5f Covalency Synergistically Boosting Oxygen Evolution of UCoO₄ Catalyst

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ABSTRACT: Electronic structure modulation among multiple metal sites is key to the design of efficient catalysts. Most studies have focused on regulating 3d transition-metal active ions through other d-block metals, while few have utilized f-block metals. Herein, we report a new class of catalyst, namely, UCoO₄ with alternative CoO₆ and 5f-related UO₆ octahedra, as a unique example of a 5f-covalent compound that exhibits enhanced electrocatalytic oxygen evolution reaction (OER) activity because of the presence of the U 5f−O₂ p−Co 3d network. UCoO₄ exhibits a low overpotential of 250 mV at 10 mA cm⁻², surpassing other unitary cobalt-based catalysts ever reported. X-ray absorption spectroscopy revealed that the Co²⁺ ion in pristine UCoO₄ was converted to high-valence Co³⁺/⁴⁺, while U⁶⁺ remained unchanged during the OER, indicating that only Co was the active site. Density functional theory calculations demonstrated that the OER activity of Co³⁺/⁴⁺ was synergistically enhanced by the covalent bonding of U⁶⁺−5f in the U 5f−O₂ p−Co 3d network. This study opens new avenues for the realization of electronic structure manipulation via unique 5f involvement.

INTRODUCTION

Increasing energy demands and environmental issues have prompted intense research on electrochemical water splitting for energy storage and conversion technologies. The sluggish four-electron kinetics of the oxygen evolution reaction (OER) becomes a bottleneck for electrochemical water splitting. Understanding the mechanism and identifying the active sites of the OER are highly important for the design and development of efficient and robust electrocatalysts. Based on the volcano-shaped experimental data, many descriptors affecting the four-electron charge transfer steps on surface-active sites have been proposed, including orbital occupancy close to unity, O 2p-band center relative to the Fermi level, charge-transfer energy, and metal–ligand covalency. These parameters are usually identified on the basis of the electronic structure of 3d transition metals (TMs) in pristine materials. However, there is increasing experimental evidence that the real active elements undergo electronic structural evolution under OER conditions, including charge, spin, orbital, and structure changes. For example, Co ions undergo a valence state transition from Co³⁺ in the tetrahedral site in Co₃O₄ to Co⁵⁺ of cobalt oxyhydroxide (CoOOH) and from Co³⁺ to Co⁴⁺ in spinel LiₓCoO₂ and in CoOOH. In addition to monometallic oxides, some bi- and trimetallic oxide catalysts have been studied, whose OER performance was enhanced by modulating the initial electronic structure of 3d metal active sites. For example, 3d Fe ion introduction can induce a change in the valence state of Co from +2.86 to +3.34 in ZnCo₂O₄, from +2 to +1.96 in CoAl₂O₄, and from +3.5 to +3.4 in perovskite Ba₀.₃₅Sr₀.₆₅CoO₃₋δ. Under applied potentials, the Co valence state changes from ~1.96 to ~2.16 in CoFe₀.₂₅Al₁.₇₅O₄ and from ~2 to ~2.12 in CoAl₂O₄. The initial valence state of cobalt may affect the evolution of the electronic structure under applied potentials and further affect the charge-transfer behavior. The low valence state of Co ions in the pristine material allows for a high possibility of oxidation during the OER. Despite these reports, the valence state evolution of Co ions during the OER process is less than 1.

Moreover, the modulation of the electronic structure of 3d metal oxide catalysts by using 4d and 5d metal dopants has been widely investigated. Previous studies have revealed that the 4d/5d metal possesses a large d electronic wave function spatial extent, producing versatile electronic structures via the interaction between 3d and 4d/5d orbitals and enhancing the OER activity. However, only a few studies have attempted adjusting the 3d electronic structure via 4f
electrons of rare earth metals because of the more localized properties of the 4f orbitals, which do not involve bonding except those of Ce4+ ions. Compared to the 4f orbitals, the extended U 5f electrons can directly participate in chemical bonding in actinide compounds. Recent research shows that uranium and iron oxide heterojunction catalysts exhibit high activity toward water oxidation because of the adjustment of band alignment induced by the “multivalence” of U and Fe ions according to density functional theory (DFT) analysis. Generally, in uranium oxides, U6+/5f and O 2p hybridization is stronger than the hybridization between U4+/5f and O 2p, which implies that U6+ modulates the band alignment more easily because of a stronger U6+–O covalent bond. However, it is unclear whether the U 5f–O 2p–Co 3d network can enhance the catalytic activity toward the OER. Based on these considerations, the structurally ordered catalysts formed by combining 3d TM ions and 5f ions are ideal structural models to explore the possible synergistic enhancement of OER activity due to 3d–5f states.

As known previously, edge-sharing CoO6 octahedra in catalysts favor OER activity and stability. For example, an increased OER activity is correlated with the surface structural conversion of CoO6 from corner-sharing to edge-sharing octahedra in Ba0.5Sr0.5Co0.8Fe0.2O3 and SrCo0.9Fe0.1O3-δ and Cr2O3.24 While the OER catalysts with the edge-shared and faced-shared networks are stable under OER conditions.25,26 Herein, we report a new class of metal oxide UCoO4 with edge-sharing CoO6 and UO6 octahedra, as a highly active and durable OER electrocatalyst in an alkaline solution. In UCoO4, the initial Co and U ions have Co2+ and U6+ valence states, respectively, and have fully ordered arrangements of the Co–O–U network. UCoO4 shows remarkable OER activity with a low overpotential of 250 mV to reach a current density of 10 mA cm−2 and a minimal Tafel slope of 47 mV dec−1, which is significantly higher than those of other B-site pure Co oxide catalysts such as LiCoO2, Li4Co3O7, Co3O4, ZnCo2O4, and WCoO4.27–29 This is unexpected according to descriptors of pristine materials because OER activity is expected at a low Co2+ valence state that has a considerable charge transfer energy (Δ) in UCoO4.30,31 Operando hard X-ray absorption spectroscopy (XAS) at the Co-K and U-L3 edges indicated that the Co ion exhibited an irreversible increase in the valence state at the applied high voltage. Its valence state remains unchanged after switching off voltage, and the U ion has no valence state transition. Soft XAS at the Co-L2,3 edge revealed that all Co2+ ions in UCoO4 are converted to high-valent Co3+ and Co4+ ions during the OER. U-M4,5 indicated strong U 5f and O 2p covalence due to the high valence state of U6+ in UCoO4. DFT calculations demonstrated that the U 5f–O 2p–Co 3d network facilitated synergistically accelerated OER performance.

**RESULTS AND DISCUSSION**

Ideal UCoO4 compounds contain edge-shared CoO6 octahedra separated by orderly-arranged 5f-related UO6 chains (Figure 1a). The crystal structures and morphologies of the synthesized UCoO4 samples were investigated through X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) (Figure 1 and Figure S1a). The diffraction pattern of structurally ordered UCoO4 can be indexed to the orthorhombic space group Imma with fully ordered Co and U ions in the lattice (Figure 1b and Figure S2); no additional peaks were observed before and after the OER. The formation process of UCoO4 was evaluated by conducting differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the precursor and XRD patterns of the sol–gel precursor calcined at different temperatures (Figure S3). We examined the atomic arrangement at the surface regions through high-resolution TEM (HRTEM); the HRTEM images are shown in Figure 1c and d. The lattice fringes with a d-spacing of 0.48 nm, corresponding to the (011) planes of UCoO4, remain unchanged before and after the OER, demonstrating a stable crystal structure of UCoO4. The Co–O–U network collapse was not observed, although the SEM-EDS and ICP-MS results (Table S1) showed small leaching of U during the OER process. Neither surface amorphization in the atomically resolved STEM (Figure S4) nor impurity in the XRD patterns was observed for the UCoO4 catalyst before and after the OER. This is because the stability of the crystal structure depends on the metal–O–metal networks, in which the edge-shared networks are widely regarded as a stable configuration.

The electrocatalytic OER activity of the UCoO4 nanoparticles in an alkaline electrolyte (1.0 M KOH) was assessed using a typical rotating disk electrode (RDE) technique. All electrode potentials were calibrated with respect to the reversible hydrogen electrode (RHE). Linear sweep voltammetry (LSV) curves were normalized by the geometric area of the electrode, as shown in Figure 2a. The LSV curves show the activity order of UCoO4 > IrO2 > Li2Co2O4 > LiCoO2 > Co3O4. The OER kinetics were studied using the corresponding Tafel slopes (Figure 2b). The lowest Tafel slope (47 mV dec−1) was obtained for UCoO4, while the other catalysts showed significantly higher values, verifying the fast intrinsic OER catalytic kinetics of UCoO4. The UCoO4 catalyst exhibited a low overpotential of 250 mV to reach a current density of 10 mA cm−2, outperforming the benchmark IrO2 catalyst (269 mV) and other Co-related catalysts (332 mV for LiCoO2, 295 mV for Li2Co2O4, and 372 mV for Co3O4). At an overpotential of 300 mV (+1.53 V vs RHE), the specific OER activity of UCoO4 was approximately 2.4 times higher than
that of IrO2 nanoparticles and nearly 513 times higher than that of typical CoOx OER catalysts and greatly exceeded that of LiCoO2 and Li2Co2O4 nanoparticles (Figure 2c). Figure 2d shows the cobalt mass activity at an overpotential of 300 mV for UCoO4, Li2Co2O4, LiCoO2, Co3O4, and IrO2. (d) Cobalt mass activities at an overpotential of 300 mV for UCoO4, Li2Co2O4, LiCoO2, Co3O4, and IrO2. (e) Tafel plots and overpotential at 10 mA cm−2 of UCoO4 and various Co-based electrocatalysts recently reported. (f) Chronopotentiometric curves at 10 mA cm−2 current densities (inset: LSV curves before and after 200 CV cycles).

Figure 2. (a) OER LSV curves. (b) Tafel plots. (c) Overpotential required at 10 mA cm−2 (left graph in c) and current density at an overpotential of 300 mV (right graph in c). (d) Cobalt mass activities at an overpotential of 300 mV for UCoO4, Li2Co2O4, LiCoO2, Co3O4, and IrO2. (e) Tafel plots and overpotential at 10 mA cm−2 of UCoO4 and various Co-based electrocatalysts recently reported. (f) Chronopotentiometric curves at 10 mA cm−2 current densities (inset: LSV curves before and after 200 CV cycles).

applied voltage. Compared to the initial state conditions at open circuit voltage (OCV), the Co-K absorption edge shifted to a higher energy level under OER conditions at 1.8 V. This indicates an increase in the Co oxidation state and demonstrates that the OER-active Co ions in UCoO4 serve as active sites. However, the valence state of U remains unchanged in the UCoO4 catalyst before and after the OER according to our XAS measurements at all U-L3 (Figure S7), M2, (Figure 3e), and N1s (Figure S8) edges. In addition, pure U oxides displayed negligible OER activity (Figure S9). These data support that U is OER inactive. The energy shift at the Co-K edge was only 0.35 eV. Using the relationship between the energy shift and Co oxidation state46 and considering the presence of Co2+ in pristine UCoO4 (Figure 3b, discussed below), we obtained an estimated Co valence state of +2.15 for UCoO4 after the OER, which could not explain the high OER activity observed for this catalyst. The reason is that the reaction layer depth strongly reduces with decreasing Co valence state.4 For UCoO4, we expect to see only <30% signal from the reacted layers because of the large particle size (~39 nm, Figure S10) against the ≤2 nm reaction layer (Figure S11). When the applied potential was removed, the energy position of the Co-K edge remained unchanged, retaining that under the OER conditions, which is consistent with the CV results (Figure S12). This is a nice case known for Li4Co3O8 because the same information about the electronic structure under the OER can be obtained after the OER by using ex situ surface-sensitive soft XAS (SXAS) spectra in the TEY mode at the Co-L2,3 and O-K edges (2–4 nm exploring depth), which can provide detailed information about the valence states,36,44 spin states,36,44 local environments45 of the Co ions, and the unoccupied O 2p states.14

The electronic structure of UCoO4 was further examined using ex situ Co-L2,3, O-K, and U-M5 XAS. The multiplet spectral feature and energy position of the Co-L3 SXAS spectrum of pristine UCoO4 in Figure 3b are very similar to those of CoO, indicating a Co2+ state with local octahedral coordination. After the OER, the Co-L3 SXAS spectra shifted to a higher energy than that of EuCoO3 suggesting mixed Co3+ and Co4+ in UCoO4 after the OER, such as Na0.75CoO2.46 Co3.2+ was observed in UCoO4 after the OER (Figure S13), which was due to U leaching (Table S1). This phenomenon has been intensively studied.10 Figure 3c shows the O-K SXAS spectra of UCoO4 before and after the OER in the TEY mode. The pre-edge peaks below 533 eV in the Co oxides are due to the unoccupied O 2p orbitals hybridized with the Co 3d states. Lower energy shift and an increase in the spectral weight of the pre-edge peaks with increasing valence state from Co2+ in Co to Co3+ in EuCoO3 and further to Co4+ in BaCoO3 were observed. In pristine UCoO4, the peak at 531 eV is mainly attributed to the U 5f states mixed with the O 2p states because Co2+ has a very weak contribution from CoO (Figure 3c), as demonstrated by our DFT calculations (magenta). After the OER, three new spectral features, α, β, and γ, appear similar to those of Na0.75CoO2.46 and Li2Co2O4,46 wherein peak α is assigned to the unoccupied eg orbitals of Co3+, while peaks β and γ are attributed to the unoccupied t2g and eg orbitals of Co4+, respectively. Both Co-L2,3 and O-K SXAS spectra demonstrate a significant increase in the valence of Co from +2 to +3.3 after the OER over UCoO4. Additionally, we also carried out the XPS analysis for UCoO4 before and after OER (Figure S14), which supports the Co2+ ions in pristine UCoO4 were converted to high-valence Co3+/4+, and U6+ remained...
unchanged during the OER. The local coordination environments of the OER-active Co ions were also investigated by the operando extended XAFS experiments. The 3D Fourier transform patterns of the Co-K edge spectra as a function of applied potential are shown in Figure 3d. However, only a small decrease in the Co–O bond length could be observed with increasing applied voltages (Figure S15 and Table S2), reflecting the small reaction depth against the considerable exploring depth of the hard X-ray.

Next, we verified the presence of U$^{6+}$ in pristine UCoO$_4$ before and after the OER to meet the charge-balance requirement. The U-M$_5$ XANES spectrum of UCoO$_4$ shifted to a higher energy of $\sim$2 eV compared to that of UO$_2$ (collected in the fluorescence mode in Figure 3e and the transmission mode in Figure S16), in agreement with the U-N$_5$ edge of UCoO$_4$ (Figure S8), thereby confirming the presence of U$^{6+}$. In addition, a weak high-energy shoulder above the main peak was observed in the UCoO$_4$ spectrum (marked by A) in Figure 3e, which is characteristic of the U 5f–O 2p covalence. A similar feature was observed at the M$_{4,5}$ edge of tetravalent rare earth metals because of the 4f-ligand 2p covalence although the U ion is OER inactive.

For Co oxides with high-valent Co$^{3+/4+}$ ions, the metal-and-lattice-oxygen-vacancy-site (MLOV) mechanism has been proven to be the most favorable scenario, wherein the adsorbates are located at both TM sites and lattice oxygen vacancy sites (Figure 4a). Based on the MLOV mechanism, the Gibbs free energy difference ($\Delta G$) of the electrochemical OER in U$_{0.8}$CoO$_4$ is shown in Figure 4b. The rate-limiting step for Co is the adsorption of $^*$OH, and the overpotential is 0.48 V in U$_{0.8}$CoO$_4$, the charge density is reduced, and the Bader charge is increased, indicating that the valence state of Co is significantly increased to Co$^{3.2+}$ states. To demonstrate the argument on the active sites of Co and U atoms, we calculated the electrochemical OER on the surface U (Figure S19) and Co atoms (Figure 4) in U$_{0.8}$CoO$_4$. For U active sites, we considered the metal-site adsorbate evolution mechanism (MAE), which is the conventional approach. The rate-limiting step for U is the adsorption of $^*$OH, and the overpotential is 0.70 V in U$_{0.8}$CoO$_4$. This large overpotential of U atoms demonstrates that the U ion is OER inactive. For Co oxides with high-valent Co$^{3+/4+}$ ions, the metal-and-lattice-oxygen-vacancy-site (MLOV) mechanism has been proven to be the most favorable scenario, wherein the adsorbates are located at both TM sites and lattice oxygen vacancy sites (Figure 4a). Based on the MLOV mechanism, the Gibbs free energy difference ($\Delta G$) of the electrochemical OER in U$_{0.8}$CoO$_4$ is shown in Figure 4b. The rate-limiting step for Co is the adsorption of $^*$OH, and the overpotential is 0.48 V in U$_{0.8}$CoO$_4$. This large overpotential of U atoms demonstrates that the U ion is OER inactive. For Co oxides with high-valent Co$^{3+/4+}$ ions, the metal-and-lattice-oxygen-vacancy-site (MLOV) mechanism has been proven to be the most favorable scenario, wherein the adsorbates are located at both TM sites and lattice oxygen vacancy sites (Figure 4a). Based on the MLOV mechanism, the Gibbs free energy difference ($\Delta G$) of the electrochemical OER in U$_{0.8}$CoO$_4$ is shown in Figure 4b. The rate-limiting step for Co is the adsorption of $^*$OH, and the overpotential is 0.48 V in
U$_{0.8}$CoO$_4$ shows an obvious overlap among U 5f, O makes the OER thermodynamically favorable. In addition, the neighboring U atom, which activates the lattice oxygen and Figure S20. The accelerated electron transfer involves the vacancy sites in U$_{0.8}$CoO$_4$ is no longer a rate-limiting step, activity enhancement. The adsorption of strong mixed with Co 3d/O 2p, as con- o oxygen becomes thermodynamically favorable if strong U 5f is participating bonding from the U$^{6+}$ state, we also calculated the charge-density differ- ences of four adsorbed species in Figure 4c, with the same 5f configuration and crystal structure but with negligible Sf–O 2p covalence. In Figure 4c, the Th Sf states are located at much higher energies and have no overlap with O 2p and Co 3d close to $E_F$ as Co ions have the same valence (+3.2 in both Th$_{0.7}$H$_2$CoO$_4$ and U$_{0.8}$CoO$_4$), the only difference between these two systems is whether the Sf orbital participates in bonding with the Co 3d/O 2p orbitals. Furthermore, the participation of the Sf orbital in covalent bonding leads to an increase in the ratio of O 2p pDOS to Co 3d pDOS near $E_F$ from $-1.4$ in Th$_{0.7}$H$_2$CoO$_4$ to approximately 3.0 in U$_{0.8}$CoO$_4$. All features in O 2p pDOS indicate that the oxidation of lattice oxygen becomes thermodynamically favorable if strong U Sf is strongly mixed with Co 3d/O 2p, as confirmed from the $\Delta G$ analysis. Moreover, in Figure 4b, the overpotential for Th$_{0.7}$H$_2$CoO$_4$ is 0.75 V, higher than 0.48 V for U$_{0.8}$CoO$_4$, confirming the important role of Sf participation toward OER activity enhancement. The adsorption of OH at lattice oxygen vacancy sites in U$_{0.8}$CoO$_4$ is no longer a rate-limiting step, unlike that in Th$_{0.7}$H$_2$CoO$_4$, because the lattice oxygen is further activated by Sf participating in covalent bonding. The higher O 2p pDOS near $E_F$ in U$_{0.8}$CoO$_4$ than that in Th$_{0.7}$H$_2$CoO$_4$ in Figure 4c is considered to be the contributor to OER activity enhancement. Thus, our theoretical results prove that OER activity can be synergistically enhanced through strong U Sf–O 2p covalent mixing.

**CONCLUSIONS**

Herein, we demonstrated that UCoO$_4$ featuring unique edge-sharing CoO$_6$ and UO$_6$ octahedra, exhibited extraordinary electrocatalytic activity toward the OER. Electrochemical measurements showed that the UCoO$_4$ catalyst displayed a low overpotential of $\sim 250$ mV at a current density of 10 mA cm$^{-2}$ in 1 M KOH solution, demonstrating the highest OER activity among unary cobalt oxides ever reported. In the UCoO$_4$ catalyst, although U is an OER-inactive ion, strong U 5f–O 2p covalence can lead to synergistically enhanced OER activity because of the Co–O–U network originating from an extremely high oxidation state U$^{6+}$. This is a particular case for U$^{6+}$ systems because the Sf orbitals in U$^{4+}$ and U$^{5+}$ compounds have insignificant covalent mixing with the O 2p states. Thus, our proof-of-concept study not only promotes the development of a highly active and stable OER electrocatalyst but also opens up new approaches to realize electronic structure modulation via unique Sf electron involvement, enabling the transformation of nuclear power plant waste into valuable products.

**EXPERIMENTAL SECTION**

**Synthesis of Catalysts.** UCoO$_4$ nanoparticles were synthesized via a facile sol–gel method. An aqueous solution of 1 mmol of cobalt nitrate and 1 mmol of uranyl nitrate was dissolved in 40 mL of water, followed by the addition of 2 mmol of citric acid and 2 mmol of urea. After decomposition at 180 °C for over 12 h, the obtained gel was sintered in a tube furnace under high-purity air, and the sintering temperature was (1) increased from room temperature to 400 °C at 1 °C/min and held for 2 h; (2) increased further from 400 °C to 700 °C at 2 °C/min and held for 24 h; and (3) allowed to cool naturally to room temperature.

**Material Characterization.** The crystal structures of the prepared catalysts were characterized by powder XRD on a Bruker D8 Advance X-ray diffractometer using a Ni-filtered Cu Kα radiation source at 40 kV and 40 mA. TEM images were acquired using an FEI Tecnai G2 F20 electron microscope operating at 200 kV. Before being transferred to the TEM chamber, the samples dispersed in ethanol were deposited onto a carbon-coated copper grid and quickly moved into a vacuum evaporator. Co-K edge operando XAS was performed at beamline 44A of the National Synchrotron Radiation Research Center (NSRRC). The electron storage ring was operated at 3.0 GeV with a constant current of $\sim 500$ mA. The corresponding data were collected in transmission mode. To have a quality spectrum, we applied the Quick-XAS mode with 120 spectra within 1 min. To get the high quality of EXAFS spectrum, we sum up 120 spectra within 1 min if they are not distorted by bubbles. U L$_y$-edge operando XAS was performed at BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring was operated at 3.5 GeV with a maximum current of $\sim 210$ mA. Ex situ XAS experiments at the Co-L$_2$ edge, O-K, and U-N$_3$ edges were carried out at the 11A beamline of the NSRRC. U M$_{4,5}$-edge XAS spectra were collected in the fluorescence mode at 16A1 of NSRRC and the transmission mode using an in-house laboratory-based X-ray absorption spectrometer with a Si (220) spherical bent crystal analyzer.

**Electrochemical Measurements.** Electrochemical measurements were performed using a three-electrode system connected to an Autolab PGSTAT302N electrochemical workstation at room temperature. A rotating disk working electrode (WE) made of glassy carbon (GC, PINE, 5 mm diameter, 0.196 cm$^2$) was used. Catalyst powder (5 mg) and carbon powder (Vulcan XC72, 5 mg) were dispersed in a mixture of water (750 μL), ethanol (250 μL), and Nafion solution (40 μL) under continuous ultrasoundation. Subsequently, 8 μL of the catalyst ink was transferred to a polished GC electrode and allowed to dry naturally. A Hg/HgO electrode in 1 M KOH aqueous solution was used as the reference electrode, and a platinum wire counter electrode was placed in a fitted glass tube. The
electrolyte was an aqueous solution of 1 M KOH, saturated with oxygen, and bubbled for 30 min before each test. OER polarization curves were obtained at a scan rate of 5 mV s⁻¹ in O₂-saturated 1 M KOH solutions. All potential versus RHE is in line with the equation
\[ E(RHE) = E(Hg/HgO) + 0.059pH + 0.096 V. \]
The pH of the 1 M KOH aqueous solution at room temperature was 13.60.

**Density Functional Simulations.** The present calculations employ the Vienna Ab initio Simulation Package (VASP)⁵⁴,⁵⁵ implementation of DFT in conjunction with the projector augmented wave (PAW) formalism. The exchange–correlation term was modeled using the general gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE)⁵⁶. For the U₀.₈CoO₄ and Th₀.₇H₂CoO₄ systems, all DFT calculations were performed with VASP in conjunction with the PAW formalism, and the exchange–correlation term was modeled using GGA with PBE. The H 1s, O 2s²2p³, Co 4s²3d⁷, U 6s²6p⁶7s²6d⁵, and Th 6s²6p⁶7s²6d⁵ states were treated as valence electrons. The electronic wave functions are expanded in plane waves using an energy cutoff of 400 eV. The force and energy convergence criteria were set to 0.02 eV/Å and 10⁻⁵ eV, respectively, and the Monkhorst–Pack k-point meshes are 2 × 2 × 1. The value of \( U_{eff} (= U – J) \) of the Co 3d, U 5f, and Th 5f states was set to 3.52, 4.00, and 4.00 eV, according to previous work.⁵²,⁵³,⁵⁸ For U₀.₈CoO₄ and Th₀.₇H₂CoO₄, we used the 1 × 1 primitive cell (lattice constants \( a = c = 6.497 \) Å, \( b = 6.952 \) Å) to build periodic slab models with 12 Co sites per surface, with two layers at the bottom that were fixed during relaxation. For Th₀.₇H₂CoO₄, we adopted the optimized 1 × 1 primitive cell by adding two H atoms in the interstitial space and then built periodic slab models with eight Co sites per surface, with two layers at the bottom that were fixed during relaxation. The thickness of the vacuum spacing was ~15 Å in the \( z \)-direction.

**Free Energy Calculations.** The elementary steps of MLOV mechanisms are listed below:

\[
\begin{align*}
\text{OH}^+ & \rightarrow [\text{OO}^* + \text{V}_\text{R}] + e^- + \text{H}^+ \quad (1) \\
\text{H}_2 \text{O} + [\text{OO}^* + \text{V}_\text{R}] & \rightarrow \text{O}_\text{R} + [\text{OO}^* + \text{OH}^\text{½}^\text{½}] + e^- + \text{H}^+ \quad (2) \\
\text{H}_2 \text{O} + [\text{OO}^* + \text{OH}^\text{½}^\text{½}] & \rightarrow [\text{OH}^* + \text{OH}^\text{½}^\text{½}] + e^- + \text{H}^+ \quad (3) \\
[\text{OH}^* + \text{OH}^\text{½}^\text{½}] & \rightarrow \text{OH}^* + e^- + \text{H}^+ \quad (4)
\end{align*}
\]

The Gibbs free energy changes (\( \Delta G \)) were calculated by the following equations:

\[
\begin{align*}
\Delta G_1 & = \Delta G_{[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - \Delta G_{[\text{OH}^\text{½}^\text{½}]} - eU \quad (5) \\
\Delta G_2 & = -2\Delta E_{\text{HHO}} + \Delta G_{i[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - \Delta G_{[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - eU \quad (6) \\
\Delta G_3 & = \Delta G_{[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - \Delta G_{[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - eU \quad (7) \\
\Delta G_4 & = \Delta G_{[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - \Delta G_{[\text{OH}^* + \text{OH}^\text{½}^\text{½}]} - eU \quad (8)
\end{align*}
\]

where \( U \) is the potential measured against RHE at standard condition (\( T = 298.15 \) K, \( p = 1 \) bar, \( \text{pH} = 0 \)) and \( \Delta E_{\text{HHO}} \) is the experimental Gibbs free energy of formation of water molecules. The \( \Delta G \) of these intermediates includes zero-point energy (ZPE) and entropy corrections (listed in Table S3) according to \( \Delta G_i = \Delta E_i + AZPE_i - T\Delta S_i \) where the energy differences \( \Delta E_i \) are calculated with respect to \( \text{H}_2 \text{O} \) and \( \text{H}_2 \) (at \( U = 0 \) and \( \text{pH} = 0 \)). The theoretical overpotential is defined as the lowest potential at which all reaction steps are thermodynamically downhill.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/jacs.1c10311.

Detailed methods, experiment process, and additional XRD, TEM, XAS, cyclic voltammetry, LSV, and DFT data (PDF)

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