Direct Dioxygen Radical Coupling Driven by Octahedral Ruthenium–Oxygen–Cobalt Collaborative Coordination for Acidic Oxygen Evolution Reaction

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ABSTRACT: The acidic oxygen evolution reaction (OER) has long been the bottleneck of proton exchange membrane water electrolyzers given its harsh oxidative and corrosive environments. Herein, we suggest an effective strategy to greatly enhance both the acidic OER activity and stability of Co$_2$O$_4$ spinel by atomic Ru selective substitution on the octahedral Co sites. The resulting highly symmetrical octahedral Ru–O–Co collaborative coordination with strong electron coupling effect enables the direct dioxygen radical coupling OER pathway. Indeed, both experiments and theoretical calculations reveal a thermodynamically breakthrough heterogeneous diatomic oxygen mechanism. Additionally, the active Ru–O–Co units are well-maintained upon the acidic OER thanks to the electron transfer from surrounding electron-enriched tetrahedral Co atoms via bridging oxygen bonds that suppresses the overoxidation and thus dissolution of active Ru and Co species. Consequently, the prepared catalyst, even with a low Ru mass loading of ca. 42.8 $\mu$g cm$^{-2}$, exhibits an attractive acidic OER performance with a low overpotential of 200 mV and a low potential decay rate of 0.45 mV h$^{-1}$ at 10 mA cm$^{-2}$. Our work suggests an effective strategy to significantly enhance both the acidic OER activity and stability of low-cost electrocatalysts.

INTRODUCTION

Water electrolysis is considered as an environmental-friendly technology for green hydrogen production. Compared with the commercially available alkaline water electrolyzer, the acidic proton exchange membrane water electrolyzer (PEMWE) possesses several advantages, including lower ohmic resistance, higher current densities, better compatibility with sustainable energy resources, etc.$^{1-3}$ The development of the PEMWE, however, has long been limited by the anodic oxygen evolution reaction (OER), due to the lack of effective and stable electrocatalysts as most known electrocatalysts would suffer from corrosion and dissolution under the strongly acidic and oxidative conditions. Even for the state-of-the-art noble metal Ru-based materials, the stability is still unsatisfactory because of the formation of soluble species (e.g., RuO$_2$) during the acidic OER.$^{4-6}$ Previous studies also demonstrated that the OER over RuO$_2$ is dominated by lattice oxygen mechanism (LOM), which involves the continuous insertion and extraction of lattice oxygens and thus would destroy the structural stability.$^{7-10}$

In addition to the severe performance decay, the high price and scarcity of Ru (ca. $17,420 kg^{-1}$) are also a big concern. The noble metal content in Ru-based catalysts (e.g., transition metal-doped RuO$_2$)$^{11-13}$ RuB$_2$,$^{14}$ Ru/RuS$_2$)$^{15}$ is usually more than 80 wt %, and the Ru mass loading is typically higher than 0.2 mg cm$^{-2}$ in three-electrode tests or 2 mg cm$^{-2}$ in PEMWE in order to achieve decent performance. Therefore, enormous efforts have been devoted to lowering the Ru usage by improving the utilization efficiency (e.g., through loading highly dispersed clusters or even single atoms on acid-resistant supports) or further, by directly using non-noble catalysts.$^{16-20}$ In this regard, Co$_3$O$_4$ has been considered as a promising alternative. Previous studies have revealed that Co$_3$O$_4$ delivers an acceptable OER stability in acidic electrolytes, yet its activity requires further enhancement.$^{21-24}$ The Co$_3$O$_4$ shares a spinel AB$_2$O$_4$ structure, where Co$^{II}$ ions occupy the tetrahedral A sites and Co$^{III}$ ions occupy the octahedral B sites, respectively. The latter has been demonstrated to be significantly more active than the former for OER.$^{25}$ This is confirmed by the fact that the ZnCo$_3$O$_4$ (where Zn atoms occupy the tetrahedral sites only) shows comparable OER activity as that of Co$_3$O$_4$,$^{26}$ while the CoAl$_2$O$_4$ (where Al atoms...
occupy the octahedral sites) possesses weaker activity than $\text{Co}_3\text{O}_4$. The engineering of octahedral Co (i.e., Co$_{\text{oct}}$) sites, for instance, by atomic substitution, therefore provides an effective way to regulate the coordination environment of Co$_3$O$_4$ and further boost the OER performance. In addition, previous studies have demonstrated a diatomic oxygen mechanism (DOM) over Co$_3$O$_4$ for OER. The DOM proceeds with direct dioxygen radicals coupling to release O$_2$, which can effectively circumvent the formation of the *OOH intermediate and thus break the *OH and *OOH scaling relationship limitation of the traditional adsorbate evolution mechanism (AEM). In this regard, the precise substitution of octahedral Co with other atoms might also enable the DOM pathway and significantly enhance the acidic OER performance, though it has not been realized yet.

In this work, we developed a modified Co$_3$O$_4$ spinel electrocatalyst with atomic Ru substitution on the Co$_{\text{oct}}$ sites (named as RuCoO$_x$ thereafter). The construction of highly symmetrical Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ collaborative coordination with a strong electron coupling effect significantly shortens the spatial distance between Ru$_{\text{oct}}$ and Co$_{\text{oct}}$, which makes the direct dioxygen radical coupling become favorable. Indeed, we confirmed both experimentally and theoretically that a thermodynamically breakthrough heterogeneous DOM driven by the Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ collaborative coordination is preferred, rather than the theoretically limited AEM and the structurally unstable LOM that are more commonly observed. More importantly, the strong interaction of the Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ collaborative coordination is also well-maintained upon the acidic OER due to the electron capture from surrounding electron-enriched tetrahedral Co (i.e., Co$_{\text{tet}}$) atoms via bridging oxygen bonds. As a result, the RuCoO$_x$ exhibits significantly enhanced OER activity and stability in acid even with a low Ru loading of ca. 42.8 $\mu$g cm$^{-2}$. Specifically, the RuCoO$_x$ delivers a small overpotential of 200 mV at 10 mA cm$^{-2}$ and can steadily operate for at least 100 h with an only 45 mV potential decay. Further, the assembled PEMWE based on the commercial 20 wt % Pt/C and RuCoO$_x$ combination also shows outstanding stability even at higher current densities.

**RESULTS AND DISCUSSION**

**Catalyst Synthesis and Structural Characterization.** The RuCoO$_x$ catalyst with Ru$_{\text{oct}}$ substitution was synthesized on carbon cloth substrate by a cation exchange strategy. In a typical synthesis, the Co(OH)$_2$ nanosheets were first electrodeposited onto carbon cloth followed by calcination to produce the porous Co$_3$O$_4$ nanosheets precursor, which was then immersed in a RuCl$_3$ aqueous solution to initiate the cation exchange. The resulting product was then annealed into the anhydrous RuCoO$_x$ nanosheet catalyst (Figure 1a, see the
principle of the cation exchange strategy in the Supporting Information). We systematically investigated the impacts of synthetic conditions and found that a cation exchange time of 9 h and a second calcination temperature of 250 °C would result in the optimal OER activity and operation stability (Figure S1). The conditions were then used for the rest of the study.

We first examined the structural difference between the Co₃O₄ and RuCoOₓ. The SEM images show that both the porous Co₃O₄ and RuCoOₓ nanosheet array uniformly covers the surface of carbon fibers (Figure 1b,c and Figure S2a–c), forming an interconnected 3D network with close surface areas (12.36 and 13.36 m² g⁻¹, respectively, Figure S3a). A careful observation further reveals that both the Co₃O₄ and RuCoOₓ nanosheets are composed of abundant micropores with the same pore diameter distribution from 5 to 60 nm (Figures S2d, S3b, and S4). Although the RuCoOₓ largely inherits the overall morphology from the Co₃O₄ precursor, the lattice distance is sensitively expanded (e.g., d(200) from 0.244 to 0.251 nm, and d(220) from 0.285 to 0.290 nm) as revealed by the high-resolution transmission electron microscopy (HRTEM) image (see comparison in Figure 1d and Figure S2e). This can be also confirmed by the X-ray diffraction (XRD) patterns (Figure 1e and Figure S5). Besides the two broad diffraction peaks originated from the carbon cloth substrate (Figure S6), all the other diffraction peaks can be assigned to spinel Co₃O₄ (JCPDS card no. 74-1656). Notably, the overall diffraction peaks of the RuCoOₓ slightly shift to lower angles in comparison to those of the Co₃O₄ implying that the lattices of the Co₃O₄ are expanded because of the incorporation of Ru atoms with a larger radius. Moreover, no other Ru species are observed even after the thermal calcination of the RuCoOₓ at 800 °C in an Ar atmosphere (Figure S5), which not only rules out the existence of amorphous Ru species but also demonstrates the high structural stability of Ru atoms in the Co₃O₄ matrix. Indeed, the selected area electron diffraction (SAED) pattern of the RuCoOₓ also confirms that all the visible polycrystalline rings belong to Co₃O₄ (Figure 1f).

Additionally, the high-angle annular dark-field scanning TEM (HAADF-STEM) image and its corresponding elemental maps reveal that the elemental distribution of the substituted Ru is highly consistent with that of Co and O signals (Figure 1g). These results suggest that the Ru atoms were doped into the Co₃O₄ lattice, instead of aggregating on the surface of the Co₃O₄ nanosheets as Ru or RuO₂ clusters.

The mass loadings of Ru and Co on carbon cloth were ca. 0.0428 and 2.3495 mg cm⁻², respectively, corresponding to a bulk Ru ratio of ca. 1.55 at. % (determined by inductively
coupled plasma mass spectrometry or ICP-MS, see details in the Supporting Information). Meanwhile, the surface Ru ratio, determined by X-ray photoelectron spectroscopy (XPS) analysis, was up to ca. 25 at.% (Figure S7). These results suggest that cation exchange reaction would lead to a concentration gradient of Ru from high to low along the surface to bulk, which improves the Ru utilization efficiency for the surface electrocatalysis reaction. The commercial RuO₂ on carbon cloth with a mass loading of 1 mg cm⁻² was also prepared for comparison (see detailed characterizations in Figure S8).

Identification of Selective Ru Sites in the RuCoOₓ. In order to reveal the selective substitution of Co sites (octahedral or tetrahedral) in the Co₃O₄ by Ru atoms, we then conducted the Raman test, which is a sensitive technology to reveal the changes in the coordination environment. The Co₃O₄ spinel presents five Raman-active modes (i.e., A₁g, E₂g and three F₂g modes, Figure 2a). The characteristic Raman peaks of the RuCoOₓ are almost identical to those of Co₃O₄ but shift to the higher frequency region. Notably, the shift of A₁g (685 cm⁻¹) is more significant than that of F₂g band (195 cm⁻¹). Since the former is related to the stretching of Co³⁺−O in the octahedral (Co₃O₄) units while the latter raises from Co⁴⁺−O in the tetrahedral (CoO₂) groups, thus we can reasonably infer that the Ru atoms preferentially occupy the position of Co₃O₄ instead of CoO₂ sites. Indeed, the decrease in peak intensity of A₁g/F₂g bands of the RuCoOₓ compared to that of the Co₃O₄ also suggests the decrease in the ratio of Co₃O₄/CoO₂ due to the RuO₂ substitution.

We also employed the Fourier transformed (FT) 3k-weighted extended X-ray absorption fine structure (FT-EXAFS) analysis to identify the bonding environment. The Ru FT-EXAFS spectra indicate that a characteristic peak at 2.49 Å observed for the RuCoOₓ in the second shell (slightly larger than the Co₃O₄−Co₃O₄ bond, 2.45 Å, without phase correction, Figure S9b) can be assigned to Ru₃O₄−Co₃O₄ coordination, suggesting that Ru atoms successfully substitute partial Co₃O₄ sites in the Co₃O₄. It is noted that the weakened and broadened FT peak at 3.13 Å in the higher shell likely belongs to the Ru₃O₄−Co₃O₄ coordination, which is obviously different from the intense FT peak at 3.19 Å that assigned to the Ru₃O₄−Ru₃O₄ coordination in the RuO₂. This can also exclude the existence of the pure RuO₂ phase in the RuCoOₓ well in line with the SAED and XRD results. Apart from the experimental spectroscopy characterizations, density functional theory (DFT) calculation also reveals that the required free energy of substituting one Ru atom into the Co₃O₄ site is 0.19 eV lower than that into the CoO₂ site (Figure 2c), further confirming the selective occupancy of Ru atoms in the octahedral Co sites of Co₃O₄.

Revelation of Strong Electron Coupling Effect in the RuCoOₓ. The Ru₃O₄ substitution in the Co₃O₄ is expected to modulate the surface electronic distribution and bonding environment. The surface-sensitive Co 2p XPS spectrum of the RuCoOₓ shows a upshift of ca. 0.1 eV compared to that of the Co₃O₄ (Figure 2d), suggesting the decrease in the Co₃O₄/CoO₂ ratio (Table S1). This is not only ascribed to the occupied octahedral sites by substituted Ru atoms as revealed before but also attributed to the partial electron transfer from Ru₃O₄ to Co₃O₄ atoms via bridging oxygen atoms in the RuCoOₓ. The later can be further verified by the complementary Ru 3p XPS spectra (Figure 2e), wherein the overall binding energy of the RuCoOₓ is 0.2 eV higher than the RuO₂ but 0.1 eV lower than that of the RuCl₃ control, and a more obvious trend was observed for the Ru 3d XPS spectra (Figure S10), meaning that the Ru oxidation state in the RuCoOₓ is between +3 and +4 (Table S1), higher than the original Co₃O₄ site (+3) in the Co₃O₄. It is noted that the existence of Ru(OH)₃ is inevitable due to the slight hydrolysis of the RuCl₃ in air. The Ru K-edge XANES and 1st derivative spectra (Figure 2f), wherein the absorption edge of the RuCoOₓ is higher than that of the RuCl₃ but lower than that of the RuO₂. Meanwhile, the energy of the maximum of 1st derivative of the RuCoOₓ displays the same trend (see detailed explanation in the Supporting Information). The lower Ru oxidation state in the RuCoOₓ than that in the RuO₂ would thus result in the longer bond length of Ru−O bonds (1.56 vs 1.47 Å, Figure 2b), which could be attributed to the increased extranuclear electron numbers of Ru centers in the RuCoOₓ. The increased electron cloud density around active Ru sites has been demonstrated to be favorable to facilitating the acidic OER progress. It is noted that the Co K-edge XANES spectra indicate that the Co oxidation state in the RuCoOₓ is almost identical to that in the Co₃O₄ (Figure S9a), and the corresponding distances of Co−O, Co₃O₄−Co₃O₄ and Co₃O₄−Co₃O₄ bonds in R space of FT-EXAFS spectra are also almost identical (Figure S9b). This is not surprising because the X-ray absorption spectroscopy is bulk sensitive, while the ion exchange most likely occurs on the surface of the Co₃O₄ given the trace amount of Ru (1.55 at.% and thus would not significantly affect the bulk properties.

Considering that the XPS and XANES only identify the overall change of electronic structure of the Co₃O₄ after Ru₃O₄ substitution, we further conducted the Bader charge analysis to explore the partial change of elemental charge distribution on the catalyst (near-)surface in detail. The substituted Ru₃O₄ atom can significantly modulate the positive charge of one of the oxygen-bridging Co₃O₄ atoms from +1.23 e to +1.18 e and slightly change the charge distribution of the other neighboring Co₃O₄ sites, yet barely affect the surrounding Co₃O₄ sites (see comparison between the RuCoOₓ and Co₃O₄ in Figure 2g,h). In addition, the Bader charge of the substituted Ru₃O₄ atom (+1.43 e) in the RuCoOₓ is obviously higher than that of the original Co₃O₄ atom (+1.23 e) in the Co₃O₄ but still lower than that of Ru atoms in the RuO₂ (e.g., +1.78, +1.70, and +1.60 e, Figure 2i), which also strongly supports the Ru 3p XPS and Ru K-edge XANES results. Both results reveal that Ru₃O₄ substitution in the Co₃O₄ would induce electron transfer from the Ru₃O₄ atom to an adjacent Co₃O₄ atom via bridging oxygen bonds, well in line with the XPS analysis. The resulted partial charge imbalance in the RuCoOₓ remarkably enhances the hybrid behavior of Ru₃O₄−O and Co₃O₄−O coordination, resulting in the strong electron coupling effect of the Ru₃O₄−O−Co₃O₄ unit with the shortened atomic distance between Ru₃O₄ and Co₃O₄ (2.61 Å) in comparison to the corresponding Co₃O₄−Co₃O₄ atomic distance (2.78 Å) in the Co₃O₄ (Figure 2g,h). The heterogeneous metal sites with shortened distance in the Ru₃O₄−O−Co₃O₄ collaborative coordination (research focus thereafter) is more beneficial than neighboring Ru₃O₄−Co₃O₄ sites (3.07 Å) to conducting direct dioxygen radical coupling for the heterogeneous DOM. It is noted that the various Bader charges of Co in the Co₃O₄ and RuCoOₓ can be attributed to the different coordination environments of (near-)surface and bulk atoms (Figure S11).

Apart from the local Bader charge analysis, we also calculated the partial band centers and adsorption ability of
The result indicates that the substituted Ru$_{\text{oct}}$ atom in the Co$_{\text{oct}}$O$_4$ can adjust the 3d band center of adjacent Co$_{\text{oct}}$ sites (from $-1.41$ to $-1.48$ eV) more significantly than that of surrounding Co$_{\text{oct}}$ sites (from $-1.27$ to $-1.23$ eV, Figure S12a,b). Additionally, the Ru$_{\text{oct}}$ 4d band center in the RuCoO$_2$ also distinctly downshifts compared with those in the RuO$_2$ ($-2.00$ vs $-1.37$ or $-1.46$ eV, Figure S12a,c). Compared with Co sites in the Co$_{\text{oct}}$O$_4$ and Ru sites in the RuO$_2$, the optimized band centers in the RuCoO$_2$ contribute to strengthening the water molecule adsorption ability of the Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ units in acid (Figure S13), which is favorable to accelerating the subsequent OER steps. Interestingly, we found that the O 2p band centers in the Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ units also display the obvious downward shift in comparison to those in the Co$_{\text{oct}}$O$_4$ and RuO$_2$ (Figure S12), suggesting that lattice oxygens would not participate in the OER pathway, i.e., the LOM pathway is not preferred. Whereas, for the RuO$_2$, its O 2p band centers are closest to the Fermi level (Figure S12c). Meanwhile, the formed strongest Ru 4d–O 2p orbital hybridization (the closest band center distance between Co 3d/Ru 4d and O 2p orbitals, Figure S12) would facilitate the lattice oxygen activation and subsequently trigger the LOM reaction pathway, thereby causing inevitable structural deformation or even collapse and further the performance decay. Indeed, our DFT calculation reveals that the rutile RuO$_2$ (110) facet with the lowest thermodynamic surface energy prefers to follow the LOM rather than the AEM reaction pathway (Figure S14, Tables S2 and S3). The LOM on the RuO$_2$ was also experimentally confirmed by $^{18}$O isotope-labeled differential electrochemical mass spectrometry (DEMS) in previous studies.$^{7-10}$ In addition to the formation of Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ collaborative coordination with a strong electron coupling effect and enhanced water adsorption ability, the substitution of Co$_{\text{oct}}$ sites by Ru atoms might also slightly cause structural distortion and thus create defects. Both the O 1s XPS spectra and electron paramagnetic resonance (EPR) analysis reveal that the RuCoO$_2$ possesses more oxygen vacancies than the Co$_{\text{oct}}$O$_4$ and RuO$_2$ (Figures S15 and S16, Table S1).

Identification of Acidic OER Mechanism of the RuCoO$_2$: Given the unique coordination environment and strong interaction of the Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ units in the RuCoO$_2$, we then conducted DFT calculation to explore the OER reaction pathway. According to the XRD result and previously reported articles, we used the spinel Co$_{\text{oct}}$O$_4$ (311) facet with Ru$_{\text{oct}}$ substitution as the model (Figure S17). We first evaluated the two well-accepted OER mechanisms (i.e., AEM and LOM) for the RuCoO$_2$ (Figure 3a and b). The calculation result indicates that the potential determining step (PDS) of the RuCoO$_2$ following the AEM reaction pathway is the dehydrogenation step on the Co$_{\text{oct}}$ sites (1.88 eV, Figure S18a, Table S2), while the O–O coupling step by lattice oxygen activation follows the LOM reaction pathway at the same sites (2.07 eV, Figure S18b, Table S3). The maximum Gibbs free energy of the AEM is lower than that of the LOM reaction pathway (Figure 3d), meaning that the AEM pathway is preferred over the RuCoO$_2$. However, we consider that the Ru sites are much more active than Co$_{\text{oct}}$ sites in theory.$^{44,45}$ In fact, the OER process over Ru$_{\text{oct}}$ sites in the RuCoO$_2$ is only significantly hindered by the transformation of $^*$O to $^*$OH intermediates (2.43 eV), while the adsorption of $^*$OH intermediate (0.25 eV) and the subsequent dehydrogenation (0.75 eV) proceed much easier (Figure S18a, Table S2). This indicates that the OER over the RuCoO$_2$ could possibly proceed with an unusual DOM reaction pathway driven by the heteroatomic Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ units. The DOM involves the adsorption of the $^*$OH intermediate, the subsequent dehydrogenation, and the final dioxygen radical coupling.
process (Figure 3c), which has been widely studied in theoretical and experimental aspects. We then further calculated the bond lengths and the bond angles of the Ru$^{\text{oct}}$–O–Co$^{\text{oct}}$ units and found that they are highly symmetrical (Figure 3e) along with shortened atomic distances (Figure 2g). Both are beneficial to conducting the final O–O radical coupling with a low thermodynamic energy barrier. Indeed, our simulation shows that the required free energy of the dioxygen radical coupling to form O$_2$ is as low as 1.17 eV (Figure S19a, Table S4), which further suggests that the OER over the RuCoO$_x$ might proceed with the DOM reaction pathway. In this case, the PDS would be the dehydrogenation of *OH intermediate on the Ru$_{\text{oct}}$ site (step III in Figure 3c), which requires a free energy of 1.74 eV (Figure 19a, Table S4), lower than that of the RuCoO$_x$ via the AEM or LOM reaction pathway (1.88 and 2.07 eV, respectively, Figure 3d) and that of the RuO$_2$ following the favorable LOM reaction pathway (2.16 eV, Figure S14). In addition, we also investigated the Ru$_{\text{oct}}$–O–Co$_{\text{tet}}$ coordination environment, and the bond lengths of Ru$_{\text{oct}}$–O and Co$_{\text{tet}}$–O are 2.00 and 1.87 Å, respectively (Figure S20). The unsymmetrical Ru$_{\text{oct}}$–O–Co$_{\text{tet}}$ units would lead to a much higher energy barrier for the dioxygen radical coupling (2.11 eV, Figure S19b, Table S4), which thus becomes the PDS. We also evaluated dual Ru$_{\text{oct}}$ sites, dual Co$_{\text{oct}}$ sites, and the combination of Co$_{\text{oct}}$ and Co$_{\text{tet}}$ sites in the RuCoO$_x$ (Figure S19c–e, Table S4). The result demonstrates that the thermodynamic free energies of these dual sites at the PDSs are higher than that of the cooperative Co$_{\text{oct}}$ and Ru$_{\text{oct}}$ sites. Accordingly, the DFT calculation results reveal that the OER over the RuCoO$_x$ catalyst proceeds with the heterogeneous DOM reaction pathway thanks to the highly symmetrical and contractive Ru$_{\text{oct}}$–O–Co$_{\text{oct}}$ collaborative coordination, which has not been discovered so far.

The dioxygen radical coupling, which can be captured by in situ electrochemical techniques, reliably distinguishes the DOM from the AEM and LOM. To experimentally confirm the O–O radical coupling, we then carried out the in situ Raman test in 0.1 M HClO$_4$. As shown in Figure 3f, when the applied potential is up to 1.66 V vs RHE (without iR correction) for the RuCoO$_x$, the Raman shift at around 1050 cm$^{-1}$ assigned to dioxygen radical coupling appears, which strongly supports the heterogeneous DOM reaction pathway of the RuCoO$_x$. We noted that the signal is relatively weak, but unfortunately failed to enhance the intensity either
by prolonging the test time or applying higher potentials, as the large amount of generated oxygen bubbles would interfere with the Raman incident light. It is also noted that the Raman signals assigned to Co−OOH (∼600 cm⁻¹) or Ru−OOH (∼720 cm⁻¹) are not detected, thereby excluding the possibility of the AEM over the RuCoOₓ. In brief, we confirmed both theoretically and experimentally that the RuCoOₓ catalyst prefers a thermodynamically breakthrough heterogeneous DOM driven by the Ru−O−Co(collaborative coordination).

Acidic OER Performance of the RuCoOₓ. Given that the DOM can effectively circumvent the thermodynamic energy barrier step (i.e., the formation of the *OH intermediate) and thus break the *OH and *OOH scaling relationship limitation of the AEM, the RuCoOₓ catalyst is expected to exhibit higher activity than the state-of-the-art RuOₓ and CoOₓ catalysts. To further verify the inference, we then conducted the acidic OER measurements in a 1 M HClO₄ electrolyte that is much harsher than the commonly used 0.1 M HClO₄. The Hg/HgSO₄ reference electrode was calibrated against reversible hydrogen electrode (RHE) using a cyclic voltammetry (CV) method (Figure S21). Linear sweep voltammetry (LSV) curves display that the RuCoOₓ only requires a small overpotential of 200 mV to reach the benchmark current density of 10 mA cm⁻², much lower than that of the RuOₓ and CoOₓ (265 and 409 mV, respectively, Figure 4a). It is noted that the activity of the commercial RuOₓ is comparable to the reported value in the literature (Table S5). Although the RuCoOₓ exhibits a comparable geometric activity to other recently reported high-performance acidic OER electrocatalysts, its mass activity (e.g., 2278 A g⁻¹ Ru at 1.48 V vs RHE, Figure 4b) is significantly higher than the RuOₓ and most of the Ru or Ir-based catalysts (Figure 4b, Table S6). We also measured the electrochemically active surface area (ECSA) by evaluating the double layer capacitance (Cdl) (Figures S22–S24). The result shows that the calculated ECSA of the RuCoOₓ (5.70 cm²) is larger than that of the RuOₓ and CoOₓ (1.58 and 5.42 cm², respectively). It is noted that the RuCoOₓ still possesses the largest ECSA or BET normalized currents (Figures S25 and S26), suggesting the highest intrinsic activity among the three catalysts. This is further confirmed by the turnover frequency (TOF), which presents the transfer number of molecules per surface active site per unit time. For example, the RuCoOₓ achieves an 8.5-fold higher TOF (0.51 s⁻¹) than the RuOₓ (0.06 s⁻¹) at 1.48 V vs RHE, while the CoOₓ has no detectable OER currents at the same potential (Figures S27 and S28).

Besides the high activity, the RuCoOₓ also possesses the smallest geometric Tafel slope among three catalysts (Figure 4c), suggesting that the Ru−O−Co(collaborative coordination) can accelerate the acidic OER kinetics. This is further confirmed by the electrochemical impedance spectroscopy (EIS) tests at a fixed potential of 1.43 V vs RHE, at which the RuCoOₓ exhibits the smallest film resistance (Rf) and charge transfer resistance (Rct) compared to the RuOₓ and CoOₓ (Figure S29, Table S7). It is noted that we also fit the OER capacitance behavior (i.e., ZCPE(fit)) of three electrodes and found that the trend is almost in accordance with the BET and roughness factor results (Table S8). All the evidence reveals that the thermodynamically breakthrough DOM contributes to the enhanced acidic OER activity of the RuCoOₓ superior to the CoOₓ and RuOₓ.

We further examined the stability of the three catalysts at the benchmark current density of 10 mA cm⁻² (Figure 4d). The operation stability of the OER electrocatalysts in acids has long been the bottleneck. Most transition metal oxides, including CoOₓ, WOₓ, and MnOₓ, cannot tolerate the harsh corrosive conditions. Even for the current state-of-the-art noble RuOₓ catalysts, the stability is still a big concern as they would easily form acidic soluble RuOₓ species with higher oxidation states under the highly oxidative and acidic environments. Indeed, our result confirms that both the RuOₓ and CoOₓ suffer from fast performance decay with quickly elevated potentials within a few hours. Impressively, the RuCoOₓ can steadily operate for at least 100 h with an average degradation rate of only 0.45 mV h⁻¹. The acidic OER performance of the RuCoOₓ evaluated by both the low potential decay rate and noble metal mass loading is superior to various recently reported high-performance Ru-based catalysts. (Figure 4e, and a more detailed comparison in Table S6). Notably, the average metal dissolution rate of the RuCoOₓ during the stability test is significantly slower than that of the RuOₓ and CoOₓ, which is only ∼1/3 and ∼1/30 as that of the latter two, respectively (determined by ICP-MS, inset of Figure 4d). The stability number (S-number), defined as the amount of evolved O₂ when a metal atom dissolves in the electrolyte, is another vital metric to evaluate the acidic OER stability and economic benefit. Since the cost of Ru (ca. $17,420 kg⁻¹) is nearly 400 times as that of Co (ca. $46 kg⁻¹), we therefore separately calculated the S-number of the RuCoOₓ based on dissolved Ru or Co metal. The calculated result indicates that the S-number of the RuCoOₓ per dissolved Ru atom (31774) is nearly 3 times as that of the RuOₓ (11297), while the S-number of the RuCoOₓ per dissolved Co atom (8895) is nearly 30 times as that of the CoOₓ (300) (Figure S30). In addition, the LSV curve of the RuCoOₓ after 1000 accelerated CV scans shows negligible changes (Figure S31), suggesting that it can withstand the frequent and intermittent power switching process.

We finally assembled a proton exchange membrane water electrolyzer (PEMWE) using two pieces of the RuCoOₓ as the anode and commercial 20 wt % Pt/C as the cathode, respectively (Figure 4f, see details in the Supporting Information). The PEMWE requires cell voltages of only 1.53, 1.56, and 1.60 V (after iR compensation) to drive the large current densities of 100, 200, and 400 mA cm⁻², respectively (Figure 4g). Moreover, the device can steadily operate at 100 mA cm⁻² for continuous 10 h without obvious voltage fluctuation (Figure 4h), and the corresponding Faradaic efficiencies of H₂ and O₂ production reach ca. 97.29 and 90.94%, respectively (determined by water drainage method, Figure S32). The reduced Faradaic efficiency of the OER might be ascribed to the bubble accumulation in the rubber tubes and the possible slight oxidation of the carbon cloth substrate. It is worthy that the mass loading of precious Ru (ca. 85.6 μg cm⁻²) used in the PEMWE is at least 20-fold less than that of other Ru-based PEMWE. 53,58,59

Origin of the Acidic OER Stability of the RuCoOₓ. The structural integrity of the RuCoOₓ after the 100 h of chronopotentiometry test was also investigated by the post physical characterizations. Electron microscope images and XRD patterns reveal no significant changes in the overall morphology and crystal structure (Figures S33 and S34). Moreover, the EPR spectra (Figure S35), together with the O 1s XPS spectra (Figure S36, Table S1), suggest an obvious
and Table S1), though the Ru requires a highly integral and symmetric structure. More durability. Ru K-edge XANES and XPS spectra (Figure 5a, Figure S37, only observed a pair of reversible and weak redox couple corresponding to the Co<sup>III</sup>/Co<sup>II</sup> redox reaction for the RuCoO<sub>x</sub> prior to the OER onset potentials. This means that the Ru<sub>oct</sub>—Co<sub>oct</sub> collaborative coordination with the strong electron coupling effect could promote the electro-oxidation behavior of the adjacent Co<sub>oct</sub> sites but not Co<sub>oct</sub> and Ru<sub>oct</sub> sites and thus capture electrons from oxidized Co<sub>oct</sub> atoms so as to avoid the overoxidation of itself, well in line with the Co 2p XPS result. It should be noted that the failure of identifying the other redox couples from the CV of the RuCoO<sub>x</sub> does not necessarily mean that these redox reactions do not proceed. The oxidation currents might simply overlap with the OER currents and thus are difficult to differentiate. The inference that the overoxidation of active Co<sup>III</sup> sites in the RuCoO<sub>x</sub> is significantly suppressed, however, is also supported by the metal dissolution result before and the in situ Raman analysis later. As a result, the RuCoO<sub>x</sub> catalyst can maintain a decent acidic OER stability at 10 or even 100 mA cm<sup>-2</sup>.

The outstanding stability of the RuCoO<sub>x</sub> can also be confirmed by the in situ Raman analysis. Besides the emerged Raman signal assigned to dioxygen radical coupling and the peak at 936 cm<sup>-1</sup> originating from ClO<sub>4</sub><sup>-</sup> in the electrolyte, the characteristic Raman peaks of the RuCoO<sub>x</sub> do not change or do not move as the potential increases (Figure 3f), suggesting the high structural stability of the RuCoO<sub>x</sub> under applied potentials. Nonetheless, we only observed a pair of reversible and weak redox couple corresponding to the Co<sup>III</sup>/Co<sup>II</sup> redox reaction for the RuCoO<sub>x</sub> prior to the OER onset potentials. This means that the Ru<sub>oct</sub>—Co<sub>oct</sub> collaborative coordination with the strong electron coupling effect could promote the electro-oxidation behavior of the adjacent Co<sub>oct</sub> sites but not Co<sub>oct</sub> and Ru<sub>oct</sub> sites and thus capture electrons from oxidized Co<sub>oct</sub> atoms so as to avoid the overoxidation of itself, well in line with the Co 2p XPS result. It should be noted that the failure of identifying the other redox couples from the CV of the RuCoO<sub>x</sub> does not necessarily mean that these redox reactions do not proceed. The oxidation currents might simply overlap with the OER currents and thus are difficult to differentiate. The inference that the overoxidation of active Co<sup>III</sup> sites in the RuCoO<sub>x</sub> is significantly suppressed, however, is also supported by the metal dissolution result before and the in situ Raman analysis later. As a result, the RuCoO<sub>x</sub> catalyst can maintain a decent acidic OER stability at 10 or even 100 mA cm<sup>-2</sup>.

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The dissolution of Co species can further be indirectly reflected by the change in the Co$^{III}$/Co$^{II}$ ratio (corresponding to integral area of A$^{18}$O/F$^{18}$O peaks) based on the in situ Raman analysis. The Co$^{III}$/Co$^{II}$ ratio of the RuCoO$_x$ only slightly elevates upon the OER potentials (Figure 5f), suggesting the highly structural integrity of the RuCoO$_x$ under positive bias, well in line with the Co 2p XPS and CV analysis (Figure 5b,d). However, the ratio of Co$^{III}$/Co$^{II}$ of the Co$_3$O$_4$ varies dramatically that it sharply rises to maximum at 1.46 V vs RHE and afterward significantly drops under higher potentials. The former can be attributed to the oxidation behavior of Co$^{III}$/Co$^{III}$, while the latter can be ascribed to the overoxidation of Co$^{III}$/Co$^{II}$ to the acidic soluble Co$^{IV}$Co$^{III}$ (i.e., Co$_2$O$_4$) that results in a sharp decrease in Co$_{oct}$ content. The difference in the Co$^{III}$/Co$^{II}$ ratio of the Co$_3$O$_4$ and RuCoO$_x$ during the dynamic OER process also confirms the highly structural integrity of the Ru$_{oct}$−O−Co$_{oct}$ collaborative coordination in the RuCoO$_x$ and thus the high acidic OER stability.

## CONCLUSIONS

In summary, we have developed a highly active and robust RuCoO$_x$ catalyst through partial substitution of Co$_{oct}$ sites in spinel Co$_3$O$_4$ by Ru atoms for enhanced acidic OER performance. Both the experimental and theoretical results confirmed that the resulted Ru$_{oct}$−O−Co$_{oct}$ collaborative coordination with strong electron coupling effect can proceed the thermodynamically breakthrough heterogeneous DOM pathway. Meanwhile, the Ru$_{oct}$−O−Co$_{oct}$ collaborative coordination can also gain electrons from surrounding electron-enriched Co$_{tet}$ sites via bridging oxygen atoms, so that the overoxidation of active Ru$_{tet}$ and Co$_{oct}$ centers into acidic soluble RuO$_4$ and Co$_2$O$_4$ species can be suppressed. As a result, the RuCoO$_x$ catalyst with an ultralow Ru loading of 42.8 µg cm$^{-2}$ delivers decent OER performance with only a 200 mV overpotential and a low degradation rate of 0.45 mV h$^{-1}$ at 10 mA cm$^{-2}$. Our work not only establishes the RuCoO$_x$ as an efficient electrocatalysts for acidic OER, but also suggests an effective strategy to dramatically boost the acidic OER performance of Co$_3$O$_4$ and potentially the big family of spinel oxides by site preferential atomic substitution.

## ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c05556.

Experimental section, theoretical calculation, and additional figures and tables (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

OER  oxygen evolution reaction
PEMWE  proton exchange membrane water electrolyzer
LOM  lattice oxygen mechanism
AEM  adsorbate evolution mechanism
DOM  diatomic oxygen mechanism
Co act  octahedral Co
Co tet  tetrahedral Co
SEM  scanning electron microscopy
SAED  selected area electron diffraction
HAADF-STEM  high-angle annular dark-field scanning transmission electron microscopy
XRD  X-ray diffraction
DFT  density functional theory
XAS  X-ray absorption spectrometry
EPR  electron paramagnetic resonance
CV  cyclic voltammetry
LSV  linear sweep voltammetry

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