Homogeneously dispersed multimetal oxygen-evolving catalysts

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Earth-abundant first-row (3d) transition metal–based catalysts have been developed for the oxygen-evolution reaction (OER); however, they operate at overpotentials substantially above thermodynamic requirements. Density functional theory suggested that non-3d high-valency metals such as tungsten can modulate 3d metal oxides, providing near-thermodynamic requirements.

We examined whether multimetal oxide OER catalysts could be improved by systematically modulating their 3d electronic structure. Prior results suggest that the introduction of additional metals has a limited impact on the behavior of the 3d metals, likely because of their undesired separation into two noninteracting metal oxide phases (16, 17). For modulation, we focus in particular on tungsten (W), which in its highest oxidation state is a structurally versatile coordination host (9, 11). We began with computational studies aimed at identifying effects of W-modulation of the local coordination environment and the impacts on the resulting electronic structure and on the consequent energetics of the OER. The OER performance of unary oxides based on iron (Fe), cobalt (Co), and nickel (Ni) is particularly promising, and OER activity often outperforms that of the corresponding single-metal oxides (5, 12–15).

E fficient, cost-effective, and long-lived electrolyzers are a crucial missing piece along the path to fuels synthesized with renewable electricity (1, 2). The bottleneck in improving water-splitting technologies is the oxygen-evolving reaction (OER), in which even the most efficient precious-metal catalysts require a substantial overpotential (i) to reach the desired current densities of ±10 mA cm⁻² (2, 3). Researchers have explored earth-abundant first-row (3d) transition metal oxides (4–9), 3d metal oxides (4, 5), oxide perovskites (10–12), and oxide perovskites (13–15) to reach the desired current densities of ±10 mA cm⁻² (2, 3). Researchers have explored earth-abundant first-row (3d) transition metal oxides (4–9), 3d metal oxides (4, 5), oxide perovskites (10–12), and oxide perovskites (13–15). The bottleneck in improving water-splitting technologies is the oxygen-evolving reaction (OER), in which even the most efficient precious-metal catalysts require a substantial overpotential (i) to reach the desired current densities of ±10 mA cm⁻² (2, 3).

We found that the OER activity of the unary pure CoOOH(01-12) surface can be improved via single-site doping with subsurface Fe atoms. This improvement can be attributed to the change in ΔG_{OH} and also in ΔE_{OH} at the Co-site and can be rationalized by the difference in electron affinity between Co^{2+} (at the surface) and Fe^{2+} (subsurface) sites. Furthermore, adding a W dopant in the vicinity of the Co active site of the FeW-doped CoOOH surface (Fig. 1B, inset) further improves the energetics for OER. The substitution of a W dopant at a Co^{2+} site results in (i) migration of protons away from W, which prefer the W^{4+} formal oxidation state, toward oxygen at Co sites, and (ii) compressive strain of larger W atoms on the surrounding Co sites. As a result of these geometric and electronic changes, we identified a favorable direct O₂ mechanism for OER with a theoretical overpotential of only 0.4 V compared with the standard electrochemical OOH mechanism [computATIONAL methodology details are provided in (19)]. In light of these findings, we sought to devise a controlled process to incorporate W^{6+} into FeCo.
oxyhydroxides in an atomically homogeneous manner. We explored a room-temperature sol-gel procedure that would feature precursors mixed in a homogeneous manner that would be hydrolyzed at a controlled rate so as to achieve atomic homogeneity. First, we dissolved inorganic metal chloride precursors in ethanol. The reagents were controllably hydrolyzed in order to produce a multimetal oxyhydroxide gel via a room-temperature sol-gel process (Fig. 2A) (21). The hydrolysis rates of CoCl₂, FeCl₃, and WCl₆ vary greatly, so very low concentrations of water and propylene oxide were used to tune their hydrolysis independently—a strategy that we anticipated could lead to the desired homogeneous spatial distribution of the three metallic elements (19).

After supercritical drying with CO₂, the gel transformed into amorphous metal oxyhydroxides powders. From inductively coupled plasma optical emission spectrometry (ICP-OES) analysis, we determined the molar ratio of Fe:Co:W to be 1:1.02:0.70. Atomic-resolution scanning transmission electron microscopy (STEM) performed in high-angle annular dark field (HAADF) mode (Fig. 2D and fig. S5A), combined with selected-area electron diffraction (SAED) analysis (Fig. 2C), revealed the absence of a crystalline phase. X-ray diffraction (XRD) (fig. S2A) further confirmed that the gelled FeCoW is an amorphous phase (19). The STEM measurements show a crumpled and entangled structure composed of nanosheets and nanopores (Fig. 2B). Electron energy loss spectroscopy (EELS) elemental maps with sub-nanometer resolution (Fig. 2E) showed a uniform, uncorrelated spatial distribution of Fe, Co, and W. The statistics of the atom-pair separation distances, obtained from the STEM elemental maps, show that the nearest-neighbor separations of all...
hydrolysis, the latter enabling the maintenance of the homogeneous phase in the final gel state without phase separation of different metals caused by precipitation. In contrast, conventional processes (17), even when their precursors are homogeneously mixed, result in crystalline products formed heterogeneously during the annealing process leading to phase separation caused by lattice mismatch. For structural comparison with prior sol-gel reports that used an annealing step (17), we annealed the samples at 500°C and

Table 1. Comparison of catalytic parameters of G-FeCoW and controls.

<table>
<thead>
<tr>
<th>Samples</th>
<th>On gold foam Overpotential* (mV)</th>
<th>On glassy carbon electrode (GCE) Overpotential* (mV)</th>
<th>TOF† (s⁻¹)</th>
<th>Overpotential* (mV)</th>
<th>ΔH (kJ mol⁻¹) at η=300 mV</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDH FeCo</td>
<td>279 (±8)</td>
<td>331 (±3)</td>
<td>0.0085</td>
<td>429 (±4)</td>
<td>81</td>
<td>This work</td>
</tr>
<tr>
<td>G-FeCo</td>
<td>213 (±6)</td>
<td>277 (±3)</td>
<td>0.0435</td>
<td>346 (±4)</td>
<td>60</td>
<td>This work</td>
</tr>
<tr>
<td>G-FeCoW</td>
<td>191 (±3)</td>
<td>223 (±2)</td>
<td>0.46 (±0.08)</td>
<td>315 (±5)</td>
<td>49</td>
<td>This work</td>
</tr>
<tr>
<td>A-FeCoW</td>
<td>232 (±4)</td>
<td>301 (±4)</td>
<td>0.17</td>
<td>405 (±2)</td>
<td>80</td>
<td>This work</td>
</tr>
<tr>
<td>Amorphous-FeCoO₂‡</td>
<td>–</td>
<td>300</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(4)</td>
</tr>
<tr>
<td>LDH NiFe</td>
<td>–</td>
<td>300</td>
<td>0.07</td>
<td>–</td>
<td>–</td>
<td>(25)</td>
</tr>
<tr>
<td>CoOOH</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>IrO₂</td>
<td>–</td>
<td>260</td>
<td>0.05</td>
<td>–</td>
<td>–</td>
<td>(25)</td>
</tr>
<tr>
<td>NiFeOOH</td>
<td>–</td>
<td>340</td>
<td>–</td>
<td>66 (-/+5)</td>
<td>–</td>
<td>(27)</td>
</tr>
<tr>
<td>Ni₆Co₄₀ oxides</td>
<td>–</td>
<td>263</td>
<td>–</td>
<td>–</td>
<td>72.6§</td>
<td>(29)</td>
</tr>
<tr>
<td>NiFe LDH/GO</td>
<td>–</td>
<td>210</td>
<td>0.1</td>
<td>–</td>
<td>–</td>
<td>(22)</td>
</tr>
</tbody>
</table>

*Obtained at the current density of 10 mA cm⁻², without iR correction. †Obtained at 95% iR corrected η = 300 mV, assuming all loaded 3d-metal atoms as active sites. ‡Obtained from the LSV plots at the current density of 4 mA cm⁻² in 0.1 M KOH aqueous solution. §Obtained at 280 mV in 1 M NaOH aqueous solution.

two-metal atom pairs are highly consistent (figs. S3, S4, and S6, A to E) (19). This homogeneity results from (i) the homogeneous dispersion of three precursors in solution and (ii) controlled hydrolysis, the latter enabling the maintenance...
then found crystalline phases (figs. S5B, high-resolution TEM images, and S2B, XRD) that included separated Fe₂O₃, Co₃O₄, and CoWO₄. Elemental mapping of this sample (fig. S6, A to E) further confirmed the phase separation of Fe from Co and W atoms (19).

We investigated the influence of incorporating W (with its high oxidation state) on the electronic and coordination structures of Fe and Co using x-ray absorption spectroscopy (XAS). We examined (i) conventionally layered double hydroxides of FeCo (LDH FeCo) that have the same structure as the state-of-the-art OER catalysts (LDH NiFe) (22), (ii) FeCo oxyhydroxides (without W) prepared via the annealing-free sol-gel process (gelled FeCo, labeled G-FeCo), (iii) gelled FeCo oxyhydroxides (G-FeCoW), and (iv) annealed G-FeCoW at 500°C (A-FeCoW).

To evaluate the change of oxidation states of metal elements during OER, we performed XAS on the G-FeCoW and A-FeCoW samples before and after OER; the latter condition was realized by oxidizing samples at +1.4 V versus the reversible hydrogen electrode (RHE) in the OER region. XAS in total electron yield (TEY) mode provides information on the near-surface chemistry (below 10 nm). We acquired TEY data at the Fe and Co L-edges on samples prepared ex situ. For comparison, on the same samples we also measured in situ XAS (during OER) at the Fe and Co K-edges via fluorescent yield, a measurement that mainly probes chemical changes in the bulk. TEY XAS spectra in Fig. 3A revealed that the surface Fe²⁺ ions in G-FeCoW had been oxidized to Fe³⁺ at +1.4 V, which is in agreement with thermodynamic data for Fe. However, the oxidation states of Co in G-FeCoW and A-FeCoW samples were appreciably different at +1.4 V. In G-FeCoW, the valence states of both surface (Fig. 3B) and bulk (Fig. 3C) Co were similar to pure Co³⁺, including only a modest admixture with Co⁴⁺ (fig. S12); in particular, the Co-K edge profile closely resembled CoO₂⁺ (23), which is consistent with our DFT model. In contrast, in A-FeCoW (in which W is phase-separated), even after a potential of +1.4 V was applied, the surface (Fig. 3B) and bulk (Fig. 3C) manifested a substantially higher Co²⁺ content (fig. S12), which is consistent with the Co₂O₃ and CoWO₄ phases. These oxides had been found to be much less reactive in DFT simulations (24, 20). The bulk and surface Fe and Co edge profiles are shown in figs. S7 to S11 and discussed in (39).

The white lines of W L₃-edge x-ray absorption near-edge structure (XANES) spectra of all samples in Fig. 3D show that W in G-FeCoW and A-FeCoW samples before and after OER has a distorted WO₆ octahedral symmetry (24). The W L₃ amplitude in pre-OER A-FeCoW was low, a finding attributable to the loss of bound water during annealing (24). When a +1.4 V bias was applied, the W L₃ intensity in G-FeCoW increased, indicating that the valence of W decreases, which is consistent with increased distortion of WO₆ octahedra (24). This result agrees with the results of DFT, in which W-doped CoOOH(01-12) is expected to produce W residing in a lower oxidation state. These results indicate that Fe and Co also inversely influence W in the homogeneous ternary metal oxyhydroxides.

In situ extended x-ray absorption fine structure (EXAFS) (figs. S3 and S4) on G-FeCoW showed a significant decrease in CO-O bond distance, from 2.06 to 1.91 Å, after a potential of +1.4 V was applied. This decrease is consistent with the reported results that the CO-O bond distance in CoOOH is shorter than that in Co(OH)₂ (23). EXAFS data at the Fe edge in G-FeCoW showed the same trend (figs. S15 and S16). Ex situ EXAFS data before OER are also shown in figs. S17 to S20 and table S3. In contrast, the local structural arrangement in A-FeCoW remains unchanged at +1.4 V. Overall, we conclude that Co in the G-FeCoW structure is more readily oxidized to high valence, which is consistent with G-FeCoW being more active than the control annealed samples.

We compared the OER performance of our gelled sample G-FeCoW with that of the reference samples G-FeCo, LDH FeCo, and A-FeCoW. Representative OER currents of the samples were measured for spin-coated thin films (thickness ~30 nm) (fig. S21) (19) on a well-defined Au(111) single-crystal electrode (Fig. 4A) in 1 M KOH aqueous electrolyte at a scan rate of 1 mV s⁻¹ (currents are uncorrected and thus include the effects of resistive losses incurred within the electrolyte). The G-FeCoW-on-Au(111) required an overpotential of only 315 mV.

**Fig. 4. Performance of G-FeCoW oxyhydroxides catalysts and controls in three-electrode configuration in 1 M KOH aqueous electrolyte.** (A and B) The OER polarization curve of catalysts loaded on two different substrates with 1 mV s⁻¹ scan rate, without iR correction: (A) Au(111) electrode and (B) gold-plated Ni foam. (C) Overpotentials obtained from OER polarization curves at the current density of 10 mA cm⁻² tested on Au(111), GCE and gold-plated Ni foam, respectively, without iR correction. (D) Arrhenius plot of the kinetic current at nₗ = 300 mV, tested on Au(111), without iR correction. (E) Chronopotentiometric curves obtained with the G-FeCoW oxyhydroxides on gold-plated Ni foam electrode with constant current densities of 30 mA cm⁻², and the corresponding metal molar ratio in G-FeCoW calculated from ICP-AES results. (F) Chronopotentiometric curves obtained with the G-FeCoW oxyhydroxides on gold-plated Ni foam electrode with constant current densities of 30 mA cm⁻², and the corresponding Faradaic efficiency from gas chromatography measurement of evolved O₂.
at 10 mA cm$^{-2}$ (Table I, all current densities based on projected geometric area). This potential is 114 mV lower than that of precipitated FeCo LDH fabricated for the present study. When W was not introduced, the resultant G-FeCo gel catalyst required an additional overpotential of 31 mV to reach a similar current density. When the gelled sample was subjected to a postsynthetic thermal treatment (500°C anneal), the overpotential of the FeCo catalyst increased to 405 mV at 10 mA cm$^{-2}$.

To assess the impact of the electrode support and compare the performance of the new catalysts with the state-of-the-art NiFeOOH, we tested on glassy carbon electrode (GCE) using the identical three-electrode system and with a catalyst loading mass of 0.21 mg cm$^{-2}$. The trend of the overpotentials remains the same (fig. S22), with overpotential of 223 mV at 10 mA cm$^{-2}$. The carrier value of 49 kJ mol$^{-1}$ continues to be distributed homogeneously in the sample was substantially improved (Fig. 4B). The G-FeCoW showed a low overpotential of 191 mV at 10 mA cm$^{-2}$ on the gold-plated nickel foam (projected geometric area) (Table I). On the basis of the above discussion and the overpotentials Au(111), gold foam, GCE, and fluorine-doped tin oxide (FTO), we can be seen that the catalytic activity of G-FeCoW is much higher than that of the annealed control (A-FeCoW), gelled FeCo without W (G-FeCo), and the LDH FeCo having the same structure as the state-of-the-art LDH NiFeOOH OER catalysts.

The operating stability of the OER catalysts is essential to their application (28). To characterize the performance of the G-FeCoW catalysts, we ran water oxidation on the catalyst deposited on gold-plated Ni foam under constant current of 30 mA cm$^{-2}$ continuously for 550 hours. We observed no appreciable increase in potential in this time interval (Fig. 4, E and F). To check that the catalyst remained physically intact, we tested in situ its mass using the electrochemical quartz crystal microbalance (EQCM) technique (figs. S31 and S32) and also assessed whether any metal had leached into the electrolyte by using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (figs. S33 to S36 and table S7). After the completion of an initial burn-in period in which (presumably unbound) W is shed into the electrolyte, we saw stable operation and no discernible W loss. EELS mapping of G-FeCoW after OER (fig. S37) indicates that the remaining W continues to be distributed homogeneously in the sample. By measuring the $O_2$ evolved from the G-FeCoW/gold-plated Ni foam catalyst, we also confirmed the high activity throughout the entire duration of stability test, obtaining quantitative (unity Faradaic efficiency) gas evolution of $O_2$ to within our available ±5% experimental error (Fig. 4F). These findings suggest that modulating the 3D transition in metal oxyhydroxides by using a suitable transition metal, one closely atomically coupled through homogeneous solid-state dispersion, may provide further avenues to OER optimization.

REFERENCES AND NOTES

Editor's Summary

Modulating metal oxides

The more difficult step in fuel cells and water electrolysis is the oxygen evolution reaction. The search for earth-abundant materials to replace noble metals for this reaction often turns to oxides of three-dimensional metals such as iron. Zhang et al. show that the applied voltages needed to drive this reaction are reduced for iron-cobalt oxides by the addition of tungsten. The addition of tungsten favorably modulates the electronic structure of the oxyhydroxide. A key development is to keep the metals well mixed and avoid the formation of separate phases.

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