Octahedral Coordinated Trivalent Cobalt Enriched Multimetal Oxygen-Evolution Catalysts

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Octahedral coordinated trivalent cobalt cations (Co\textsubscript{Oh\textsuperscript{3+}}) in metal oxyhydroxides are highly active catalytic sites for the oxygen evolution reaction (OER), a critical bottleneck for efficient water splitting; however, previous synthetic methods have limited control over these sites. Herein, a scalable electrodeposition method coupled with in situ oxidation to produce amorphous Co–Fe–W trimetallic oxyhydroxides enriched with Co\textsubscript{Oh\textsuperscript{3+}} is developed. X-ray absorption, in operando spectroscopic analysis, and computational studies reveal that 72% of the Co atoms are present in Co\textsubscript{Oh\textsuperscript{3+}} sites. Fe and W synergistically affect the electronic structure of Co and provide a favorable coordination environment. The Co–Fe–W oxyhydroxides exhibit superior OER catalytic performance with an impressive turnover frequency of 1.96 s\textsuperscript{-1} at an overpotential of 300 mV, a low Tafel slope of 32 mV dec\textsuperscript{-1}, and small activation energy of 53 kJ mol\textsuperscript{-1} in alkaline electrolyte. The catalyst directly deposited on Ni foams can serve as a robust OER electrode in two-electrode water electrolyzers; they deliver a current density of 100 mA cm\textsuperscript{-2} at a small overpotential of 234 mV in alkaline electrolyte with excellent durability under 100 mA cm\textsuperscript{-2} over 120 h. These catalysts are excellent for practical water splitting applications.

1. Introduction

Green hydrogen (H\textsubscript{2}) can be produced from water electrolysis as a promising clean fuel to enable a more sustainable society.[1] Anodic oxygen evolution reaction (OER) in water electrolyzers is slow and requires substantial energy inputs.[2] Catalysts are necessary to deliver a high current density under a low overpotential (\(\eta_0\)) of 191 mV (supported on Au plated Ni foams (NiFs) or 223 mV supported on glassy carbon electrodes) at 10 mA cm\textsuperscript{-2} in alkaline electrolyte, demonstrating a very promising OER catalyst.[2c] In another study, Fe was found to play a critical role in regulating the catalytic activity of Co–Fe–W oxyhydroxides, and the optimized W\textsubscript{0.5}Co\textsubscript{0.4}Fe\textsubscript{0.1} exhibited an overpotential of 310 mV at 100 mA cm\textsuperscript{-2}.[2b] Furthermore, recent in situ mechanistic studies suggest that Co catalysts would undergo structure transformations during OER to form CoOOH, in which high valence Co ions in the octahedral coordination (Co\textsubscript{Oh\textsuperscript{3+}}) serve as active catalytic sites for OER.[8] However, the abundance of Co\textsubscript{Oh\textsuperscript{3+}} in the previously reported Co–Fe–W oxyhydroxides was not controlled. Thus, we envision that creating Co–Fe–W oxyhydroxides enriched with Co\textsubscript{Oh\textsuperscript{3+}} may deliver a high-performance catalyst for OER.

A key challenge is how to synthesize Co–Fe–W oxyhydroxides with a high abundance of Co\textsubscript{Oh\textsuperscript{3+}}, which have homogenously dispersed metal components without phase segregation so that different metal atoms can actively interact with each other. The previously used sol–gel method by hydrolyzing the mixture of CoCl\textsubscript{2}, FeCl\textsubscript{3}, and WCl\textsubscript{6}, mainly resulted in Co\textsuperscript{2+} species in the resulting Co–Fe–W oxyhydroxides.[9] Hydrothermal synthesis involving WCl\textsubscript{6} often leads to the formation of a segregated WO\textsubscript{3} phase due to the spontaneous hydrolysis.[9b] In comparison, electrodeposition is a versatile technique to synthesize...
Co catalysts with uniform elemental distribution and tunable structures.\[^{5a,9}\] Co catalysts can be deposited on various conductive and mechanically robust porous substrates without polymeric binders. Such porous electrodes can also enable efficient mass transfer for reaction intermediates and generated gases.\[^{10}\] Further, an aqueous oxidation method has been used to oxidize Co\(^{3+}\) to Co\(^{4+}\) through Co Fenton reaction in catalyst synthesis.\[^{11}\] Along these lines, we propose that it may be possible to in situ generate Co\(^{4+}\) and use it for electrodeposition.

Herein, we demonstrate a fast and scalable electrodeposition method to synthesize amorphous Co–Fe–W oxyhydroxides enriched with Co\(_{oix}\) as a highly efficient OER catalyst. Peroxide ligands released from the WO\(_4(O_2)\)\(^{4-}\) precursor oxidize Co\(^{2+}\) to Co\(^{3+}\), which was then electrodeposited together with Fe\(^{3+}\), WO\(_4\)\(^{2-}\), and OH\(^-\) to form Co–Fe–W oxyhydroxides. Detailed characterization by X-ray absorption spectroscopy (XAS) elucidates local environments and the average valence state of Co atoms in the deposited catalysts. The abundance of Co\(^{4+}\) was determined by X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) analysis, and electron energy loss spectroscopy (EELS). The catalytic performance of synthesized amorphous Co–Fe–W oxyhydroxides was comprehensively examined and compared with several reference catalysts. Further, the in operando electrochemical impedance spectroscopy (EIS), Fourier transformed alternative current voltammetry (FTACV) together with density functional theory (DFT) calculations reveal how Fe and W modulate electronic structures of Co, affording superior OER performance. Finally, using catalysts directly deposited on NiFs as an anode, a two-electrode water electrolyzer demonstrates excellent performance in an alkaline electrolyte and neutral seawater.

2. Results and Discussion

The synthesis of catalysts by the electrodeposition method is illustrated in Figure 1a. Experimental details are described in the Experimental Section. Briefly, we prepared an electrodeposition bath by an equimolar mixing of H\(_2\)O\(_2\) and Na\(_2\)WO\(_4\) to form WO\(_4(O_2)\)\(^{4-}\).\[^{12}\] followed by adding Co(NO\(_3\))\(_2\) and Fe(NO\(_3\))\(_3\). According to the elemental optimization reported in a previous study,\[^{7b}\] the concentration of Co, Fe, and W in the bath solution was set at 20, 5, and 20 \times 10\(^{-3}\) m, respectively. The electrodeposition was carried out at –0.2 V versus Ag/AgCl (3 m KCl) for 10 min on cleaned Ni foams (NiFs).\[^{11}\] During the electrodeposition, peroxide ligands (O_2\(^{2-}\)) released from WO\(_4(O_2)\)\(^{4-}\) oxidize Co\(^{2+}\) to Co\(^{3+}\), according to reactions that can be written as:

\[
\text{WO}_4(O_2)^{4-} + 2\text{H}^+ \rightarrow \text{WO}_4 + O_2^{2-} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{Co}^{3+} + O_2^{2-} + 4\text{H}^+ + e^- \rightarrow \text{Co}^{2+} + 2\text{H}_2\text{O} \quad (2)
\]

At the same time, the reduction of NO\(_3^-\) ions generates OH\(^-\) and leads to the deposition of amorphous tertiary Co–Fe–W oxyhydroxides enriched with Co\(^{4+}\) (denoted as CoFeWO\(_4\)). The reactions can be expressed as:

\[
\text{NO}_3^- + 7 \text{H}_2\text{O} + 8e^- \rightarrow \text{NH}_4^+ + 10 \text{OH}^- \quad (3)
\]

\[
a\text{Co}^{2+} + b\text{Fe}^{3+} + c\text{WO}_4(O_2)^{4-} + \text{mOH}^- \rightarrow \text{CoFeWO}_x \quad (4)
\]

We also optimized the electrodeposition time. As shown in Figure S1a (Supporting Information), there is a linear relationship between the mass of deposited catalysts on NFs and the deposition time. Analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) shows minor elemental composition changes when the deposition time increases from 2 to 30 min (Figure S1b, Supporting Information). OER performance tests (see Figure S1c,d and the related discussion in Supporting Information) indicate that 10 min is the optimal deposition time, which was used for the rest of the study.

After electrodeposition, Figure 1b shows that pale yellow-green color solids appear on NiFs with a geometric areal mass loading of 0.31 ± 0.06 mg cm\(^{-2}\). Several reference catalysts were also synthesized for comparison. Catalysts with reduced Co\(^{1+}\) abundance (denoted as CoFeWO\(_x\)R) were also synthesized by adding reductive ascorbic acid in the electrodeposition bath (see Figure S2 and the related discussion in Supporting Information). Ascorbic acid is found to consume peroxide ligands competitively, resulting in a lower Co\(^{4+}\) abundance in CoFeWO\(_x\)R. A crystallized and phase segregated catalyst (denoted as CoFeWO\(_x\)A) was obtained by thermal annealing CoFeWO\(_x\) at 500 °C in Ar for 1 h. Bimetallic (CoFeO\(_x\)) and monometallic (CoO\(_x\)) were synthesized by electrodeposition under similar experimental conditions (see details in the Experimental Section). Overall, the electrodeposition method is time-efficient. Including the time required to prepare electrodeposition bath electrolytes, it took less than 1 h to complete the whole process. Additionally, this method is scalable for making large electrodes. A large area electrode of 60 cm\(^2\) was fabricated as a demonstration (see the photo in Figure S3, Supporting Information).

Various techniques were used to characterize the physicochemical properties of catalysts. Scanning electron microscope (SEM) images shown in Figure 1c suggest that CoFeWO\(_x\) was deposited uniformly on NiFs. Energy-dispersive X-ray spectroscopy (EDX, Figure S4, Supporting Information) analysis indicates a Co:Fe:W atomic ratio of 1.00: 0.95: 1.15, which agrees with results obtained by XPS and ICP-AES (see Table S1, Supporting Information). The atomic ratio between Co and Fe in CoFeWO\(_x\) is similar to the optimal result reported for Fe–Co based OER electrocatalysts.\[^{6b}\] Nitrogen physisorption analysis shows that CoFeWO\(_x\) has a Brunauer–Emmett–Teller (BET) surface area of 75.3 m\(^2\) g\(^{-1}\), and the Barrett–Joyner–Halenda (BJH) pore size distribution indicates the existence of mesopores around 5–10 nm (see Figure S5, Supporting Information). In conjunction with large macropores in NiFs, the hierarchically porous structure in the FeCoWO\(_x\)/NiF electrodes is beneficial for OER by providing a large accessible surface area and fast mass transfer for electrolyte ions and gaseous products.\[^{10,13}\]

The high-resolution transmission electron microscope (TEM) image in Figure 1d shows that CoFeWO\(_x\) is composed of thin nanoplates without apparent lattice fringes. The selected area electron diffraction (SAED) analysis in the inset of Figure 1d shows no crystalline lattice fringes. X-ray diffraction (XRD) in Figure S6 (Supporting Information) shows featureless XRD patterns. These results confirm that CoFeWO\(_x\) is amorphous. Further, no high-contrast spots were found in the high-angle annular dark-field (HAADF) mode of our scanning
TEM (STEM) analysis, as displayed in Figure 1e. The corresponding EDX maps confirm the uniform elemental distribution in CoFeWOx. In comparison, XRD and TEM characterization results of CoFeWOx-R (Figure S7, Supporting Information) show structural properties similar to those of CoFeWOx, suggesting that adding ascorbic acid in the electrodeposition bath does not affect the amorphous structure and uniform element distribution in CoFeWOx. On the contrary, Figure S8 (Supporting Information) shows evident crystal phase segregation in the thermally annealed CoFeWOx-A.
XAS was applied to elucidate the coordination environment of Co in CoFeWO\textsubscript{x} using extended X-ray absorption fine structure (EXAFS) at the Co K-edge, for comparison with several reference structures. Figure 1f displays the $k^3$-weighted Fourier-transformed EXAFS (FT-EXAFS) spectra. The first shell coordination number of Co (CN\textsubscript{Co}) was obtained by fitting the FT-EXAFS spectra, with results listed in Table S2 (Supporting Information). CoFeWO\textsubscript{x} and CoFeWO\textsubscript{x}-R have similar CN\textsubscript{Co} of 5.8 ± 0.4 and 5.9 ± 0.2, respectively, indicating that Co atoms mostly occupy octahedral sites (Co\textsubscript{Oh}). In contrast, the EXAFS spectra of CoFeO\textsubscript{x} and CoO\textsubscript{x} show split peaks at the second Co–Co shell ($R = 2$–$3.5$ Å), indicating the co-existence of Co\textsubscript{Oh} and Co atoms at fourfold tetrahedral sites (Co\textsubscript{Td}). A linear combination fit reveals that 38 and 74 at\% of Co atoms are at Co\textsubscript{Oh} sites in CoFeO\textsubscript{x} and CoO\textsubscript{x}, respectively. Additionally, the Co–O bond length of CoFeWO\textsubscript{x} at 1.921 ± 0.012 Å is shorter than that of CoFeWO\textsubscript{x}-R, CoFeO\textsubscript{x}, and CoO\textsubscript{x} at 1.977 ± 0.025, 1.953 ± 0.042, 2.008 ± 0.037 Å, respectively. The contracted Co–O bond length in CoFeWO\textsubscript{x} is similar to that of CoOOH at 1.900 ± 0.011 Å, suggesting a high average Co valence state in CoFeWO\textsubscript{x}.

Several spectroscopic methods further confirm the formation of abundant Co\textsuperscript{3+} in CoFeWO\textsubscript{x}. First, Figure 2a displays the XPS spectra of the catalysts. Their Co\textsubscript{2p\textsubscript{3/2}} peaks can be deconvoluted into contributions from Co\textsuperscript{3+} and Co\textsuperscript{2+} at the binding energy of ≈780.2 and 782.2 eV, respectively. Due to in situ oxidation by $O_2$, the abundance of Co\textsuperscript{3+} in CoFeWO\textsubscript{x} is 72 at\%, which is much higher than that in CoFeWO\textsubscript{x}-R (23 at\%), CoFeO\textsubscript{x} (41 at\%), and CoO\textsubscript{x} (12 at\%). Second, the pre-edge position shift observed in the Co K-edge XANES spectra displayed in Figure S10 (Supporting Information) is consistent with the changing trend of Co\textsuperscript{3+} abundance revealed by XPS. Third, the valence state of Co was quantified by Co L-edge EELS. Figure 2b shows a TEM image of CoFeWO\textsubscript{x} with four marked spots at different sample thicknesses. EELS spectra collected at the four spots in Figure 2c show an identical line shape and peak positions for Co L\textsubscript{3} and L\textsubscript{2} edges, suggesting that the valence state of Co is similar at the surface and in the bulk of CoFeWO\textsubscript{x}. The L\textsubscript{2}
and $L_2$ intensity ratio can be correlated with the valence state of Co.\cite{14} We calculated the intensity ratio of Co $L_3$ and $L_2$ edges for different catalysts and compared them in the inset of Figure 2c. The ratio of CoFeWO$_x$ at 2.93 is higher than 2.46 of CoOOH. A linear interpretation shown in Figure S11 (Supporting Information) indicates that Co in CoFeWO$_x$ has a valence of 2.74, which is similar to the value obtained by the surface sensitive XPS (Figure 2a). In comparison, CoFeWO$_x$-R and CoFeO$_x$ have $L_3/L_2$ intensity ratios of 3.78 and 3.61 (Figure S11, Supporting Information), corresponding to a Co$^{3+}$ abundance of 30 and 43 at%, respectively. These ratios are close to those determined from the XPS results shown in Figure 2a at 23 and 41 at%. Based on our EXAFS analysis results and spectroscopic valence state assessment of Co, we conclude that all Co$^{2+}$ and Co$^{3+}$ in CoFeWO$_x$ and CoFeWO$_x$-R are at octahedral sites. The Co$^{3+}$ in CoFeO$_x$ (41 at%) would preferentially occupy octahedral sites, agreeing with EXAFS fitting results (38 at%).\cite{15} Meanwhile, the abundant Co$^{2+}$ in CoO$_x$ (88 at%) would situate at both octahedral and tetrahedral coordination sites.

XPS was also used to examine the electronic structure of W and Fe. Figure 2d shows that W4f$_{7/2}$ (36.1 eV) and W4f$_{5/2}$ (38.2 eV) XPS spectra of CoFeWO$_x$ and CoFeWO$_x$-R are about 0.3–0.2 eV lower than that in WO$_x$. This result is similar to recent reports that W doped in CoOOH resides at lower oxidation states due to substantial structural distortions from Co sites.\cite{5c,7c} Meanwhile, Fe2p XPS spectra of CoFeWO$_x$, CoFeWO$_x$-R, and CoFeO$_x$ are comparable with that of Fe$_2$O$_3$ (Figure S12, Supporting Information), indicating that Fe$^{3+}$ is the dominate Fe species.\cite{6c} Further, the deconvolution of O1s XPS spectra confirms the co-existence of M–O and M–OH bonds. Detailed deconvolution analysis further proves that they exhibit a similar level of O vacancies (see Figure S13 and the related discussion in Supporting Information). Thus, we rule out that oxygen vacancy would play a significant role in their observed different OER performance.

The catalytic performance for OER was evaluated by depositing catalysts (removed from NiFs) on rotating disk glassy carbon electrodes (GCEs) with an areal mass loading of 0.2 mg cm$^{-2}$ in a three-electrode configuration in O$_2$ saturated 1 m KOH electrolytes. Figure 3a displays linear sweep voltammetry (LSV) polarization curves collected under a scan rate of 2 mV s$^{-1}$. Among the tested catalysts and references, CoFeWO$_x$ exhibits the highest catalytic activity with the lowest overpotential ($\eta$) at 231 mV at 10 mA cm$^{-2}$, which is lower than that of CoFeWO$_x$-R at 249 mV, CoFeO$_x$ at 303 mV, and commercial RuO$_2$ at 324 mV (see Table 1). After thermal annealing at 500 °C, the phase-segregated CoFeWO$_x$-A shows significantly reduced activity with $\eta$ at 332 mV, suggesting that amorphous crystallinity is important for the observed high catalytic activity of CoFeWO$_x$. We further normalized our measured current densities from the catalysts based upon their electrochemically active surface area (ECSA). The ECSA was determined by measuring the double-layer capacitance ($C_{dl}$) of the catalysts, as shown in Figure S14 and Table S3 (Supporting Information).
Figure S15 (Supporting Information) shows that the trend observed for catalytically active based on normalized current density is similar to what is displayed in Figure 3a. This confirms that the observed variance in the catalytic activity of the catalysts originates from their intrinsic catalytic activity rather than their different specific surface areas. In particular, CoFeWOx and CoFeWOx-R have similar morphology and elemental composition. The observed difference in their catalytic activity can be directly attributed to the higher abundance of CoO\(_{\text{H}}\)\(_{3}\) in CoFeWOx, which serves as active catalytic sites for OER.[8a,b]

The catalytic activity of the catalysts was further compared based upon their mass-based activities and turnover frequencies (TOFs). Details of these methods are described in the Experimental Section. The results are listed in Table 1 and Table S4 (Supporting Information). At \(\eta\) of 300 mV, CoFeWOx delivers a mass-based activity of 781.6 A g\(^{-1}\) (based on the total mass of the catalyst) and a TOF of 0.57 s\(^{-1}\) (assuming all 3d metals are active), which is nearly two times higher than that of CoFeWOx-R (391.5 A g\(^{-1}\) and 0.29 s\(^{-1}\)). The TOF was also calculated based on the total moles of surface 3d metals, determined from cathodic peaks in cyclic voltammetry curves of catalysts at 10–50 Hz, suggesting that OER is primarily initiated at CoOH. It should be noted that the locus of CoFeWOx and reference catalysts at 10 Hz and 100 mV are compared in Figure 4b. Three distinctive sets of peaks can be assigned to different electron transfer steps along the OER pathway.[17,22a,23b] Region I (1–1.2 V vs RHE) and II (1.2–1.5 V vs RHE) can be assigned to the redox of Co\(^{2+}\)/Co\(^{3+}\) and the abundant Co\(^{3+}\) in octahedral coordination.[20] The higher carrier density is expected to facilitate fast electron transfer and improve OER performance. We also measured the apparent OER activation energy (\(E_a\)) of the catalysts (Figure S18, Supporting Information). Figure 3d shows that CoFeWOx has the lowest \(E_a\) of 53 kJ mol\(^{-1}\) (see Table 1), further confirming its superior OER activity.

To better understand the OER mechanisms on CoFeWOx, we used in operando EIS and FTACV to investigate the role of CoO\(_{\text{H}}\)\(_{3}\) sites on the superior OER catalytic activity of CoFeWOx in comparison with several other catalysts. The in operando Bode plots of the catalysts were collected under applied potentials from 1.03 to 1.68 V versus RHE as displayed in Figure S19 (Supporting Information) along with the corresponding Nyquist plots. Figure 4a displays 2D contour Bode plots of CoFeWOx and reference catalysts. The peak loci of phase angles are marked by dashed arrows on the plots to distinguish OH\(^{-}\)adsorption sites and identify the OER active Co coordination geometries.[15] The structure-defined spinel CoO\(_4\) displays two distinctive loci between 0.1 and 10 Hz, and 30–50 Hz, which can be assigned to Co\(_{\text{H}}\)\(_{2}\) and CoO\(_{\text{H}}\)\(_{3}\) sites, respectively.[15] CoFeWOx and CoO\(_{x}\) also have both Co\(_{\text{H}}\)\(_{2}\) and CoO\(_{\text{H}}\)\(_{3}\) loci, similar to those in CoO\(_{x}\) which agree with the EXAFS results in Figure 1f, confirming the co-existence of CoO\(_{\text{H}}\)\(_{2}\) and CoO\(_{\text{H}}\)\(_{3}\) in CoFeWOx and CoO\(_{x}\).[21] In contrast, CoFeO\(_x\) exhibits a single-phase angle peak locus decaying at 20–50 Hz, suggesting that OER is primarily initiated at CoO\(_{\text{H}}\). It should be noted that the locus of CoFeWOx is similar to that of spinel ZnCo\(_2\)O\(_4\), which is the only active catalytic site (see Figure S20, Supporting Information).[15,22] Further, CoFeWOx-R has a single local locus that of CoFeWOx.

The high-order harmonic components are generally avoided in FTACV to avoid the non-Faradaic process and signify currents related to electron transfer and catalytic reactions (Figure S21, Supporting Information).[23] Thus, the 6th harmonic FTACV components of CoFeWOx and reference catalysts at 10 Hz and 100 mV are compared in Figure 4b. Three distinctive sets of peaks can be assigned to different electron transfer steps along the OER pathway.[17,22a,23b] Region I (1–1.2 V vs RHE) and II (1.2–1.5 V vs RHE) can be assigned to the redox of Co\(^{2+}\)/Co\(^{3+}\) and the subsequent structure rearrangement toward the formation of Co\(^{3+}\)/Co\(^{4+}\) active center, respectively.[8b,17,24] The region beyond 1.5 V (region III) is associated with the fast water dissociation and O\(_2\) production under a high overpotential.[17,21b] CoFeWOx has a very low Co\(^{3+}\)/Co\(^{3+}\) redox current in the region I, which can be attributed to its high Co\(^{3+}\) abundance, where few Co\(^{2+}\) sites

### Table 1. OER catalytic performance parameters of CoFeWOx and reference catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>(\eta_{0}^{\text{a}}) [mV]</th>
<th>Tafel slope [mV dec(^{-1})]</th>
<th>Mass activity ((\text{A g}^{-1}))</th>
<th>TOF (s(^{-1}))</th>
<th>(R_{CT}^{\text{b}}) [(\Omega)]</th>
<th>(E_{a}^{\text{c}}) [kJ mol(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFeWOx</td>
<td>231</td>
<td>32</td>
<td>781.6</td>
<td>0.54</td>
<td>7.6</td>
<td>53</td>
</tr>
<tr>
<td>CoFeWOx-R</td>
<td>249</td>
<td>38</td>
<td>391.5</td>
<td>0.28</td>
<td>11.4</td>
<td>58</td>
</tr>
<tr>
<td>CoO(_{x})</td>
<td>303</td>
<td>47</td>
<td>45.5</td>
<td>0.014</td>
<td>26.8</td>
<td>74</td>
</tr>
<tr>
<td>CoFeWOx-A</td>
<td>342</td>
<td>57</td>
<td>13.4</td>
<td>0.0031</td>
<td>55.6</td>
<td>92</td>
</tr>
<tr>
<td>CoFeO(_{x})</td>
<td>332</td>
<td>64</td>
<td>20.7</td>
<td>0.012</td>
<td>51.2</td>
<td>86</td>
</tr>
<tr>
<td>RuO(_{x})</td>
<td>324</td>
<td>70</td>
<td>31.6</td>
<td>0.011</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(\eta_{0}\) Obtained from LSV scans without iR correction; \(\eta_{0}\) Obtained with 95%-iR correction at \(\eta = 300\) mV based on the total mass of catalysts; \(\eta_{0}\) Obtained with 95%-iR correction at \(\eta = 300\) mV based on total 3d metals (Co/Fe) in catalysts; \(\eta_{0}\) Determined at \(\eta = 250\) mV; \(\eta_{0}\) Obtained with 95%-iR correction at \(\eta = 250\) mV on Au RDEs.

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**Adv. Energy Mater. 2020, 2002593**

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are oxidized to Co$^{3+}$. In contrast, other reference catalysts have higher Co$^{2+/3+}$ redox currents in the region I, suggesting that Co$^{3+}$ is oxidized to Co$^{3+}$ as active catalytic sites for OER. Importantly, CoFeWO$_x$ with abundant pre-generated Co$^{3+}$ sites exhibits nearly two-times higher current ($\approx 17 \mu A$) in the region II than that of CoFeWO$_x$-R ($\approx 9 \mu A$). This observation is indicative of its faster structural transformation toward the Co$^{3+/4+}$ active center, which is beneficial for the fast OER process. It should be noted that the redox of Fe$^{3+/4+}$ ($\approx 1.9$ V vs Ag/AgCl) only overlaps with the rapid catalytic water oxidation in the region III.[25] Additionally, the redox of W$^{5+/6+}$ in WO$_3$ ($\approx 0.35$ V vs RHE) is also outside our tested potential window from 1.0 to 1.7 V versus RHE. Therefore, we can rule out any contribution from Fe and W to the measured currents in FTACV.[26]

The intensity of measured currents in FTACV is correlated with the reaction rate on our catalysts. We further examined the kinetics of OER to determine the potential RDS.[23b] CoFeWO$_x$ has a relatively low current intensity in the region III, suggesting that the RDS of OER on CoFeWO$_x$ is the formation of the O$_2^*$ intermediate, agreeing with its small Tafel slope of 32 mV dec$^{-1}$ (Table I).[56,27] In comparison, CoFeO$_x$, CoO$_x$, and Co$_3$O$_4$ exhibit a much lower current in region II. This indicates that the formation of OOH$^*$ is the RDS.[17,22a,28] Agreeing with their higher Tafel slopes of 50–70 mV dec$^{-1}$.

DFT calculations were carried out to understand how electronic interactions among different metal elements in CoFeWO$_x$ contribute to its excellent catalytic activity. Figure 4c illustrates three models used for the calculations. The three oxide surfaces (CoFeWO$_x$, CoFeO$_x$, and CoO$_x$) were modeled as two-layer (221) slabs. The surface of the CoFeWO$_x$ was modeled by replacing two W atoms with Fe on the surface of CoWO$_4$. Figure S22 (Supporting Information) displays the projected density of states (PDOS) of Co, Fe, W, and O in the three models. The Co$^{3d}$ electrons are the main contributor to the PDOS near the Fermi level, suggesting that Co would have higher activity in CoFeWO$_x$.[29] Figure 4d compares the PDOS of Co$^{3d}$ and O$^{2p}$ electrons of the three models. The incorporation of Fe and W gradually tunes the electronic structures of Co and O. The $d$-band center of Co is shifted upward from –2.01 eV in the monometallic CoO$_x$ model to –1.55 eV after doping Fe in the CoFeO$_x$ model, which is further lifted to –1.45 eV in the CoFeWO$_x$ model. This up-shift in the $d$-band center is expected to strengthen the adsorbate binding energies at Co sites, leading to more favorable OER thermodynamics.[30] Therefore, the modulation of the $d$-band center of Co can optimize the interaction between Co and OER intermediates, resulting in improved catalytic activity for OER.[11] Meanwhile, Figure 4d also shows that O $p$-electrons are lifted closer to their Fermi level, which is beneficial for improving the antibonding state and promoting catalytic activity for OER.[8a,32] The calculated energy gaps between Co $d$-band and O $p$-band centers show a declining trend with 1.17 eV in CoFeWO$_x$, 1.22 eV in CoFeO$_x$, and 1.31 eV in CoO$_x$, indicating a lower electron transfer resistance in CoFeWO$_x$, which is also beneficial in promoting catalytic activity for OER.[35,33]
To demonstrate the practical application potential of FeCoWOx, we tested the performance of CoFeWOx directly electrodepositing on NiFs (denoted as CoFeWOx/NiF). Figure 5a shows that the LSV curve of CoFeWOx/NiF measured in a three-electron configuration in 1 M KOH electrolyte has a rapid current increment. In contrast, the bare NiF displays negligible catalytic activity. CoFeWOx/NiF requires an overpotential of 211 mV to reach the current density of 10 mA cm⁻². It delivers 100 mA cm⁻² at 234 mV and 500 mA cm⁻² at 280 mV, outperforming most recently reported earth-abundant transition metal-based OER catalyst electrodes (see the detailed comparison in Table S5, Supporting Information). Furthermore, CoFeWOx/NiF can also work in near-neutral seawater electrolyte (pH = 8.4, conductivity = 32 mS cm⁻¹), requiring an overpotential of 422 mV to deliver the current density of 100 mA cm⁻².

A two-electrode water electrolyzer was assembled using CoFeWOx/NiF as the anode and a NiMoO₄/NiF electrode (Figure S23, Supporting Information) as the cathode. As shown in Figure 5b, multi-step chronopotentiometric tests performed in both 1 M KOH and seawater electrolyte exhibit fast and steady responses, and generated gas bubbles can quickly dissipate from the electrode surfaces (see the inset image of Figure 5b). The stability of CoFeWOx/NiF was assessed by continuous discharge at 100 mA cm⁻² for 120 h in 1 M KOH electrolyte. Figure 5c shows that the applied overpotential remains stable during the test, indicating excellent stability. The Faradaic efficiency measured by quantifying O₂ produced using gas chromatography is close to 100% during the entire stability test. Periodic elemental analysis of the KOH electrolyte by ICP-AES confirms that there is minimum leaching of Co and Fe during the 120-h test. However, we found about 10 wt% of W was leached in the first 24 h of the electrolysis, and then the W content remained stable in the next 96 h. After the stability test, CoFeWOx/NiF shows minor morphological changes and remains amorphous without element/crystal phase segregations (see Figure S24, Supporting Information). XPS analysis of CoFeWOx/NiF after the stability test shows that the abundance of Co³⁺ increases from 72 to 85 at%. At the same time, the electronic structures of Fe and W are largely unchanged (Figure S25, Supporting Information). We further tested the stability of this CoFeWOx/NiF electrode in a 10 M KOH electrolyte at 80 °C to simulate the working condition of practical alkaline water electrolyzers. The electrolyzer can work steadily during the 48-h test performed at 500 mA cm⁻², and the voltage has merely increased by ≈20 mV (Figure S26, Supporting Information). Meanwhile, similar elemental retention performance can be observed.

3. Conclusion

In summary, we demonstrate an efficient synthetic method to electrodeposit trimetallic Co–Fe–W oxyhydroxides enriched...
with Co\(^{3+}\). The in situ oxidation by peroxide ligands released from WO\(_4\)\(^{2-}\) precursors play a crucial role in obtaining a high abundance of Co\(^{3+}\). Spectroscopic characterization reveals that 72 at% of Co occupied the catalytic active octahedral coordinated Co\(^{3+}\) site in CoFeWO\(_x\). On a glassy carbon RDE, the high Co\(^{3+}\) abundance renders extraordinary OER performance with an ultralow overpotential of 231 mA\(\mathrm{cm}^{-2}\) at 10 mA cm\(^{-2}\), a fast reaction kinetics with a low Tafel slope of 32 mV dec\(^{-1}\), and a high TOF of 1.96 s\(^{-1}\) per surface 3d metal in 1 m KOH electrolyte, outperforming most of the recently reported earth-abundant transition metals based OER catalysts. The mechanistic investigation by in operando EIS and FTACV analysis indicates that abundant Co\(^{3+}\) sites are highly active catalytic sites for OER. DFT calculation results show the optimization of Co electronic structures by Fe and W. Benefiting from the excellent intrinsic catalytic activity and hierarchical pore structures, CoFeWO\(_x\)/NiF electrodes deliver a current density of 100 mA cm\(^{-2}\) over 120 h. This work demonstrates an easily scalable route of H\(_2\)O\(_2\) and Na\(_2\)WO\(_4\). The mixture was further stirred for 30 min before Fe(NO\(_3\))\(_3\) and Co(NO\(_3\))\(_2\) stock solutions were added. The final molar concentration of Co\(^{2+}\), Fe\(^{3+}\), and W\(^{6+}\) in the electrodeposition bath was kept at 20, 5, and 20 \times 10\(^{-3}\) M, respectively, and its pH was adjusted to 1.5 by adding 3 M HNO\(_3\). The NiFs were cleaned by bath sonication in acetone for 15 min and then rinsed with DI water. After drying, the NiFs were further bath sonicated in 0.1 M HCl for 15 min to remove surfaceoxide layers. The electrodeposition of CoFeWO\(_x\) on cleaned NiFs was carried out in the three-electrode configuration using a Pt mesh and an Ag/AgCl (saturated KCl) electrode as the counter and reference electrodes, respectively. The deposition was limited to a 2 \times 2 cm\(^2\) area, and the region adjacent to the electrodeposition area was sealed by a waterproof sealant, as illustrated in Figure 1b. The potential of –0.2 V versus Ag/AgCl was applied to NiFs for 10 min using an electrochemical workstation (CHI, 660E). After electrodeposition, NiFs were rinsed with DI water and dried in an oven overnight.

CoFeWO\(_x\)-R was prepared by adding 20 \times 10\(^{-3}\) M ascorbic acid to the electrodeposition bath (the concentration of ascorbic acid was optimized as described in the Supporting Information). Although WO\(_4\)\(^{2-}\) was stable in solutions containing a small amount of citric acid, O\(_2\)\(^{-}\) would be competitively consumed by ascorbic acid and Co\(^{3+}\), resulting in lower Co\(^{3+}\) concentration. Further, bimetallic CoFeO\(_2\) and monometallic CoO\(_2\) were also prepared under the same electrodeposition condition. However, the electrodeposition condition bath was changed to have 20 \times 10\(^{-3}\) M Co\(^{2+}\) and 5 \times 10\(^{-3}\) M Fe\(^{3+}\) or only 20 \times 10\(^{-3}\) M Co\(^{3+}\), respectively.

**Materials Characterization:** SEM imaging and EDX were performed on an SEM (Zeiss Ultra Plus). TEM images of samples deposited on Cu grids were taken on a TEM (FEI Tecnai Z). EELS spectra were collected on another TEM (Joel JEM-2100) at 200 kV. The surface area was measured by liquid N\(_2\) physisorption on a surface analyzer (QuantaChrome, Autosorb-1). BET and BJH methods were used to calculate the specific surface area and pore size distribution, respectively. XRD patterns were recorded on an X-ray diffractometer (Shimadzu XRD-6000). XPS spectra were measured using an XPS spectrometer (Thermo Fisher, K-Alpha+) equipped with an Al-K\(_\alpha\) (1486.3 eV) radiation source. XAS spectra were collected on the beamline BL-12B2 in the fluorescence mode at National Synchrotron Radiation Research Center (NSRRC, Taiwan). Data analysis and fitting were performed by the Demeter Software package using the FEFF 9.0 code.

**Working Electrode Preparation:** Catalyst ink at the concentration of 5 mg mL\(^{-1}\) was prepared by dispersing the catalyst (removed from NiFs) in a water/isopropanol (v/v = 1/9) solution containing 0.05 wt% Nafion 117. The ink was then dropped cast on GCEs (Pine instrument, 5 mm in diameter) with an areal mass loading of 0.2 mg cm\(^{-2}\). The catalytic performance of catalysts was tested in the three-electrode configuration in O\(_2\) saturated 1 m KOH electrolyte on an electrochemical workstation (CHI 760E), using a Pt mesh and a saturated Ag/AgCl electrode as counter and reference electrodes, respectively. A water circulator controlled the electrolyte temperature in a jacketed electrochemical cell. All measured potentials were corrected to the RHE by adding E\(_0\)(Ag/AgCl) + 0.0591 × pH. The Ag/AgCl reference electrode was also calibrated in the three-electrode configuration using Pt foils (99.9%, Sigma-Aldrich) as working and counter electrodes in 0.5 m H\(_2\)SO\(_4\) electrolyte saturated with 99.99% H\(_2\). CV scans were performed between –100 and +100 mV to calibrate HER and hydrogen oxidation reaction. The average zero current points were used to calibrate the Ag/AgCl reference electrode. It should be noted that the filling electrolyte in Ag/AgCl reference electrodes was replaced and performed calibration to minimize their drifting. The catalysts using a 1 m KOH Hg/HgO reference electrode were tested. The LSV curves obtained after averaging three-consecutive tests by using the different types of reference electrodes overlapped. It was concluded that the results were not affected by the stability of Ag/AgCl reference electrodes, as reported in some other studies. The apparent activation energy was estimated from temperature-dependent catalytic activity, which used catalyst loaded Au rotary disk electrodes (Pine instrument, 5 mm in diameter). Catalysts deposited on NiFs (with a geometric surface area of \(~0.5 \text{cm}^2\)) were also directly used as working electrodes to measure their electrocatalytic performance. It should be noted that NiFs were fully covered by deposited materials. No bare NiFs were exposed to electrolytes after the electrodeposition. Next, LSV and Tafel plots were collected under the scan rate of 2 mV s\(^{-1}\) with or without a 95%-IR correction. Nyquist plots were obtained under an overpotential of 250 mV. ECSA of catalysts loaded on GCEs was estimated by their CV scans in a non-Faradaic region in 1 m KOH electrolyte at scan rates from 2 to 50 mV s\(^{-1}\). The cathodic and anodic currents at the mid-point were fitted linearly. The average absolute slopes were used as their double-layer capacitance (\(C_d\)). A specific capacitance (\(C_s\)) of 0.04 mF cm\(^{-2}\) for metal oxides was used. ECSA was estimated by the ratio of \(C_s\) to \(C_d\). In operando Bode plots were collected at 1.03–1.68 V (vs RHE) with a step of 0.05 V at an amplitude of 5 mV from 10\(^3\) to 0.1 Hz. FTACV was performed from 0.1 to 0.7 V versus Ag/AgCl electrode under a potential amplitude of 100 mV and an AC frequency of 10 Hz. The first to the 6th harmonic transformed \(i–V\) curve was derived from 32 768 data points collected using the CHI software.

**Carrier Density Calculation:** The carrier density in Co catalysts and commercial CoO\(_2\) crystalline nanoparticles were determined by EIS, which was performed at applied potentials from 0 to 0.4 V vs Ag/AgCl. Capacitance was calculated at 0.1 Hz and plotted against the potential to develop the Mott–Schottky plot. The fitted slope of the linear part was used to calculate the carrier density by Equation (5):

\[
\frac{1}{C_d^2} = \frac{2}{e^2e_0N_a}\left(V - V_f - \frac{kT}{e}\right)
\]

\(C_d\) was calculated by dividing \(C\) with measured ECSA, \(e\) is the charge of an electron (1.602 \times 10\(^{-19}\) C), \(e_0\) is the free space permittivity (8.85 \times 10\(^{-12}\) F cm\(^{-1}\)), and \(e\) is the dielectric constant of metal oxides (an estimated value of 20 was used).
Turnover Frequency: TOF of catalysts was calculated by Equation (6):

\[ \text{TOF} = \frac{i_x E_{p}}{4 \times F \times n} \]  

(6)

where \( i \) (A) is the current obtained under the overpotential of 300 mV, \( E_p \) is the Faradaic efficiency, and \( F \) is Faraday constant (96 485 C mol\(^{-1}\)). \( n \) is the molar number of Fe or Co catalytic active sites, which was determined by EDX elemental analysis.

The second method was based on the assumption that all surface Co and Fe atoms are active sites. One-electron redox reactions for Co and Fe were assumed, the number of active 3d metal surface sites \( n_{\text{Co/Fe}} \) was calculated from redox features of \( \text{Co}^{3+}/\text{Co}^{4+} \) in CV scans by Equation (8):

\[ n_{\text{Co/Fe}} = \frac{4 \times 10^{-3} \times (r_{\text{Co/Fe}} + 1)}{M_w} \]  

(7)

where \( 4 \times 10^{-3} \) (g) is the total mass of the catalyst; \( r_{\text{Co/Fe}} \) is the molar ratio of Fe and Co in catalysts; and \( M_w \) is the molar mass of catalysts determined by EDX elemental analysis.

\[ n_{\text{Co/Fe}} = \frac{Q}{F_{\text{r}}} \times (r_{\text{Co/Fe}} + 1) \]  

(8)

where \( Q \) is the amount of charge from the \( \text{Co}^{3+}/\text{Co}^{4+} \) redox peak, \( F_{\text{r}} \) is Faraday constant.

**Apparent Activation Energy:** The apparent enthalpy of activation \( \Delta H^a \), can be simply treated as the activation energy, \( E_a \) of catalysts was determined by temperature-dependent measurements. The experiments were carried out in the water-jacketed electrochemical cell, and its temperature was controlled by a water circulator. A thermal meter was submerged in electrolytes to measure their temperature. The cell was sealed to minimize evaporation. LSV curves were recorded at 2 mV s\(^{-1}\) and corrected with 95% of internal resistances as determined from EIS measurement at 0 V. The current obtained at \( \eta = 300 \) mV was used to calculate \( \Delta H^a \) of various electrocatalysts using the Arrhenius equation:

\[ k = A e^{-\frac{\Delta H^a}{RT}} \]  

(9)

where \( k \) is the reaction rate, as represented by the current \( i_x \) obtained from the electrochemical test. \( A \) is a pre-factor for a given chemical reaction. \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is the temperature. The equation can be reorganized as:

\[ \frac{\partial \log(i_x)}{\partial(1/T)} |_{\text{ip}} = -\frac{\Delta H^a}{2.3R} \]  

(10)

The slope obtained by the linear fitting of \( \log(i_x) \) against \( 1/T \) can be used to calculate \( \Delta H^a \).

**Computational Method:** All DFT calculations were performed using the VASP code including spin-polarization. DFT+U was used to describe the on-site Coulomb interaction of localized electrons. \( U_{\text{eff}} \) values of 3.32, 5.30, and 6.20 eV for Co, Fe, and W, respectively. Core electrons were described by the projector augmented wave method.[35] Electronic exchange and correlation were described by the generalized gradient approximation method with the functional developed by Perdew, Burke, and Ernzerhof.[36] Valence electrons were described by the Kohn–Sham wave functions expanded in a plane wave basis[37] with an energy cutoff set to 400 eV. Structures were considered relaxed when all the force on each atom was lower than 0.05 eV Å\(^{-1}\). The Brillouin zone was sampled by a \( (3 \times 3 \times 1) \) k-point mesh via the Monkhorst–Pack method.[38] Each calculated d- or p-band center value was the average of d-/p-band centers of spin-up and spin-down electrons. The band centers of the Co and O atoms in different models were calculated by:

\[ \text{Band center} = \frac{\int_{-\infty}^{\text{F}} (\varepsilon - E_p) n(\varepsilon) d\varepsilon}{\int_{-\infty}^{\text{F}} n(\varepsilon) d\varepsilon} \]  

(11)

where \( \varepsilon \) is the energy of state, \( E_p \) is the Fermi level, and \( n \) is the number of states.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

J.C. and H.L. contributed equally to this work. This work was supported by the Australian Research Council under the Future Fellowships scheme (FT160100107). The calculations were supported by the Welch Foundation (F-1841) and the Texas Advanced Computing Center.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

cobalt oxyhydroxide, electrodeposition, oxygen evolution reaction, tungstate, water splitting