Tuning Ni-based hydroxide into efficient hydrogen evolution electrocatalyst by fluoride incorporation

Bowei Zhang, Shan Hu*

Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, USA

*Corresponding to: shanhu@iastate.edu

Abstract

Ni-based oxides/hydroxide have been extensively reported for oxygen evolution reaction and the fluoride precursor was frequently used in its synthesis. However, there is no work studied the effect of fluoride in Ni based oxide/hydroxides for hydrogen evolution reaction (HER) as it is generally considered inactive for HER. Recently the HER activities of Ni based oxide/hydroxides have been improved by anions doping (-P, -S, and -Se). However, these compounds are chemically unstable in HER and can be converted into the corresponding oxide/hydroxides. Herein, we discovered an interesting phenomenon that the NiFe hydroxide can be tuned into active HER material by incorporating fluoride into it. In 1M KOH, a significant shift of ~ 91 mV was observed in the HER overpotential at -10 mA/cm^2 due to the enhanced charge transfer ability that is triggered by fluoride. This discovery provides a new strategy to turn the normally inactive materials, whose catalytic activities are mainly hindered by their low intrinsic conductivity, into electrocatalysts and will lead to the discovery of new catalysts.

Keywords: Ni-based hydroxide; Hydrogen evolution; Fluoride incorporation; Charge transfer; Electrocatalysis

1. Introduction

With the high energy density and environmentally friendly nature, hydrogen fuel is expected to be a promising resource to solve the issues of environmental pollution and fossil fuel depletion in our age. With this regard, generating hydrogen by water electrolysis has been investigated extensively as a next-generation energy conversion way [1]. To substitute the high cost and scarce electrocatalyst of Pt that has superior hydrogen evolution reaction (HER) activity, the scientific community has devoted much effort into developing efficient, stable, and earth-abundant HER electrocatalyst and a series of exciting progresses have been achieved in recent years. Among various earth-abundant HER electrocatalysts, nickel-based nanomaterials including chalcogenides (-Se and -S) and phosphides (-P) have been widely reported in literature as attractive HER catalysts [2–4]. These compounds are usually thought as stable for HER and the chemical instability of them only exhibited under oxidative condition [5]. However, recently some works reported that these materials are chemically unstable and can be converted into the corresponding amorphous oxides/hydroxides during HER process [6–8]. This prompts us to explore nickel based oxide/hydroxide as more stable HER electrocatalysts.

Ni based oxide/hydroxides are very stable, but few works of them for HER have been reported. This is because the Ni-based oxide/hydroxide is generally considered as HER inactive material owing to its inappropriate hydrogen atom adsorption energy, namely excessively strong H adsorption on O but extremely weak H adsorption on Ni. Considering the Volmer step in alkaline condition, the ideal HER electrocatalyst should have relative high adsorption energy for H and good desorption ability of hydroxyl (OH) [3]. Inversely, as one of the most active oxygen evolution electrocatalysts, NiFe hydroxide can effectively adsorb OH species and accordingly has extremely weak ability for H adsorption [3,9].

Nonetheless, Wang et al. have improved the HER activity of NiFe oxides by Li^+ insertion and extraction to break off the oxide [10]. In 2017, NiFe hydroxide was grown on copper nanowires and this composite shows an enhancement of HER activity compared to NiFe hydroxide [11]. These methods are effective but too complicated and uneconomical for synthesis in large-scale and application in industrial productions. Therefore, proposing simpler, low-cost, and scalable method is of great significance for the practical hydrogen generation.

Herein, we fabricated fluoride incorporated NiFe hydroxide (NiFe-OH-F) and NiFe hydroxide (NiFe-OH) nanosheets on nickel foam by a simple one-step method, respectively, and then investigated the effects of fluoride incorporation in NiFe hydroxide for HER in alkaline condition.

2. Material and methods

2.1 Materials and chemicals

Ni foam (thickness: 1.6 mm; bulk density: 0.45 g/cm^3), NH_4F, and urea were provided by Sigma Aldrich. $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were purchased from Fisher Scientific. The water used in this work was purified by Milli-Q system.

2.2 Synthesis of NiFe-OH-F and NiFe-OH

The materials were synthesized according to the methods we reported previously [12,13]. Ni foams (2 cm × 3 cm) were cleaned under the assistance of sonication in 6 M HCl, ethanol, and Milli-Q water for 10 min, respectively. To synthesis NiFe-OH-F, 4 mmol NH_4F, 10 mmol urea, and 4 mmol total amount of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 40 mL water with the Fe/Ni ratio of 7:3. Then the solution and the cleaned Ni foam were transferred into a 50 mL Teflon-lined stainless steel autoclave, then sealed and kept at 120 °C for 6 h with a heating rate of 3 °C min^{-1}, followed by washing the obtained samples with water under the

assistance of sonication and dried in vacuum oven at 60 °C for 6 h. NiFe-OH was synthesized according to the above procedures without adding NH_4F.

2.3 Materials characterization

The crystallographic information was characterized by XRD (Siemens D500 X-ray diffractormeter) using Cu Kα radiation. The morphology and structure of the materials were characterized using a FEI Quanta 250 field-emission scanning electron microscopy (FE-SEM) and a FEI Titan Themis 300 Cubed probe aberration corrected STEM. X-ray photoelectron spectroscopy (XPS, AMICUS ESCA 3400) measurements were performed with Mg Kα 1253.7eV radiation for the composition analysis.

2.4 Electrochemical measurements

All electrochemical measurements were conducted on a Gamry Interface 1000 potentiostat in a three-electrode setup using electrocatalysts electrode as the working electrode, a graphite rod as the counter electrode, and Ag/AgCl electrodes as the reference electrode. Polarization curves were obtained using linear sweep voltammetry (LSV). The long-term stability tests were carried out using the chronopotentiometric measurements. The loading mass of NiFe-OH-F and NiFe-OH on nickel foam are about 3.3 mg/cm^2 and 2.1 mg/cm^2, respectively. The current densities were calculated using the widely used geometry area (projected area) of the electrode. The electrode area used in this work is 2 cm × 2 cm (width × length).

3. Results and discussion

Both NiFe-OH (Fig. 1a) and NiFe-OH-F nanosheets (Fig. 1b and c) are fabricated on 3D Ni foam frameworks by a one-step hydrothermal method at 120 ℃, respectively. The inset side-view image in Fig. 1b shows the thickness of the NiFe-

OH-F layer, which is about 2 μm. The lattice fringe of 0.27 nm in the inset HR-STEM image in Fig. 1c index to the (101) facet of NiFe hydroxide [14]. The XRD measurements on NiFe-OH and NiFe-OH-F were conducted to confirm the crystalline nature. Except for the three peaks of Ni substrate, all the other peaks in Fig. 1d are index to the typical facets of NiFe hydroxide: (003), (006), (101), (012), (015), (018), (110), and (113) [13,15,16]. These results indicate that the incorporation of F^- did not affected the original nature of NiFe-OH. Then, the energy-dispersive X-ray (EDX) characterization was employed in the NiFe-OH-F surface, as shown in Fig. 1e. The inset EDX spectrum reveals the coexistence of Ni, Fe, O, and F and the elemental mapping images suggest the homogeneous distribution of these elements. The Iridium (Ir) peaks in the inset EDX spectra are originated from the Ir layer that was coated on the sample surface before SEM characterization. The molar ratio of Ni: Fe: F is about 8.0: 3.4: 5.2, this ratio was estimated by inductively coupled plasma emission spectrometer (ICP-MS) and EDX.

To further probe the chemical composition and the effect of F^- in NiFe hydroxide, XPS was used. Note that all the XPS high-resolution spectrums were calibrated by C1s. The high-resolution Ni $2p_{3/2}$ spectrums (Fig. 2a) of NiFe-OH-F and NiFe-OH were fitted into two peaks and corresponding to Ni^{2+} (855.65 eV and 855.30 eV) and its satellite peaks (861.78 eV and 861.23 eV), respectively [17,18]. After carefully checking the binding energies of these peaks, we realized that the significant positive shifts of the Ni $2p_{3/2}$ peaks were generated by F^- incorporation in NiFe-OH-F compared to NiFe-OH. The positive binding energy shifts of 0.35 eV at Ni^{2+} and 0.55 eV at its satellite indicates the significantly enhanced electron transfer ability of NiFe-OH-F [19]. In the spectrum of Fe 2p (Fig. 2b), the binding energies at 731.5 eV are index to Fe $2p_{3/2}$ [20]. As both NiFe-OH-F and NiFe-OH show hydroxide

nature, the O 1s spectrum needs to be analyzed. The high-intensity peaks of O 1s at 530.92 to 530.97 eV can be assigned to -OH groups [18,21]. Therefore, this detailed analysis further confirmed the hydroxide nature of NiFe-OH-F and NiFe-OH. Moreover, the XPS F 1s spectra in Fig. 2d manifested the successful incorporation of F^- in NiFe-OH-F [22]. Overall, the XPS analysis and the above XRD characterization of NiFe-OH-F are consistent with our previous report [13].

Electrocatalytic performance of NiFe-OH-F, NiFe-OH, and Ni foam toward HER were evaluated in argon saturated 1M KOH solution using three-electrode system. Note that a graphite rod was used as the counter-electrode rather than the conventional Pt to avoid the influence of the oxidation-dissolution of Pt on the samples' HER activates [23]. Fig. 2a shows the iR-corrected polarization curves of various electrodes at a scan rate of 5 mV/s. Compared to NiFe-OH, NiFe-OH-F just needs a ~ 91 mV lower overpotential of -206 mV to drive a typical current density of -10 mA/cm^2. This performance is comparable to the recently reported non-noble metal based HER compounds, including exfoliated NiFe hydroxide/defective graphene ($\eta_{-10\ mA/cm^2}$ = -210 mV) [24], CoSe/NiFe hydroxide/Ni foam ($\eta_{-10\ mA/cm^2}$ = -260 mV) [25], Janus Co/CoP ($\eta_{-10\ mA/cm^2}$ = -193 mV) [26], MA-MoS_2 ($\eta_{-0.9\ mA/cm^2}$ = -200 mV) [27], $NiSe_2$/CNT ($\eta_{-35.6\ mA/cm^2}$ = -250 mV) [28], and $NiCo_2S_4$ NWS/Ni foam ($\eta_{-10\ mA/cm^2}$ = -210 mV) [29]. Ni foam shows a poor HER activity and the performance of NiFe-OH is even slightly lower than Ni foam in the current density range of < 20 mA/cm^2, indicating the active sites on Ni foam surface might be partially blocked by the NiFe-OH layer.

To gain more insight into the HER reaction kinetics, the electrochemical impedance spectroscopy (EIS) tests were performed from 20 kHz to 0.1 Hz at a potential of -0.2 V vs RHE (Fig. 3b). Nyquist plot of NiFe-OH-F shows a much smaller semicircle in the low-frequency region compared to NiFe-OH, revealing that

the F^- lowered the charge transfer resistance during HER process. The intercept of the Nyquist plot with the real axis in the high-frequency region represents the ohmic resistance (R_Ω), which is the sum of the electrode and electrolyte resistance. We can observe that the R_Ω of NiFe-OH-F is smaller than that of NiFe-OH, indicating NiFe-OH-F electrode has higher electrical conductivity than NiFe-OH. In summary, we can conclude that the incorporation of F^- enhances the charge transfer during HER and enhanced the conductivity of NiFe-OH-F. These beneficial effects of fluoride incorporation afford a better HER electrocatalyst.

The stability of the NiFe-OH-F electrode was examined by a long-term test at a current density of -20 mA/cm^2, the electrode maintained a steady potential for over 12 hours (Fig. 3c) and exhibited a good stability. After finishing the stability measurement, the corresponding sample was further characterized by SEM and XRD. As shown in the inset images in Fig. 3d, both the morphology and typical XRD peaks of the post-HER sample remain the same with the original sample. Therefore, the NiFe-OH-F electrode has a good durability for HER in alkaline condition.

4. Conclusion

In summary, we have discovered that the NiFe-OH can be tuned into active HER electrocatalyst by F^- incorporation without altering its materials structure or hydroxide nature. By the F^- incorporation, the charge transfer ability in NiFe-OH-F during HER can be greatly enhanced and its ohmic resistance can be reduced. This work broadens the design strategy for low-cost and scalable HER electrocatalyst, which is a promising substitution of the low-efficient metallic nickel catalyst used in industrial hydrogen production. As mentioned previously, existing works always improve the electric conductivity of the Ni-based oxides/hydroxides by converting

them into the chalcogenides and phosphides. However, the chalcogenides and phosphides are chemically unstable during HER and will be converted to the corresponding hydroxides. This method provides an alternative way for improving the performance of transition metal oxide/hydroxide electrodes whose electrochemical activities have been greatly hindered by their low intrinsic conductivity. Hence, this work will generally benefit research on high-performance electrode materials for supercapacitors, batteries, electrocatalysts, etc.

Acknowledgements

This material is based upon the work supported by the National Science Foundation (Grant No. CMMI-1663509). B. Z. was supported by the Catron Fellowship from the College of Engineering, Iowa State University (USA).

Conflict of interest

The authors declare no conflict of interest.

References

[1] S. Xu, Y. Chen, Y. Li, A. Lu, Y. Yao, J. Dai, Y. Wang, B. Liu, S.D. Lacey, G.R. Pastel, Y. Kuang, V.A. Danner, F. Jiang, K.K. Fu, L. Hu, Universal, in situ transformation of bulky compounds into nanoscale catalysts by high-temperature pulse, Nano Lett. 17 (2017) 5817–5822. doi:10.1021/acs.nanolett.7b03019.

[2] V. Vij, S. Sultan, A. M. Harzandi, A. Meena, J.N. Tiwari, W.G. Lee, T. Yoon, K.S. Kim, Nickel–based electrocatalysts for energy related applications: oxygen Reduction, oxygen evolution, and hydrogen evolution reactions, ACS Catal. 7 (2017) 7196-7225. doi:10.1021/acscatal.7b01800.

[3] M. Gong, D.Y. Wang, C.C. Chen, B.J. Hwang, H. Dai, A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction, Nano Res. 9 (2016) 28–46. doi:10.1007/s12274-015-0965-x.

[4] Y. Shi, B. Zhang, Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction, Chem. Soc. Rev. 45 (2016) 1529–1541. doi:10.1039/C5CS00434A.

[5] S. Jin, Are metal chalcogenides, nitrides, and phosphides oxygen evolution catalysts or bifunctional catalysts?, ACS Energy Lett. 2 (2017) 1937–1938. doi:10.1021/acsenergylett.7b00679.

[6] X. Wang, W. Li, D. Xiong, D.Y. Petrovykh, L. Liu, Bifunctional nickel phosphide nanocatalysts supported on carbon fiber paper for highly efficient and stable overall water splitting, Adv. Funct. Mater. 26 (2016) 4067–4077. doi:10.1002/adfm.201505509.

[7] W. Li, X. Gao, D. Xiong, F. Wei, W.G. Song, J. Xu, L. Liu, Hydrothermal synthesis of monolithic Co_3Se_4 nanowire electrodes for oxygen evolution and overall water splitting with high efficiency and extraordinary catalytic stability, Adv. Energy Mater. 7 (2017) 1602579. doi:10.1002/aenm.201602579.

[8] H. Liang, A.N. Gandi, D.H. Anjum, X. Wang, U. Schwingenschlo gl, H.N. Alshareef, Plasma-assisted synthesis of NiCoP for efficient overall water splitting, Nano Lett. 16 (2016) 7718–7725. doi:10.1021/acs.nanolett.6b03803.

[9] J. Hu, C. Zhang, L. Jiang, H. Lin, Y. An, D. Zhou, M.K.H. Leung, S. Yang, Nanohybridization of MoS_2 with layered double hydroxides efficiently synergizes the hydrogen evolution in alkaline media, Joule. 1 (2017) 383–393. doi:10.1016/j.joule.2017.07.011.

[10] H. Wang, H.-W. Lee, Y. Deng, Z. Lu, P.-C. Hsu, Y. Liu, D. Lin, Y. Cui, Bifunctional non-noble metal oxide nanoparticle electrocatalysts through lithium-induced conversion for overall water splitting, Nat. Commun. 6 (2015) 7261. doi:10.1038/ncomms8261.

[11] Y. Luo, H. Zhou, J. Sun, F. Qin, F. Yu, J. Bao, Y. Yu, S. Chen, Z. Ren, Cu nanowires shelled with NiFe layered double hydroxide nanosheets as bifunctional electrocatalysts for overall water splitting, Energy Environ. Sci. 10 (2017) 1820–1827. doi:10.1039/C7EE01571B.

[12] B. Zhang, Y.H. Lui, H. Ni, S. Hu, Bimetallic $(Fe_xNi_{1-x})_2P$ nanoarrays as exceptionally efficient electrocatalysts for oxygen evolution in alkaline and neutral media, Nano Energy. 38 (2017) 553–560. doi:10.1016/j.nanoen.2017.06.032.

[13] B. Zhang, Y.H. Lui, L. Zhou, X. Tang, S. Hu, An alkaline electro-activated Fe–Ni phosphide nanoparticle-stack array for high-performance oxygen evolution under alkaline and neutral conditions, J. Mater. Chem. A. 5 (2017) 13329–13335. doi:10.1039/C7TA03163G.

[14] Y. Zhu, J. Ren, X. Yang, G. Chang, Y. Bu, G. Wei, W. Han, D. Yang, Interface engineering of 3D $BiVO_4$/Fe-based layered double hydroxide core/shell nanostructures for boosting photoelectrochemical water oxidation, J. Mater. Chem. A. 5 (2017) 9952–9959. doi:10.1039/C7TA02179H.

[15] H.D. M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, An advanced Ni−Fe layered double hydroxide electrocatalyst for water oxidation, J. Am. Chem. Soc. 135 (2013) 8452–8455.

[16] F. Dionigi, P. Strasser, NiFe-based (oxy)hydroxide catalysts for oxygen

evolution reaction in non-acidic electrolytes, Adv. Energy Mater. 6 (2016) 1600621. doi:10.1002/aenm.201600621.

[17] J.-J. Wang, J. Wang, K. Feng, H.-H. Zhang, Z.-J. Li, B. Liu, C.-H. Tung, L.-Z. Wu, Enhanced visible-light-driven hydrogen generation by in situ formed photocatalyst RGO–CdS–Ni_xS from metal salts and RGO–CdS composites, J. Mater. Chem. A. 5 (2017) 9537–9543. doi:10.1039/C7TA00336F.

[18] B. Zhang, H. Ni, R. Chen, W. Zhan, C. Zhang, R. Lei, Y. Zha, A two-step anodic method to fabricate self-organised nanopore arrays on stainless steel, Appl. Surf. Sci. 351 (2015) 1161–1168. doi:10.1016/j.apsusc.2015.06.083.

[19] J. Yu, Q. Li, Y. Li, C.Y. Xu, L. Zhen, V.P. Dravid, J. Wu, Ternary metal phosphide with triple-layered structure as a low-cost and efficient electrocatalyst for bifunctional water splitting, Adv. Funct. Mater. 26 (2016) 7644–7651. doi:10.1002/adfm.201603727.

[20] Z. Lu, W. Xu, W. Zhu, Q. Yang, X. Lei, J. Liu, Y. Li, X. Sun, X. Duan, Three-dimensional NiFe layered double hydroxide film for high-efficiency oxygen evolution reaction, Chem. Commun. 50 (2014) 6479–6482. doi:10.1039/C4CC01625D.

[21] C. Xia, Q. Jiang, C. Zhao, M.N. Hedhili, H.N. Alshareef, Selenide-based electrocatalysts and scaffolds for water oxidation applications, Adv. Mater. 28 (2016) 77–85. doi:10.1002/adma.201503906.

[22] L.F. Chen, Z.Y. Yu, J.J. Wang, Q.X. Li, Z.Q. Tan, Y.W. Zhu, S.H. Yu, Metal-like fluorine-doped β-FeOOH nanorods grown on carbon cloth for scalable high-performance supercapacitors, Nano Energy. 11 (2015) 119–128. doi:10.1016/j.nanoen.2014.10.005.

[23] R. Chen, C. Yang, W. Cai, H.-Y. Wang, J. Miao, L. Zhang, S. Chen, B. Liu, Use of platinum as the counter electrode to study the activity of nonprecious metal catalysts for the hydrogen evolution reaction, ACS Energy Lett. 2 (2017) 1070–1075. doi:10.1021/acsenergylett.7b00219.

[24] Y. Jia, L. Zhang, G. Gao, H. Chen, B. Wang, J. Zhou, M.T. Soo, M. Hong, X. Yan, G. Qian, J. Zou, A. Du, X. Yao, A heterostructure coupling of exfoliated Ni–Fe hydroxide nanosheet and defective graphene as a bifunctional electrocatalyst for overall water splitting, Adv. Mater. 29 (2017) 1–8. doi:10.1002/adma.201700017.

[25] Y. Hou, M.R. Lohe, J. Zhang, S. Liu, X. Zhuang, X. Feng, Vertically oriented cobalt selenide/NiFe layered-double-hydroxide nanosheets supported on exfoliated graphene foil: an efficient 3D electrode for overall water splitting, Energy Environ. Sci. 9 (2016) 478–483. doi:10.1039/C5EE03440J.

[26] Z.H. Xue, H. Su, Q.Y. Yu, B. Zhang, H.H. Wang, X.H. Li, J.S. Chen, Janus Co/CoP nanoparticles as efficient mott–schottky electrocatalysts for overall water splitting in wide pH range, Adv. Energy Mater. 7 (2017) 1–7. doi:10.1002/aenm.201602355.

[27] D. Wang, Z. Wang, C. Wang, P. Zhou, Z. Wu, Z. Liu, Distorted MoS_2 nanostructures: an efficient catalyst for the electrochemical hydrogen evolution reaction, Electrochem. Commun. 34 (2013) 219–222. doi:10.1016/j.elecom.2013.06.018.

[28] B. Wang, X. Wang, B. Zheng, B. Yu, F. Qi, W. Zhang, Y. Li, Y. Chen, $NiSe_2$ nanoparticles embedded in CNT networks: scalable synthesis and superior electrocatalytic activity for the hydrogen evolution reaction, Electrochem.

Commun. 83 (2017) 51–55. doi:10.1016/J.ELECOM.2017.08.022.

[29] A. Sivanantham, P. Ganesan, S. Shanmugam, Hierarchical $NiCo_2S_4$ nanowire arrays supported on Ni foam: an efficient and durable bifunctional electrocatalyst for oxygen and hydrogen evolution reactions, Adv. Funct. Mater. 26 (2016) 4661–4672. doi:10.1002/adfm.201600566.

Figure Legends:

Fig. 1. SEM images of (a) NiFe-OH and (b, c) NiFe-OH-F nanosheets on nickel foam; (d) XRD patterns of NiFe-OH and NiFe-OH-F; (e) EDX elemental mapping of NiFe-OH-F nanosheets; Inset in (b), (c), and (e) are the side-view, HR-STEM lattice fringe, and the EDX spectrum of NiFe-OH-F.

Fig. 2. High-resolution XPS spectrums of (a) Ni 2p, (b) Fe 2p, (c) O 1s of NiFe-OH-F and NiFe-OH, respectively; (d) F 1s spectrum in NiFe-OH-F.

Fig. 3. (a) LSV curves for various samples and (b) Nyquist plots of NiFe-OH and NiFe-OH-F; (c) Stability test for NiFe-OH-F; Inset in (c) is the SEM image and XRD pattern of post-HER NiFe-OH-F.