Dopants fixation of Ruthenium for boosting acidic oxygen evolution stability and activity

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Designing highly durable and active electrocatalysts applied in polymer electrolyte membrane (PEM) electrolyzer for the oxygen evolution reaction remains a grand challenge due to the high dissolution of catalysts in acidic electrolyte. Hindering formation of oxygen vacancies by tuning the electronic structure of catalysts to improve the durability and activity in acidic electrolyte was theoretically effective but rarely reported. Herein we demonstrated rationally tuning electronic structure of RuO₂ with introducing W and Er, which significantly increased oxygen vacancy formation energy. The representative W₀.²Er₀.₁Ru₀.₇O₂₋δ required a super-low overpotential of 168 mV (10 mA cm⁻²) accompanied with a record stability of 500 h in acidic electrolyte. More remarkably, it could operate steadily for 120 h (100 mA cm⁻²) in PEM device. Density functional theory calculations revealed co-doping of W and Er tuned electronic structure of RuO₂ by charge redistribution, which significantly prohibited formation of soluble Rux>₄ and lowered adsorption energies for oxygen intermediates.
Electrochemical splitting water into $\text{H}_2$ is considered as a promising technology for storing renewable and sustainable energy\textsuperscript{1–7}. Acidic proton exchange membrane (PEM) water electrolyzers is highly desirable because the reaction rate in acidic electrolyte is three or more orders of magnitudes speedier than pH-neutral and alkaline electrolysers owing to its higher voltage efficiency, more compact designing system, lower ohmic loss, and wider partial load range\textsuperscript{8–11}. For decades, anode catalyst for PEM is mainly concentrated on IrO$_2$ with the compromise between stability and activity in acidic electrolyte\textsuperscript{12–17}. However, the low mass activity and the high cost extremely hindered its practical applications at large scale. Compared with IrO$_2$, Ru-based materials usually exhibit the relatively higher activity owing to the suitable binding ability of oxygenated intermediate species ($^*$OH, $^*$O, and $^*$OOH) with the surface active sites\textsuperscript{18–22}, but with a poor stability. Recently, a series of Ru-based oxides, including oxide perovskites\textsuperscript{23,24}, 3d metals doped RuO$_2$\textsuperscript{25}, heterostructured Ru@IrO$_2$\textsuperscript{3} and Ru$_3$-Pt$_2$Cu\textsuperscript{18} with compressive strain, were explored to simultaneously enhance their activities and stabilities in acidic electrolyte by regulating the compositions and surface strain. Although the activities of Ru-based catalysts are attractive, the stability is still only dozens of hours in acidic electrolyte. It has been proven that the over-oxidation of Ru-based materials results in soluble Ru$^{2+}$ (e.g. RuO$_4$) derivatives\textsuperscript{14,26,27}, which seriously hinders the application of RuO$_2$ in the commercial PEM devices.

The over-oxidation of Ru-based catalysts in acidic electrolyte is mainly caused by the oxidation of lattice oxygen, resulting in oxygen vacancies (V$_O$) during OER\textsuperscript{19,28}. The generation of V$_O$ would expose Ru atoms on the surface\textsuperscript{3,29–32}, which will be over-oxidized to soluble high valence Ru$^{2+}$ (e.g. RuO$_4$) materials. The over-oxidation of Ru unavoidably leads to the collapse of the crystal structure, damaging the stability\textsuperscript{28,29}. Therefore, it is reasonable to speculate that the over-oxidation of Ru-based catalysts could be thermodynamically hindered during OER if we can tune the electronic structure of RuO$_2$ to make the formation energy of V$_O$ much higher than the redox $\text{H}_2\text{O}/\text{O}_2$ energy. Foreign elements doping is the classical and effective strategy to enlarge the localized gap between O 2p band centers and Fermi level\textsuperscript{28,33,34}. This would enhance the energy barrier for oxidation of lattice oxygen, prohibiting the formation of V$_O$.

Herein, W and Er are co-doped into the lattice of RuO$_2$ to modify its electronic structure, avoiding over-oxidation of Ru. By down-shifting O 2p-band centers, the energy (ΔG) for the V$_O$ formation in W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ is significantly increased, preventing the generation of soluble high valence Ru$^{2+}$ (Fig. 1d). As a result, the representative W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ offers a record low overpotential of 168 mV to achieve 10 mA cm$^{-2}$ accompanied with a stability at least 500 h in 0.5 M H$_2$SO$_4$ electrolyte. It can also be applied as anode catalyst in acidic PEM with a high current of 100 mA cm$^{-2}$ for over 120 h. Thus, tuning the electronic structure of RuO$_2$ to prevent the over-oxidation and dissolution of Ru opens a feasible route to keep Ru$^{4+}$ active sites for acidic OER. This work provides the insight to understand the stability of metal oxide catalysts in acidic electrolyte and a strategy to promote their activity and stability by fixing the catalysts.

Results and discussion
Mechanisms of W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ toward acidic OER. As for the metal dissolution in acidic electrolyte, it is mainly correlated with the adsorbate evolution and lattice oxygen oxidation mechanisms\textsuperscript{9,18,35}. For lattice oxygen oxidation, there are four electrochemical steps as well as a non-electrochemical step for desorption of O$_2$. In lattice oxygen oxidation route, the origin for releasing oxygen was occurred in step III (O$^*$ + H$_2$O + O$_2$ + 2H$^+$ + e$^-$ → $\text{O}_V$ + O$_2$ + H$_2$O + 2H$^+$ + e$^-$, L represents lattice). With releasing oxygen from the lattice of electrocatalysts, the oxygen vacancies were created, in turn beneficially enhancing the OER activity (Fig. 1a, c)\textsuperscript{28}. However, in acidic electrolyte, the existing oxygen vacancies would accelerate the over-oxidation of the exposed Ru, leading to the highly soluble Ru$^{2+}$ (e.g. RuO$_4$) derivatives. Therefore, the structure of Ru-based materials on anodic side would be destroyed with releasing lattice oxygen from catalysts. As compared with lattice oxygen oxidation, there are only four electrochemical steps in the adsorbate evolution way toward OER (Fig. 1b)\textsuperscript{9,36,37}. Simultaneously, in the adsorbate evolution route, O–O coupling from H$_2$O in steps I and III was the origin for releasing O$_2$ (step I: W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ + H$_2$O → W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$–OH$^*$ + H$^+$ + e$^-$, step III: W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$–O$^*$ + H$_2$O → W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$–OH$^*$ + H$^+$ + e$^-$) (Fig. 1d). The structures of catalysts would not be destroyed without releasing lattice oxygen. Therefore, effectively enhancing the energy for formation of oxygen vacancies and inhibiting the direct O–O coupling together from the lattice of W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ would be beneficial for maintaining the stability of Ru-based materials in acidic electrolyte (Fig. 1b, d).

Density functional theory (DFT) calculations. In light of the reacted ways toward acidic OER, we carried out DFT studies aiming at rationally tuning the electronic of RuO$_2$. To enhance the acidic OER stability, the energy for V$_O$ formation should be thermodynamically suppressed. Density of states (DOS) from DFT was established to investigate how W and Er synergistically rationalize the Ru 4d and O 2p orbitals in RuO$_2$ (Fig. 2a and Supplementary Fig. 1). The DOS spectra shows that O 2p band center ($\epsilon_p$) moves from −3.31 eV (RuO$_2$) to −4.12 eV with W and Er introduction. And the gap between $\epsilon_p$ and Fermi level is obviously enlarged\textsuperscript{28}.

This result indicates the covalency of Ru–O bond is decreased by introduction of W and Er\textsuperscript{37}. Therefore, the O–O coupling on O 2p states above the Fermi level will be not thermodynamically favored, which could be seen from ΔG for formation of OH$^*$ (Fig. 2b, right). This result will make AG for formation of V$_O$ higher than that of RuO$_2$ (Fig. 2b, left). Further, the DFT results also reveal ΔG for formation of V$_O$ at the pyramid vertex of W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ shifts from lower energy band of 0.67 eV (RuO$_2$) to higher energy band of 2.29 eV (Fig. 2c). These results indicate W and Er could effectively enhance the energy for formation of V$_O$ in W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ toward acidic OER. Therefore, the dissolution of Ru in acidic electrolyte will be suppressed. Moreover, Bader charge analyses also prove the downshift of $p$ band centers, resulting in the negative charge of the lattice O (Supplementary Fig. 2). Consequently, this electronic state could effectively enhance AG for the formation of V$_O$ and suppress the lattice O binding with oxygen intermediates to release O$_2$. Besides that, the corresponding model structures were established for oxidation of lattice oxygen on surface of (110) in W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ (Supplementary Fig. 3). However, the OH$^*$ adsorbed on W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ was not stable and transferred to Ru, W, or Er sites after optimization of the models (step II in Fig. 1c and Supplementary Fig. 3). Therefore, the lattice oxygen in W$_{0.2}$Er$_{0.1}$Ru$_{0.7}$O$_{2–δ}$ will not participate in acidic OER process. This result also confirmed that introducing W and Er into RuO$_2$ could suppress the dissolution rate of Ru.

DFT calculations were then performed to rationalize the acidic OER performance (Fig. 2d and Supplementary Figs. 4–12). As also motivated by the experimental results of synthesized samples, all the models were established based on (110) surface. Besides that, the solvation was not considered in our calculation because the DFT was intended to understand trends when doping the...
RuO$_2$ surface with foreign metal atoms. All potential determining steps (PDS) for these designed samples were between OOH$^*$ and O$^*$. The calculated $\Delta G$ for PDS followed the order of $W_{0.2}Er_{0.1}Ru_{0.8}O_2$ $\leq$ $W_{0.2}Er_{0.2}O_2$ $\leq$ $W_{0.2}Ru_{0.8}O_2$ $\leq$ $Er_{0.1}Ru_{0.8}O_2$ $\leq$ $Er_{0.2}O_2$ (0.53 eV) $< W_{0.2}Ru_{0.8}O_2$ $< W_{0.2}Er_{0.2}O_2$ (0.6 eV) $< Er_{0.1}Ru_{0.8}O_2$ (0.72 eV) $< Ru_{0.1}O_2$ (0.79 eV) (Fig. 2d and Supplementary Figs. 4–6), revealing that simultaneously doping W and Er could reduce energy barriers for boosting activities. This phenomenon also agreed well with the upshift of Ru 4d band centers, which tuned the adsorption energy of oxygen intermediates on active sites. Moreover, the surface of preferential and established models for these RuO$_2$-based materials was not bare anymore at $U$ $\geq$ 1.23 V vs. RHE. And there should be neighboring intermediates around active sites, which influenced on the energetics of the elementary processes in the OER (Supplementary Figs. 9–11). According to the calculations, the energy barrier for PDS significantly decreased (Supplementary Figs. 10 and 11), compared with the traditional models without considering the neighboring intermediates (Supplementary Figs. 4–6). Therefore, these results also indicated that the neighboring intermediates around active sites could also contribute to enhancing the activity of $W_{0.2}Er_{0.1}Ru_{0.8}O_2$ toward OER. Besides that, $\Delta G_2$ for formation of OH$^*$ has always acted as a descriptor for indicating the activity trends of the modeled materials. The scaling relation of $\Delta G_2$ and $\Delta G_3$ for formation of OH$^*$ and OOH$^*$ should be also coupled: 2.6 eV $\leq$ $\Delta G_2 + \Delta G_3$ $\leq$ 3.6 eV.

**Synthesis and characterization.** To experimentally probe the predictions, $W_{0.2}Er_{1−m}Ru_{m}O_2$ nanosheets with various ratios were synthesized by a hydrothermal method, in which ethylenediaminetetraacetic acid (EDTA), ruthenium(III) acetate, WCl$_6$, ErCl$_3$, and citric acid were used as precursors (Fig. 3a). Supplementary Fig. 13 shows that these as-synthesized materials are of the rutile ruthenium oxides ($RuO_2$). PDF#40-1290 along with the dominant (110) peak. Transmission electron microscopy (TEM) exhibited that the prepared $W_{0.2}Er_{1−m}Ru_{m}O_2$ nanosheets possessed the ultrathin nanosheet morphology (Fig. 3b, c, and Supplementary Figs. 14–19). The corresponding elemental mapping confirmed that Er, W, and Ru were uniformly distributed in these nanosheets (Fig. 3d). High-resolution TEM (HR-TEM), fast Fourier transform (FFT), and selected area electron diffraction (SAED) revealed that $W_{0.2}Er_{1−m}Ru_{m}O_2$ nanosheets possessed a face centered cubic (FCC) crystal face along (110) direction (Fig. 3e, f). The atomic ratios of Ru, W, and Er in these as-prepared samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The results revealed the atomic ratio of these elements was close to the expected values (Supplementary Tables 1–6).

**Oxidation state analysis.** X-ray photoelectron spectra (XPS) was carried out on these prepared Ru-based nanosheet catalysts to analyze their compositions and chemical states (Supplementary Fig. 20). From Fig. 4a, the Ru 3d spectra for RuO$_2$–δ, $W_{0.2}Ru_{0.8}O_2$–δ, $Er_{0.1}Ru_{0.9}O_2$–δ, and $W_{0.2}Er_{0.1}Ru_{0.8}O_2$–δ could be deconvoluted into
two kinds of doublets. The binding energies of lower energy couples situated at 280.6 (Ru 3d\(_{5/2}\)) and 284.8 eV (Ru 3d\(_{3/2}\)) were, respectively, attributed to Ru\(^{3+}\) and Ru\(^{4+}\). Simultaneously, the higher energy couples situated at 282.2 and 286.7 eV were, respectively, ascribed to the satellite peaks. The average area and intensity ratios for Ru 3d\(_{5/2}\) and Ru 3d\(_{3/2}\) were, respectively, higher (2:1.2) and lower (2:3.3) than the expected value of 2:3. This should be ascribed to the fact that the C 1s peak was coincided with Ru 3d\(_{3/2}\). For W 4f\(_{7/2}\), the binding energies were deconvoluted into W \(5d\) and W \(4f\) peaks at 37.4 and 35.5 eV, respectively, in a valence state of \(W^{6+}\). Similarly, the average area and intensity ratios for W 4f\(_{5/2}\) and W 4f\(_{7/2}\) doublet were, respectively, 15:17 and 9:10, which were close to the expected value of 3:4. Moreover, compared with \(W_{0.2}Ru_{0.8}O_{2-\delta}\), the binding energies of W 4f\(_{5/2}\) and W 4f\(_{7/2}\) were, respectively, negatively shifted with 0.74 and 0.60 eV (Fig. 4b), confirming that W in \(W_{0.2}Ru_{0.8}O_{2-\delta}\) exhibited a lower valence state than \(W^{6+}\). From Fig. 3c, the binding energies for Er 4d could be fitted with two peaks, which should be, respectively, assigned to Er 4d\(_{5/2}\) (170.0 eV) and Er 4d\(_{3/2}\) (168.5 eV), revealing the Er element in these samples was in Er\(^{3+}\) valence state. Interestingly, as compared with \(W_{0.2}Ru_{0.8}O_{2-\delta}\), the Er 4d\(_{5/2}\) and Er 4d\(_{3/2}\) were, respectively, positively shifted with 0.20 and 0.47 eV (Fig. 4c). This indicates that Er\(^{3+}\) in \(W_{0.2}Ru_{0.8}O_{2-\delta}\) was a little more positively charged. Besides that, O 1s peaks around at 532, 530.5, and 529.3 eV are, respectively, confirmed as hydroxyl groups, lattice oxygen, and M–O bonds. The lattice oxygen and M–O bonds in \(W_{0.2}Ru_{0.8}O_{2-\delta}\) and \(Er_{0.1}Ru_{0.9}O_{2-\delta}\) nanosheets were slightly positively shifted compared with Ru\(^{2+}\), approximately (Fig. 4d), indicating O 1s was positively charged. Through above analyses, it could be concluded that some electrons were transferred from Er to Ru and W through O in \(W_{0.2}Er_{0.1}Ru_{0.9}O_{2-\delta}\), confirming the electronic interactions among Ru, W, Er, and O.

**Electrochemical OER in acid electrolyte.** To establish correlation between the electrocatalytic performances and the specific electronic structure, the OER activities of the prepared \(W_{m}Er_{n}\), \(Ru_{1-\delta}O_{2-\delta}\) nanosheets and C-RuO\(_2\) were investigated in 0.5 M H\(_2\)SO\(_4\) (Supplementary Figs. 21 and 22). The linear sweep voltammetry (LSV, scan rate: 5 mV s\(^{-1}\)) was corrected with iR and normalized with geometrical area, respectively. It was seen that the performances of prepared electrocatalysts followed an order of \(W_{0.2}Er_{0.1}Ru_{0.9}O_{2-\delta}\) > \(Er_{0.1}Ru_{0.9}O_{2-\delta}\) > \(W_{0.2}Ru_{0.8}O_{2-\delta}\) nanosheets > C-RuO\(_2\) NPs as shown in Fig. 6a. Simultaneously,
the representative $W_{0.2}Er_{0.1}Ru_{0.7}O_2$ nanosheet exhibited a record performance toward OER with an overpotential ($\eta$) as low as 168 mV at 10 mA cm$^{-2}$ (Fig. 6a), remarkably preceding other prepared Ru-based nanosheets. Simultaneously, $W_{0.2}Er_{0.1}Ru_{0.7}O_2$ also exhibited the fastest reaction rate among these prepared samples with a small Tafel slope of 66.8 mV dec$^{-1}$ (Fig. 6b). The current density of $W_{0.2}Er_{0.1}Ru_{0.7}O_2$ nanosheets could achieve 500 mA cm$^{-2}$ at $\eta = 275$ mV, which was 28.6-folds higher than that of C-RuO$_2$. It should be noted that the performance for the representative $W_{0.2}Er_{0.1}Ru_{0.7}O_2$ was also superior to those of the catalysts reported recently (Supplementary Table 9).

To reveal the origin of the performances for prepared samples, electrochemical double-layer capacitance ($C_d$) was performed to measure the surface area and roughness factor ($R_d$) (Fig. 6c and Supplementary Figs. 23–27). Moreover, CV curves for these materials supported on glass carbon electrode were also measured to confirm $C_d$ (Supplementary Figs. 26 and 27). As listed in Supplementary Table 8, the calculated $C_d$, $R_d$ and surface area exhibited a similar trend as activity. $W_{0.2}Ru_{0.8}O_2$, $Er_{0.1}Ru_{0.9}O_2$, and $W_{0.2}Er_{0.1}Ru_{0.7}O_2$ nanosheet structures revealed successively increased roughness compared with RuO$_2$ nanosheets. The representative $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ (1231.8 m$^2$ g$^{-1}$) exhibited much larger surface area than $Er_{0.1}Ru_{0.9}O_2$ (494.9 m$^2$ g$^{-1}$), $W_{0.2}Ru_{0.8}O_2$ (326.3 m$^2$ g$^{-1}$), and RuO$_2$ (166.7 m$^2$ g$^{-1}$), probably originating from more active sites exposure with co-doping of W and Er into RuO$_2$ nanosheets (Supplementary Fig. 21d). The calculated specific activity followed an order of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ ($1.23$ mA cm$^{-2}$) > $W_{0.2}Ru_{0.8}O_2$ ($1.15$ mA cm$^{-2}$) > $Er_{0.1}Ru_{0.9}O_2$ ($0.98$ mA cm$^{-2}$) > C-RuO$_2$ ($0.50$ mA cm$^{-2}$). Simultaneously, $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ also possessed the highest mass activity of 1518.6 A g$^{-1}$, which was 2.7, 2.8, and 28.5-folds higher than $Er_{0.1}Ru_{0.9}O_2$, $W_{0.2}Ru_{0.8}O_2$, and C-RuO$_2$, respectively (Supplementary Fig. 21d). The highest specific and mass activities for $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ among these samples indicated the highest intrinsic activity of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$.

Nyquist plots in Fig. 6d were applied to fit the equivalent circuit diagram for the electrochemical impedance spectroscopy, revealing the reaction impedance between the electrode and solution. Figure 6d shows that the charge-transfer resistance ($R_{ct}$) for $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ was 3.3 $\Omega$, which was much smaller than those of $Er_{0.1}Ru_{0.9}O_2$ (13.8 $\Omega$), $W_{0.2}Ru_{0.8}O_2$ (20.2 $\Omega$), and RuO$_2$ (50.8 $\Omega$). These results further confirmed the co-doping of W and Er into RuO$_2$ nanosheets enhanced the intrinsic OER property of the samples. Additionally, Faraday efficiency for OER on $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ could reach 99.5%, indicating the current mainly came from OER as shown in Supplementary Fig. 28.

Stability for acidic OER and PEM. The stability in acidic electrolyte is a critical factor to evaluate the performances of OER electrocatalysts due to highly oxidative operating conditions and corrosive electrolytes. The stability of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ could be assessed by $\Delta\eta = \eta_{final}-\eta_{initial}$, the gap between the final and initial overpotential ($\eta$) can be calculated from a chronopotentiometric test of 10 mA cm$^{-2}$. From Fig. 7a, the chronopotentiometric line exhibited a highly durable stability for 250 h with a small increase of $\Delta\eta = 83$ mV, indicating the excellent stability of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ (Fig. 7b and Supplementary Table 9). Remarkably, from 250 to 500 h during the stability test, the operation ran stably with a tiny increase of $\Delta\eta = 5$ mV, confirming the durable properties of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ in acidic electrolyte. Besides that, the stability of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ loaded on glass carbon electrode also revealed the durable stability in acidic electrolyte (Supplementary Fig. 29). As a contrast, the C-RuO$_2$ could only run 24 h with the large loss of $\Delta\eta = 615$ mV (Supplementary Fig. 30). To confirm the fixation of Ru in $W_{0.2}Er_{0.1}Ru_{0.9}O_2$, ICP-MS was performed to analyze the concentration of the dissolved W, Er, and Ru in the solution during the 500 h stability test at an interval of 100 h (Fig. 7c). The results of ICP-MS revealed that the Ru cations in the solution were <12 ppb after 500 h (Supplementary Tables 10–18). More significantly, $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ as anodic electrocatalyst could also operate steadily for 120 h at high current of 100 mA cm$^{-2}$ in acidic PEM (Fig. 7d, e).

Charge redistribution of $W_{0.2}Er_{0.1}Ru_{0.9}O_2$ for the long-durable acidic OER stability. To prove the highly improved
Furthermore, wavelet transform (WT) for Ru K-edge EXAFS in Fig. 5c showed the adsorption energy of the prepared W0.2Er0.1Ru0.7O2 nanosheets. In order to precisely analyze the valence state of Ru, X-ray absorption near-edge spectroscopy (XANES) was applied to characterize RuO2−δ and W0.2Er0.1Ru0.7O2−δ. Ru foil and C-RuO2 were employed as reference materials. Compared with Ru K-edge position of Ru foil, the C-RuO2, RuO2−δ, and W0.2Er0.1Ru0.7O2−δ all shifted to higher energy, resulting from the Ru–O bonds in these materials (Fig. 5a). Additionally, the Ru K-edge spectra in Fig. 5a showed the adsorption energy of the prepared RuO2−δ and W0.2Er0.1Ru0.7O2−δ were different from that for C-RuO2. This result mainly resulted from the fact that Ru valence state in RuO2−δ and W0.2Er0.1Ru0.7O2−δ were mainly dominated Ru4+ accompanied with Ru2+ (δ < 1). Simultaneously, compared with adsorption energy of RuO2−δ, the adsorption energy for W0.2Er0.1Ru0.7O2−δ shifted to lower energy region, indicating that Ru valence state in W0.2Er0.1Ru0.7O2−δ was a little lower than that in RuO2−δ due to introduction of W and Er. Additionally, the adsorption energy (Es) for RuO2−δ (22.119.99 eV) was also a little higher than that for W0.2Er0.1Ru0.7O2−δ (22.118.92 eV). These results were consistent with the valence state analysis in XPS. Furthermore, extended X-ray absorption fine structure (EXAFS) with Fourier transform as well as its counterpart (k3-weighted EXAFS) was applied to analyze the structure of RuO2−δ and W0.2Er0.1Ru0.7O2−δ (Fig. 5b). Compared with the bond of Ru–Ru in Ru foil (2.68 Å), W0.2Er0.1Ru0.7O2−δ exhibited a slightly longer interatomic distance (2.71 Å), which could be related with the strained effect in HRTEM5 (Supplementary Table 7). Additionally, the Ru–Ru and Ru–O bonds in RuO2−δ and W0.2Er0.1Ru0.7O2−δ showed different interatomic distances is due to the existence of lower Ru4+ valence state, compared with that in C-RuO2 (3.12 and 3.56 Å). Besides that, the different Ru–Ru, Ru–O bonds between RuO2−δ and W0.2Er0.1Ru0.7O2−δ should be related with introducing W and Er into RuO2−δ. Furthermore, wavelet transform (WT) for Ru K-edge EXAFS in Fig. 5c was applied to exhibit the length changes of Ru–Ru and Ru–O bonds in W0.2Er0.1Ru0.7O2−δ. The intensities at ±6.5 Å−1 increased gradually, indicating that Ru4+ had strong influence on W0.2Er0.1Ru0.7O2−δ compared with that for C-RuO2. Besides that, compared with RuO2−δ, the intensities changed slightly at ±13.5 Å−1 in W0.2Er0.1Ru0.7O2−δ is due to the coordination of Ru-W/Er.

**Fig. 4 XPS characterization for W0.2Er0.1Ru0.7O2−δ.** a) Ru 3d spectra, b) W 4f spectra, c) Er 4d spectra, d) O 1s spectra for the prepared W0.2Er0.1Ru0.7O2−δ, Er0.1Ru0.7O2−δ, W0.2Ru0.8O2−δ, W0.2Er0.1Ru0.9O2−δ, and RuO2−δ nanosheets. In order to precisely analyze the valence state of Ru, X-ray absorption near-edge spectroscopy (XANES) was applied to characterize RuO2−δ and W0.2Er0.1Ru0.7O2−δ. Ru foil and C-RuO2 were employed as reference materials. Compared with Ru K-edge position of Ru foil, the C-RuO2, RuO2−δ, and W0.2Er0.1Ru0.7O2−δ all shifted to higher energy, resulting from the Ru–O bonds in these materials (Fig. 5a). Additionally, the Ru K-edge spectra in Fig. 5a showed the adsorption energy of the prepared RuO2−δ and W0.2Er0.1Ru0.7O2−δ were different from that for C-RuO2. This result mainly resulted from the fact that Ru valence state in RuO2−δ and W0.2Er0.1Ru0.7O2−δ were mainly dominated Ru4+ accompanied with Ru2+ (δ < 1). Simultaneously, compared with adsorption energy of RuO2−δ, the adsorption energy for W0.2Er0.1Ru0.7O2−δ shifted to lower energy region, indicating that Ru valence state in W0.2Er0.1Ru0.7O2−δ was a little lower than that in RuO2−δ due to introduction of W and Er. Additionally, the adsorption energy (Es) for RuO2−δ (22.119.99 eV) was also a little higher than that for W0.2Er0.1Ru0.7O2−δ (22.118.92 eV). These results were consistent with the valence state analysis in XPS. Furthermore, extended X-ray absorption fine structure (EXAFS) with Fourier transform as well as its counterpart (k3-weighted EXAFS) was applied to analyze the structure of RuO2−δ and W0.2Er0.1Ru0.7O2−δ (Fig. 5b). Compared with the bond of Ru–Ru in Ru foil (2.68 Å), W0.2Er0.1Ru0.7O2−δ exhibited a slightly longer interatomic distance (2.71 Å), which could be related with the strained effect in HRTEM5 (Supplementary Table 7). Additionally, the Ru–Ru and Ru–O bonds in RuO2−δ and W0.2Er0.1Ru0.7O2−δ showed different interatomic distances is due to the existence of lower Ru4+ valence state, compared with that in C-RuO2 (3.12 and 3.56 Å). Besides that, the different Ru–Ru, Ru–O bonds between RuO2−δ and W0.2Er0.1Ru0.7O2−δ should be related with introducing W and Er into RuO2−δ. Furthermore, wavelet transform (WT) for Ru K-edge EXAFS in Fig. 5c was applied to exhibit the length changes of Ru–Ru and Ru–O bonds in W0.2Er0.1Ru0.7O2−δ. The intensities at ±6.5 Å−1 increased gradually, indicating that Ru4+ had strong influence on W0.2Er0.1Ru0.7O2−δ compared with that for C-RuO2. Besides that, compared with RuO2−δ, the intensities changed slightly at ±13.5 Å−1 in W0.2Er0.1Ru0.7O2−δ is due to the coordination of Ru-W/Er.
The binding energies for W and Er in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after OER were positively shifted compared with those before OER, respectively. This suggested that W and Er in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after OER were positively charged (Fig. 8b, c). Compared with $O_{1s}$ in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ before OER, the lattice O and M–O groups in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after OER were slightly positively shifted, indicating $O_{1s}$ were slightly positively charged after OER (Fig. 8d). Simultaneously, the ratio between the area of the lattice oxygen and M–O groups of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after OER stability became smaller, compared with that for $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ before OER. Additionally, the hydroxyl groups disappeared in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after OER, suggesting the hydroxyl groups were oxidized during OER. The surface rearrangement in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ during acidic OER should be responsible for the shift in these electron states (Fig. 8a–d). Simultaneously, after the surface rearrangement, partial electrons from W and Er were transferred to Ru atoms, achieving a charge redistribution among Ru, W, Er, and O. The similar redistribution was also observed in IrO$_2$/SrIrO$_3$ for acidic OER. Remarkably, after electron charge redistribution, Ru $4d$ still keeps Ru$^{4+}$ without the generation of soluble Ru$^{x+}$ ($x > 4$) derivatives. Therefore, charge redistribution among W, Er, Ru, and O is one reason for achieving the long-durable stability of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ in acidic OER.

Characterization of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after acidic OER. To prove there was no generation of oxygen vacancies on $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ during acidic OER, electron spin resonance (ESR) was further applied to characterize $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ after the stability test (Fig. 8e). ESR spectra revealed that there were no obvious peaks around 3275 G (oxygen vacancies) in $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$, confirming that there were no generation of oxygen vacancies during acidic OER. The similar redistribution was also observed in IrO$_2$/SrIrO$_3$ for acidic OER. Remarkably, after electron charge redistribution, Ru $4d$ still keeps Ru$^{4+}$ without the generation of soluble Ru$^{x+}$ ($x > 4$) derivatives. Therefore, charge redistribution among W, Er, Ru, and O is one reason for achieving the long-durable stability of $W_{0.2}Er_{0.1}Ru_{0.7}O_{2-\delta}$ in acidic OER.
that the O–O coupling was from H₂O, rather than from lattice oxygen (Fig. 1). Consequently, there was no generation of high-valance RuO₄, avoiding collapsing the crystal structure of W₀.₂Er₀.₁Ru₀.₇O₂₋.delta. Additionally, the morphology of the W₀.₂Er₀.₁Ru₀.₇O₂₋.delta remained intact after 500 h operation under acidic electrolyte (Fig. 8f, g). The fractional lattice spacing of W₀.₂Er₀.₁Ru₀.₇O₂₋.delta also kept at ~0.356 nm, which may be due to the surface rearrangement during acidic OER (Fig. 8f and Supplementary Fig. 32). The elemental mappings of W₀.₂Er₀.₁Ru₀.₇O₂₋.delta revealed that W, Er, Ru, and O were still distributed uniformly in the sample (Fig. 8g), suggesting the unchanged composition. Moreover, XRD pattern of W₀.₂Er₀.₁Ru₀.₇O₂₋.delta after OER did not change obviously, implying that the structure kept unchanged (Supplementary Fig. 33).

In summary, we applied doping engineering with W and Er for simultaneously boosting the OER activities and stabilities of RuO₂ in acidic electrolyte by tuning electronic structure of RuO₂. The generation of oxygen vacancies during OER was thermodynamically difficult due to the obviously downshift O 2p band centers, which improved the dissolution and oxidation resistance of Ru. Remarkably, the representative W₀.₂Er₀.₁Ru₀.₇O₂₋.delta OER catalyst only required a 168 mV overpotential to reach 10 mA cm⁻² accompanied with long-durable stability of 500 h in acidic electrolyte, overwhelmingly outperforming other Ru-based electrocatalysts reported so far. Particularly, the obtained sample could also operate stably for 120 h at a high current of 100 mA cm⁻² in acidic PEM, further pushing its applications in industrial field. This study not only offers deep insights into tuning electronic properties of catalysts to enhance stabilities, but also opens a new-record horizon for designing electrocatalysts with super activity applying in acidic PEM.

**Methods**

**Materials**: Ruthenium(III) acetate (C₁₄H₂₁O₁₄Ru₃), Tungsten(VI) chloride (WCl₆), and Erbium(III) chloride (ErCl₃) were all directly obtained from Aladdin Reagent (Shanghai) Co., Ltd. HCl and H₂SO₄ was purchased from Sinopharm Co., Ltd. EDTA and citric acid were provided with Shanghai Macklin Biochemical Co., Ltd. Carbon paper (CP) was supplied with Shanghai Hesen Electric Co., Ltd. Ultra-pure (18.2 MΩ cm⁻¹) water was applied to deal with the prepared electrodes and electrolytes.

**Preparation of RuO₂, W₀.₂Ru₀.₈O₂₋.delta, W₀.₂Ru₀.₇O₂₋.delta, W₀.₁Ru₀.₉O₂₋.delta, Er₀.₁Ru₀.₉O₂₋.delta, and W₀.₂Er₀.₁Ru₀.₇O₂₋.delta nanosheets.** All samples were prepared by the hydrothermal method. Firstly, C₁₄H₂₁O₁₄Ru₃ (0.07 mol, 5.02 g), WCl₆ (0.002 mol, 0.79 g), and ErCl₃ (0.001 mol, 0.27 g) were added into ultra-pure water with vigorous stirring. Then, EDTA (0.01 mol, 1.92 g) and citric acid (0.01 mol, 1.92 g) was added into ultra-pure water with regulating pH to 9 by NH₄OH. Finally, the solution containing EDTA and citric acid was added drop-wise into the metal salt solution for reaction for 12h at 353 K. The obtained precursors were tiled in a treated porcelain boat and heated to 573 K for 4 h and then cooled to 303 K. The methods for preparation of the RuO₂, W₀.₂Ru₀.₈O₂₋.delta, W₀.₂Ru₀.₇O₂₋.delta, W₀.₁Ru₀.₉O₂₋.delta, and W₀.₂Er₀.₁Ru₀.₇O₂₋.delta nanosheets were the same as that of W₀.₂Er₀.₁Ru₀.₇O₂₋.delta nanosheets.

**Characterization.** The XRD patterns for prepared electrocatalysts were all obtained on a X-pert Powder (PAAnalytical B.V., Netherlands) with PIXcel 1D detector and Cu-Kα (λ = 1.54178 Å) radiation. Additionally, Tecnai G2 F20 S-TWIN (FEI, America) was used to obtain the TEM, HR-STEM, and elemental mapping at a voltage of 200 kV. For XPS analysis, X-ray photoelectron spectrometer (Thermo Scientific Escalab Xi+, England) was used to characterize these representative electrocatalysts. For ESR, JEOL FA200 was applied to characterize
these samples. ICP-MS (Agilent ICP-OES730) was employed to show the ratios of these elements in W0.2Er0.1Ru0.7O2 nanosheets in 0.5 M H2SO4. ICP-OES analysis for W0.2Er0.1Ru0.7 O2−δ after 500 h operation in acidic electrolyte. Additionally, the samples were analyzed via a GC calibrated O2. Each injection into GC was repeated to eliminate error.

**Electrochemical measurements.** These prepared electrodes were characterized by Bio-Logic VSP potentiostat. The mass-loading for prepared electrocatalysts on CP was 0.33 mg cm−2. The prepared C-RuO2/CP, RuO2−δ/CP, W0.3Ru0.7O2−δ/CP, W0.2Ru0.8O2−δ/CP, W0.1Ru0.9O2−δ/CP, Er0.1Ru0.9O2−δ/CP, and W0.2Er0.1Ru0.7O2−δ/CP, W0.3Er0.7O2−δ/CP (1 × 0.5 cm2) were, respectively, applied as working electrodes. Meanwhile, the platinum column electrode and Hg/HgSO4 (0.645 V) were, respectively, employed as counter and reference electrodes. Besides that, LSV measured with the three-electrode configuration as well as detected by Faraday constant (96,485.33289 C/mol), t stands for the applying current, t is the total time for OER, and VM represents the molar volume of the generated O2.

**Theoretical calculations.** Spin-polarized DFT calculations were conducted on projector-augmented wave (PAW) in the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange-functional functional was applied. The cut-off energy for plane-wave basis set was set as 450 eV. A 20 Å vacuum slab in a direction perpendicular to the surface of catalyst was adopted to avoid periodic interactions. The Brillouin zone integration was performed with 3 × 3 × 1 Monkhorst-Pack k-point sampling for geometry relaxation. For the calculations of DOS, the k-point mesh was increased to 6 × 6 × 1. The convergence threshold for force and energy during optimization were set as 0.03 eV Å−1 and 10−6 eV, respectively. A p(4 × 4) unit cell of RuO2 (110) surface with three layers in their slab was comprised. In the main text and supplementary information, the influence of neighboring intermediates on the energetics was not considered when free-binding energies were calculated without special instructions. Additionally, the influence of aqueous solvent in calculation were not considered. The first two layers as well as the adsorbate intermediates were relaxed with the fixation of other atoms for geometry optimization. For Er and W doping, three different initial structures are considered, +3 and +6 valences of Er and W are taken into account, respectively. It is worth mentioning that the model of Er-doped exhibited a relatively lower energy as compared with Er and W co-doped, because of the larger distortion of the adjacent O at the Er defect position, another more reasonable structural model is selected. On this basis, we simulated the adsorption behavior of *O, *OH, and *OOH intermediates for each catalyst, and each model was optimized to convergence. ΔG for each OER step was calculated through the model of computational hydrogen electrode along with the equation as following:

\[
\Delta G = \Delta G_{\text{prod}} + \Delta E - T \times \Delta S.
\]

The formula for calculation of VO:

\[
\Delta G(V_O) = G(V_O) + (G(H_2O) - G(H_2)) - (G(*O)),
\]

where

\[
\eta(t) = \frac{1}{F} \frac{\Delta G(V_O)}{C_0}.
\]

Fig. 7 The long-durable stability investigation for OER and PEM in acidic electrolyte. a The current-time (500 h) stability of W0.2Er0.1Ru0.7O2−δ and W0.3Ru0.7O2−δ (diameter: 3 mm). The detector is thermal conductivity detector (TCD). The electrolyte under stirring was firstly degassed by Ar gas for half an hour. Then, the gaseous sample was taken out with a gas tight syringe every 20 min at 10 mA. Additionally, the samples were analyzed via a GC calibrated O2. Each injection into GC was repeated to eliminate error.
where $\Delta E$ refers to DFT energy difference; $\Delta S$ and $\Delta E_{ZPE}$ refer to corrections with entropy through vibrational analysis and zero point energy at 300 K, respectively; $G(V_O)$ refers to the energy of the structure after leaving a vacancy; $G(\ast O)$ refers to the energy that adsorbs the structure of $\ast O$ intermediate; $G_{H2O}$ and $G_{H2}$ are the energy for water molecules and hydrogen molecules, respectively.

Data availability
All of the authors claim that the presented data in this work will be available for the contacts from corresponding author with reasonable request.

Received: 23 March 2020; Accepted: 23 September 2020; Published online: 23 October 2020

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