Hydration-Effect-Promoting Ni–Fe Oxyhydroxide Catalysts for Neutral Water Oxidation

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Adv. Mater. 2020, 1906806

DOI: 10.1002/adma.201906806
is several orders of magnitude lower than in the alkaline electrolyte. OER in pH-neutral electrolyte therefore requires additional water adsorption and dissociation processes to provide the adsorbed water molecules (H₂O*)—and the OER steps under neutral-pH conditions:[12]

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

Catalysts including iridium oxide (IrO₂)[13] as well as Co-based,[14] Ni-based,[15,16] and Mn-based[17] materials, have each shown recent progress in OER performance in pH-neutral electrolytes. Nevertheless, these catalysts have yet to fulfill the requirement of sub-350 mV overpotentials and prolonged durability (≥ 500 h typically for initial stability studies).[18]

We took the view that efficiently capturing and dissociating water molecules at the catalyst/water interface could improve OER performance in pH-neutral electrolytes. Prior studies have shown that noncovalent interactions between hydrated metal cations (Mⁿ⁺) and *OH form OHad-Mnⁿ⁺(H₂O)x and enhance the adsorption of OH⁻ at the catalyst/electrolyte interface. These methods can accelerate the oxygen reduction reaction.[19–24] Mg²⁺ is an example of a metal that can support another beneficial strategy: it possesses a high hydration energy that offers the prospect of enhancing the bond strength between the catalyst surface and molecular water.[23] We hypothesized that introducing ions of this kind into the catalyst framework could lead to a higher hydration level of the system, improving thereby the OER rate.

Theoretical studies of the hydration effect on Ni–Fe based catalyst. Using the Ni–Fe system as a prototypical framework,[25,26] we investigated the effect of introducing metal cations with strong hydration capacity and small atomic diameters. We focus on whether water adsorption onto the surface of Ni–Fe catalyst can be enhanced.

We first studied the effect of Mg²⁺ (a relatively small size cation) and compared it with Ba²⁺ (a relatively large size cation) doping (Figure 1). In each case we examined the water adsorption properties of the doped Ni–Fe catalyst.

Starting from a stable metal oxyhydroxide model, we constructed the slab β-NiOOH as the catalyst framework (Figure S1, Supporting Information).[27,28] Mg atoms remain at the catalyst surface, and are directly exposed to the aqueous solution during OER (Figure S2, Supporting Information).

We then considered the immersion of this catalyst into aqueous solution: we assumed that two (015) facets were exposed to interfacial water. One of the two (015) facets was modified to replace half of the surface Ni²⁺ with the relatively small Mg²⁺ or the larger Ba²⁺ cations (Figure 1a,d), while the other facets of the catalyst were kept the same as controls. Water adsorption on each catalyst was investigated using molecular dynamic simulations in the canonical ensemble at 300 K (details in the Supporting Information). We accumulated a 12 ps trajectory and recorded the final 10 ps trajectory to produce a map of the water-catalyst distance under dynamic conditions. Specifically, we report

\[
\frac{1}{\sqrt{\pi}} \exp\left(-\frac{(-a_i-a_o)^2}{\xi^2}\right)
\]

where \(d\) is the shortest distance between the interfacial water oxygen and any metal ion at slab surface, \(a_o\) is the \(x\)-\(y\) coordinate of this water oxygen, \(a_i\) is the grid on the surface, and \(\xi = 1.0 \text{ Å}\) determines the resolution of the map (Figure 1b,c,e,f).

In the absence of the Mg²⁺ cation, the surface OH terminal groups of the Ni–Fe catalyst determine the interfacial water
distribution via hydrogen-bonding interactions. When surface Mg$^{2+}$ is added, it attracts interfacial water molecules, leading to a shorter distance between the oxygen atom in water and the metal ions (red patches in Figure 1c). These interfacial water molecules no longer reflect the structure of surface OH terminal groups. By contrast, when Ba$^{2+}$ is introduced, the water-catalyst distance is dominated by the hydrogen-bonding network (Figure 1f).

Using this simple model, we are able to suggest a trend: pursuing experimental doping using cations having a high hydration capacity could potentially offer more water molecules for dissociation reactions.

Synthesis and OER activity of hydration-effect catalysts. We synthesized hydration-effect-promoting (HEP) oxyhydroxides and hydration-effect-limiting (HEL) Ni–Fe–Ba oxyhydroxides. We used a room-temperature sol–gel process previously reported.[29] Energy-dispersive X-ray spectroscopy mapping shows a uniform distribution of Ni, Fe, and Mg (Figure S3, Supporting Information). From inductively coupled plasma optical emission spectra, we determined the molar ratio of Ni:Fe:Mg to be 7:1:0.2 (Figure S4, Supporting Information). The catalysts present a porous structure (Figure S5, Supporting Information) without evidence of crystallinity (Figure S6, Supporting Information).

We evaluated catalytic properties using a three-electrode electrochemical cell containing CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte. Compared with the HEL catalyst, the HEP exhibited a significant improvement in catalytic activity on glass carbon electrode (GCE). Linear sweep voltammetry (LSV) polarization measurements indicate that optimized Ni–Fe–Mg requires only 514 mV overpotential to reach 10 mA cm$^{-2}$ on GCE, which outperforms the best oxide catalysts previously reported (Figure 2a; Table S1 and Figure S7, Supporting Information). The decreased Tafel slope (210 mV dec$^{-1}$→150 mV dec$^{-1}$, Table S2, Supporting Information) indicates a higher OER reaction rate when Mg$^{2+}$ is incorporated (Figure 2b). Charge-transfer resistance ($R_{ct}$), determined using electrochemical impedance spectroscopy (Figure 2c), shows that incorporating Mg$^{2+}$ decreases the $R_{ct}$ (580 $\Omega$→480 $\Omega$) and gives rise to faster electrode kinetics. The Ni is in an oxidation state higher than 3$^{+}$ as seen in previous reports (Figure S8, Supporting Information).[30,31]

Next, we investigated further electrochemical behaviors of the best catalysts compared to controls in order to characterize intrinsic activity. First, we normalized the current density using the electrochemically active surface area (ECSA) obtained using the double-layer capacitance ($C_{dl}$) technique.[32,33] The ECSA-normalized current density of the HEP catalyst is fully 1.3-times and 1.8-times higher than those of reference Ni–Fe catalyst and HEL Ni–Fe–Ba catalyst, respectively, at 1.7 V versus RHE (Figure S9, Table S3, Supporting Information). The activation energy (Figure 2d) and turnover frequency[29,31,34–36]
confirm the same trend: the HEP catalyst exhibits the lowest activation energy of 64 kJ mol\(^{-1}\) and the highest TOF of 0.3 s\(^{-1}\).

We also built and compared the catalysts on Au-coated Ni foam and Ni foam. In neutral electrolyte, the HEP catalyst outperforms both IrO\(_2\) and other relevant controls (Figure 2e; Table S1 and Figure S11, Supporting Information). The HEP catalyst on Au-coated Ni foam achieves a 310 mV at current density 10 mA cm\(^{-2}\) compared to 344 mV for Ni–Fe and 360 mV for HEL Ni–Fe–Ba. We measured \(R_s\) and \(R_{ct}\) to identify the effect of supports on catalytic performance. The Au-coated Ni foams have the lowest \(R_s\) and \(R_{ct}\), consistent with the view that it provides faster charge transfer (Table S5 and Figure S12, Supporting Information).

We further tested the \(iR\)-corrected LSV curves on GCE and Au-coated Ni foam to exclude the effects of cell geometry measurement and conductivity on performance (Figure S13, Supporting Information). The HEP Ni–Fe–Mg catalyst requires of 290 mV overpotential at 10 mA cm\(^{-2}\) on Au-coated Ni foam after \(iR\)-correction, which is 35 mV lower than that of Ni–Fe catalyst and 50 mV lower than that of HEL Ni–Fe–Ba catalyst). Ni and Fe K-edge X-ray absorption near-edge structure spectroscopy and Fourier-transformed extended X-ray absorption fine structure spectra of catalysts showed no obvious change for Ni–Fe–Mg versus relevant controls (Figures S8c–f and S14 and Table S6, Supporting Information). This indicates that the effects of dopants on the electronic structure of Ni and Fe sites do not play a principal role in the observed catalytic enhancement.

We characterized the operating stability of the HEP catalyst at 10 mA cm\(^{-2}\) and found that it retained its overpotential to within 10 mV following 900 h of continuous water splitting operation (Figure 2f). The Faradaic efficiency for oxygen production remained at 98% ± 2% throughout.

Investigations of the HEP effect. To explore further the relationship between the hydration effect and catalyst activity, we examined the role of Mg and Ba in water adsorption and water dissociation. When we increase pH, the catalytic advantage from HEP Ni–Fe–Mg is reduced, consistent with the abundance of OH\(^-\) at high pH (Table S7, Supporting Information; Figure 3a,b), and also in accordance with the viewpoint that alkaline earth cations cannot improve the alkaline catalytic performance.[37,38] The Tafel slope decreased from 150 mV dec\(^{-1}\) (pH = 7.2) to 120 mV dec\(^{-1}\) (pH = 8.5) and 80 mV dec\(^{-1}\) (pH = 14, Figure 3c), which again supports the view that the HEP advantage is occurred in neutral electrolyte.[39–41]

We next proceeded to characterize the effect of HEP/HEL metal cations on water adsorption. Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (TOF, Figure S10 and Table S4, Supporting Information) confirm the same trend: the HEP catalyst exhibits the lowest activation energy of 64 kJ mol\(^{-1}\) and the highest TOF of 0.3 s\(^{-1}\).
(XPS) were used to compare the adsorbed water on HEP Ni–Fe–Mg and relevant controls (Figure 4a,b). The enhanced peak intensity at \(\approx 3400 \text{ cm}^{-1}\) indicates that the HEP Ni–Fe–Mg catalyst favors water molecule adsorption (Figure 4a; Figure S15, Supporting Information).[43] XPS curves indicate large quantities of water adsorbed on the HEP catalyst (Figure 4b).[44,45]

Contact angles measurements results show that the addition of Mg\(^{2+}\) improves the contact between the electrolyte and the catalyst surface, resulted by the enhanced water-adsorption ability (Figure S16, Supporting Information).

To challenge the role of hydration effect metal cations, we doped other alkaline earth metals into the Ni–Fe framework and characterized OER catalytic activity under identical conditions. The doping concentration of M (Mg, Ca, Sr, and Ba) ratio was fixed at similar value to avoid the effect of dopant concentration on electrochemical activity and water adsorption (Table S8, Supporting Information). The HEP Ni–Fe–Mg and Ni–Fe–Ca catalysts exhibit better performance than HEL Ni–Fe–Sr and Ni–Fe–Ba (Figure 4c). To investigate the hydration-promotion effect further, we performed FTIR and XPS of Ni–Fe–Ca catalyst. The obtained results indicate that the Ni–Fe–Ca catalyst provides improved water-adsorption ability compared to Ni–Fe (Figure 4a,b). Its overpotential of 330 mV at the current density of 10 mA cm\(^{-2}\) on Au-coated Ni foam is also lower than that of reference sample (345 mV) (Figure S17, Supporting Information).

In summary, a series of Ni–Fe based catalysts were prepared via a sol–gel method at room temperature, and then used as electrocatalysts for OER in neutral electrolyte. By combining electrochemical characterization with density functional theory (DFT) studies, we found that incorporating hydration effect metal cations into a Ni–Fe framework—namely, the Ni–Fe–Mg catalysts—influences water adsorption and enhances OER performance in neutral electrolytes. Specifically, OER activities on the RHE scale for Ni–Fe based catalysts are increased when we decrease the metal–oxygen distance, consistent with the view that the hydration-effect-promoting water adsorption triggers more favorable OER reaction pathways. In the future, the hydration-effect-promoting phenomenon can be extended to provide enhanced water adsorption for other electrochemical reactions, such as in CO\(_2\) reduction to hydrocarbons, N\(_2\) reduction to ammonia, and other reactions involving water molecules.

**Experimental Section**

See the details in the Supporting Information.

**Supporting Information**

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

N.W., Z.C., and X.Z. contributed equally to this work. This work was supported by the Ontario Research Fund – Research Excellence Program, the Natural Sciences and Engineering Research Council of Canada, and the CIFAR Bio-Inspired Solar Energy program. N.W. and X.D.Z. acknowledge support from International Cooperation Projects of the Ministry of Science and Technology (2014DFE60170), National Natural Science Foundation of China (61774065), and (61674084), Tianjin Ministry of Science and Technology (2017KJRC610), and the CIFAR Bio-Inspired Solar Energy program. N.W. and X.D.Z. contributed equally to this work. This work was performed using the KAUST supercomputer (HPC).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

hydration effect, neutral electrolytes, Ni–Fe catalysts, oxygen evolution reaction

Received: October 16, 2019
Revised: December 11, 2019
Published online: