the adjacent peaks with BEs of 64.1 and 68.7 eV correspond to their shake-up satellites [24]. High oxidation state of Ir^{5+} in pristine Pr_3IrO_7 makes the BEs of Ir 4f higher than those of commercial IrO_2 , which is similar to $\text{Ba}_2\text{PrIrO}_6$ (Ir^{5+}) reported by Cherevko and

Figure 1 Characterization of the fluorite-type Pr_3IrO_7 . (a) XRD pattern; (b) SEM image; (c) HRTEM image; (d) magnified HRTEM image; (e) SAED pattern; (f) atomic-resolution HAADF-STEM image; (g–j) EDS elemental mappings of Ir, Pr and O.

coworkers [19]. The doublet of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ peaks with BEs of 62.3 and 65.5 eV are related to $\text{Ir } 4f_{7/2}$ and $\text{Ir } 4f_{5/2}$, and the peaks with BEs of 63.8 and 68.0 eV are their shake-up satellites. After OER testing, the doublet peaks for $\text{Ir } 4f_{7/2}$ and $\text{Ir } 4f_{5/2}$ of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ shift to lower energy compared with that of Pr_3IrO_7 , which is caused by the formation of IrO_x instead of IrO_2 . As we know, the peak with BE of $\text{Ir } 4f_{7/2}$ for IrO_2 is usually less than 62.0 eV [25]. Meanwhile, the peaks related to $\text{Pr } 3d_{5/2}$ and $\text{Pr } 3d_{3/2}$ are both shifted by 0.2 eV toward high binding energies, which may be attributed to the slight oxidation of Pr^{3+} during the oxygen evolution (Fig. 2b) [26]. Deconvolution of the O 1s spectrum affords signal of Ir–OH in Pr_3IrO_7 , which appears at BE of 531.1 eV (Fig. S4) [27]. A weak peak positioned at 532.4 eV is related to oxygen-containing adventitious carbon species, and the peak at 529.2 eV is assigned to the lattice oxygen bound to the Pr ion in Pr_3IrO_7 [13], which shows an obvious decrease in proportion from 53.1% to 16.7%, along with extensive leaching of surface Pr during electrochemical process (Fig. S4). This behavior is similar to that observed after leaching of Pr in $\text{Ba}_2\text{PrIrO}_6$ [19], Ni in Ir–Ni oxide [28], and Co in IrCo nanodendrites [29]. After the OER test,

the O 1s XPS spectrum of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ displays one small peak assigned to oxygen from adventitious H_2O and carbon species at high BE of 535.1 eV [27], as well as a broad main peak with a BE of 531.8 eV assigned to IrOH, which contains much higher OH content (67.7%) than that of Pr_3IrO_7 (39.6%), indicating more Ir catalytic active sites in $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ compared with Pr_3IrO_7 .

Fig. 2c shows the Ir L_{III} -edge XANES spectrum of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ compared with the pristine Pr_3IrO_7 , commercial Ir foil, IrO_2 , and IrCl_3 measured under the same conditions. The white line peak position of Pr_3IrO_7 is located at 11,221.0 eV, which is shifted to higher energy than the absorption peak of IrO_2 , indicating a higher Ir oxidation state than that of IrO_2 [16,25]. While the white line peak position of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ exhibits a clear shift toward lower photon energy compared with Pr_3IrO_7 , which is almost same as that of IrO_2 , implying the oxidation state of Ir on the surface is closer to +4. This trend in the change of Ir oxidation state is consistent with the XPS results. The corresponding Fourier transform of EXAFS oscillations gives further insight into the oxidation state of Ir on the surface of Pr_3IrO_7 and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ using the Ir–O bond distances as a descriptor [30,31]. In Fig. 2d,

Figure 2 High-resolution XPS spectra of Pr_3IrO_7 and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$. (a) Ir 4f, (b) Pr 3d. (c) Ir L_{III} -edge XANES spectra and (d) the corresponding k^3 -weighted Fourier transforms of Ir L_{III} -edge EXAFS spectra for Pr_3IrO_7 , $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, and references Ir foil, IrCl_3 , IrO_2 . (e) Pr L_{III} -edge XANES spectra and (f) the corresponding k^3 -weighted Fourier transforms of Pr L_{III} -edge EXAFS spectra for Pr_3IrO_7 , and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$.

the main peak of Pr_3IrO_7 at 1.57 Å belongs to the Ir–O bond derived from electron backscattering of the octahedral O environment around the central Ir ion. The shorter Ir–O bond in Pr_3IrO_7 than that of commercial IrO_2 (1.61 Å) convincingly confirms an oxidation state of Ir that is higher than +4. For $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, the resulting peak related to Ir–O corresponds to a bond length similar to that of IrO_2 , further confirming an oxidation state of approximately +4. The reduced oxidation state of Ir may be attributed to the loss of oxygen on the surface according to the equation [12]:

The Pr L_{III} -edge XANES and EXAFS spectra of Pr_3IrO_7 and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ can be found in Fig. 2e and f. For Pr_3IrO_7 , the XANES spectrum is characterized by strong white line, and the peak position locates at 5966.6 eV, much close to that of the trivalent Pr [32]. After OER testing, the white line of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ shows a slight change. Correspondingly, the Fourier transform Pr L_{III} -edge EXAFS spectrum of Pr_3IrO_7 shows two main peaks at 1.86 and 3.48 Å, respectively. Compared with Pr_3IrO_7 , the peak positions and intensity of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ change obviously, which locate at 1.92 and 3.42 Å, respectively.

After electrochemical pre-treatment for 100 cyclic voltammetry (CV) cycles, the OER activity of the $\text{IrO}_x/$

Pr_3IrO_7 catalyst was evaluated in acidic media with scanning potentials from 1.20 to 1.65 V (vs. RHE) using a standard three-electrode configuration. As a reference, the activity of commercial IrO_2 toward the OER was also investigated under the same conditions. The polarization curve of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ produces an extremely small onset potential of 1.45 V (vs. RHE), beyond which the anodic current rises sharply (Fig. 3a). A relatively low overpotential of 305 mV was observed for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ at the current density of 10 mA cm^{-2} , whereas IrO_2 required a higher overpotential (320 mV) to deliver the same current density, indicating higher catalytic activity of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$. Furthermore, as demonstrated by the Tafel plots (Fig. 3b) derived from linear sweep voltammetry (LSV) (Fig. 3a), Tafel slopes of 37 and 94 mV dec^{-1} for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ and IrO_2 , respectively, indicate faster kinetics of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ for the OER. In addition to high catalytic activity per geometric area, $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ also delivers outstanding mass activity (normalized by the mass of iridium) (Fig. 3c). The current density ($\text{A g}_{\text{Ir}}^{-1}$) of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ is

approximately 4.8 times that of IrO_2 at 1.58 V (vs. RHE), further highlighting the superior OER activity of the prepared $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ catalyst relative to IrO_2 . We also explored the optimal preparation temperature of Pr_3IrO_7 catalysts by varying the annealing temperature from 1000 to 1400°C . Evidently, the Pr_3IrO_7 prepared at 1200°C exhibits the highest activity (Fig. S5), the largest electrochemical active surface area (ECSA) determined by C_{dl} (Fig. 3d, Fig. S6), and the smallest charge transfer resistance (R_{ct}) (120Ω) (Fig. 3e) among the three catalysts. The OER activities of the catalysts prepared with different molar ratios of Pr to Ir were also evaluated. As confirmed by Fig. S7, the catalyst with the Pr/Ir molar ratio of 2:1 in the reactant shows the highest OER activity. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of the electrolyte was applied to detect the amount of dissolved Pr and Ir ions during the OER process, which provides further insight into the changes of structure and composition on the surface of the catalyst. Fig. 3f shows that the initial molar ratio of Pr to Ir in the electrolyte is

Figure 3 OER performance in $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ medium. (a) Polarization curves of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ and commercial IrO_2 , (b) Tafel slopes, (c) mass activities (normalized to the mass of Ir, $\text{A g}_{\text{Ir}}^{-1}$) of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ and IrO_2 . (d) Capacitive currents as a function of the scan rate for Pr_3IrO_7 catalysts prepared at different annealing temperatures varied from 1000 to 1400°C . (e) Nyquist plots for Pr_3IrO_7 prepared at 1000, 1200, 1400°C , respectively. (f) Time-dependent concentrations of Ir and Pr in the electrolyte. (g) The durability testing by the chronopotentiometry at a benchmark of 10 mA cm^{-2} .

approximately 7.56, which is obviously higher than the theoretical ratio in Pr_3IrO_7 , suggesting that Pr ions are more easier to be dissolved in the acidic medium under an open circuit than Ir ions. As the OER process proceeds, the molar ratio of Pr to Ir increases to 30:1 after 7 h, demonstrating the more dissolution of Pr ions into the electrolyte, but from 7 to 10 h, the ratios of Pr/Ir dissolution are relatively unchanged. The electrochemical durability of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ and IrO_2 were also examined *via* chronopotentiometry at a constant current density of 10 mA cm^{-2} (Fig. 3g). For $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, the initial potential increases by less than 0.07 V after continuous OER testing over 60,000 s. In contrast, IrO_2 becomes nearly inactive for the OER in less than 20,000 s. The overpotential of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ at 10 mA cm^{-2} was then compared with those of recently reported electrocatalysts in

acidic media (Table S1), further confirming the competitive performance of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$.

DFT calculations were performed to explore the energetically preferred catalytic reaction pathway and reveal a possible catalytic reaction mechanism. The structural models and further DFT calculation details are available in the Supplementary information (Figs S8–S10). The adsorbate evolution mechanism (AEM) is classic and universal. Based on previous research, we first assumed that a four-step OER mechanism proceeds as follows: $\text{H}_2\text{O} \rightarrow * \text{OH} \rightarrow * \text{O} \rightarrow * \text{OOH} \rightarrow \text{O}_2$ (see Equations (S1)–(S4) in the Supplementary information) [33]. The Equations (S5)–(S8) in the Supplementary information show the steps of lattice oxygen participation mechanism. As shown in Fig. 4a, c, e, the free energy barrier for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$ is 2.62 eV to form the $* \text{OOH}$ at a rate-

Figure 4 OER free energy diagrams via AEM and LOM, respectively, for (a) IrO_2 , (c) Pr_3IrO_7 , (e) $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, in which the corresponding Gibbs free energy differences of the potential-determining step (ΔG_{max}) denoted by dashed arrows. (b), (d), (f) show the PDOS of surface active Ir 5d orbitals and O 2p orbitals for IrO_2 , Pr_3IrO_7 and $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, respectively. The corresponding band centers of O 2p and Ir 5d are denoted by dash lines.

determining step, which is higher than those of $\text{IrO}_2(110)$ and $\text{Pr}_3\text{IrO}_7(002)$. The free energy barriers for $\text{IrO}_2(110)$ and $\text{Pr}_3\text{IrO}_7(002)$ of $^*\text{OOH}$ formation are 1.81 and 2.44 eV, respectively. However, the electrochemical testing results indicate that $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$ shows higher activity than IrO_2 , suggesting that the $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$ does not follow the AEM, and thus we tried the lattice oxygen mechanism (LOM) with surface Ir atoms as the active sites. The computed results in Fig. 4e show that there is a lower OER barrier of 1.76 eV for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$ following the LOM, which is much lower than that of 4.51 and 2.49 eV for $\text{IrO}_2(110)$ and $\text{Pr}_3\text{IrO}_7(002)$, respectively. The minimum theoretical overpotential (η^{OER}) is calculated as 0.53 V for the $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$ based on LOM mechanism, which is smaller than that of $\text{IrO}_2(110)$ (0.58 V) based on AEM, making the theoretical calculated OER activity of $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$ relative to $\text{IrO}_2(110)$ consistent with the experimental data. To better understand the appropriate mechanism to describe $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$, we further explored their surface structures and electronic properties. As shown in Fig. 4b, d, and f, the projected density of states (PDOS) of Ir 5d orbitals and O 2p orbitals for surface active Ir ions and lattice oxygen atoms that participate in the OER for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$, $\text{IrO}_2(110)$ and $\text{Pr}_3\text{IrO}_7(002)$ were calculated. The OER reaction mechanism can be affected by the relative position of oxygen 2p orbitals and metal d orbitals [34,35]. For $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$, the surface active Ir 5d orbitals shows a lower energy level than the 2p orbitals of oxygen that will reduce the charges on oxygen. The charge-reduced oxygen atom will be easy to escape from the lattice to participate the OER process. Thus, it can be concluded that the LOM is a preferred reaction pathway than the AEM for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7(002)$.

CONCLUSIONS

In summary, we expanded a new member of family for the IrO_x -type OER electrocatalyst, which exhibits an enhanced OER activity with a low overpotential of 305 mV compared with that of IrO_2 (320 mV) and a better stability. Particularly, the increase of overpotential within 0.07 V over continuous testing for 60,000 s at a benchmark of 10 mA cm^{-2} for $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, in contrast to the inactivation of commercial IrO_2 within 20,000 s using glass carbon as the working electrode. The DFT studies reveal that LOM is followed by the $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ system. Based on the PDOS analysis, the energy level of active Ir 5d orbitals is obviously lower than that of ligand O 2p orbitals in $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$, which endows the enough activity of oxygen to participate in the OER process, and

thus contributes to the higher OER activity.

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Author contributions Liu X proposed the research ideas and designed the experiments. Qin Q and Liu X wrote the manuscript and performed the analysis. Wang Y, Liu H, Zhang L, Wei T, and Li H carried out the synthetic, electrochemical experiments and physical characterizations. Liu S carried out the DFT calculations. All the authors participated in this research project.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Materials characterization and supporting data are available in the online version of the paper.

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锆铱氧化物高效催化酸性介质析氧反应

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摘要 非晶态铱氧化物(IrO_x)在酸性介质中具有高的电催化析氧反应(OER)活性, 但其稳定性不如商业 IrO_2 . 近年来, 多种非贵金属-铱混合氧化物展现出高效催化析氧反应的性能. 本文报道了一种含 IrO_x 高活性表面层的立方萤石结构锆铱氧化物(Pr_3IrO_7)催化剂. 该催化剂在 $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ 溶液中, 表现出高的析氧反应催化活性和良好的稳定性, 优于商业 IrO_2 和目前报道的大多数催化剂. 在电流密度为 10 mA cm^{-2} 时, 该催化剂的过电位为 305 mV , 并具有低的Tafel斜率, 约为 37 mV dec^{-1} , 表明该催化剂具有更快的反应动力学. 在持续 60000 s 的稳定性测试后, 该催化剂的初始电位仅增加了 0.07 V , 而 IrO_2 只经过 20000 s 测试就几乎丧失活性. 密度泛函理论计算表明, $\text{IrO}_x/\text{Pr}_3\text{IrO}_7$ 催化析氧反应遵循晶格氧机理(LOM). 这项工作拓展了 IrO_x 型酸性OER电催化剂的种类.