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

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ABSTRACT

The use of Ni-based oxides/hydroxides in the oxygen evolution reaction has been extensively reported and fluoride precursors have frequently been used in their synthesis. However, there have been no studies of the effect of fluoride in Ni-based oxides/hydroxides on the hydrogen evolution reaction (HER) as these materials are generally considered inactive for HER. Recently the HER activities of Ni-based oxides/hydroxides have been improved by doping with anions ($-P$, $-S$, and $-Se$). However, these compounds are chemically unstable during HER and can be converted into the corresponding oxides/hydroxides. In this paper we discovered an interesting phenomenon: the NiFe hydroxide can be turned into an active HER material by incorporating fluoride into it. In 1 M KOH, a significant shift of ~91 mV was observed in the HER overpotential at $-10\ \text{mA/cm}^2$ due to the enhanced charge transfer ability triggered by fluoride. This discovery provides a new approach to turning normally inactive materials, whose catalytic activity is hindered by low intrinsic conductivity, into electrocatalysts, and will lead to the discovery of new catalysts.

1. Introduction

With its high energy density and environmentally friendly nature, hydrogen is seen as a promising fuel in the light of the problems of environmental pollution and fossil fuel depletion in our age. In this context, hydrogen generation by water electrolysis has been investigated extensively as a next-generation approach to energy conversion [1]. The scientific community has devoted much effort to developing efficient, stable, and earth-abundant electrocatalysts to replace the high cost and scarce electrocatalyst Pt, with its superior hydrogen evolution reaction (HER) activity, and a series of exciting advances have been made 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 the literature as attractive HER catalysts [2–4]. These compounds are usually thought of as stable for HER, with chemical instability only being exhibited under oxidative conditions [5]. However, it has recently been reported that these materials are chemically unstable and can be converted into the corresponding amorphous oxides/hydroxides during the HER process [6–8]. This prompted us to explore nickel-based oxides/hydroxides as more stable HER electrocatalysts.

Ni-based oxides/hydroxides are very stable, but few applications involving HER have been reported. This is because Ni-based oxides/ hydroxides are generally considered as HER inactive materials owing to their inappropriate hydrogen atom adsorption energy, i.e. excessively strong H adsorption on O but extremely weak H adsorption on Ni. Considering the Volmer step in alkaline conditions, the ideal HER electrocatalyst should have a relatively high adsorption energy for H and good hydroxyl (OH) desorption properties [3]. Conversely, one of the most active oxygen evolution electrocatalysts, NiFe hydroxide, can effectively adsorb OH species and accordingly has extremely weak H adsorption [3,9].

Nonetheless, Wang et al. have improved the HER activity of NiFe oxides by Li^+ insertion and extraction to detach 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 large-scale synthesis and industrial applications. Developing simpler, low-cost, and scalable methods is therefore of great importance for practical hydrogen generation.

In this work we fabricated NiFe hydroxide nanosheets incorporating fluoride (NiFe-OH-F) and NiFe hydroxide (NiFe-OH) nanosheets on nickel foam by a simple one-step method. We then investigated the effects of fluoride incorporation on HER in alkaline media.

2. Material and methods

2.1. Materials and chemicals

Ni foam (thickness: 1.6 mm; bulk density: 0.45 g/cm³), NH₄F, and urea were provided by Sigma Aldrich. Ni(NO₃)₂·6H₂O and Fe (NO₃)₃·9H₂O were purchased from Fisher Scientific. The water used in this work was purified with the 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 sonication in 6 M HCl, ethanol, and Milli-Q water for 10 min each. To synthesise NiFe-OH-F, 4 mmol NH₄F, 10 mmol urea, and 4 mmol total amount of Ni(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in 40 mL water with a Fe/Ni ratio of 7:3. The solution and the cleaned Ni foam were then transferred into a 50 mL Teflon-lined stainless steel autoclave, sealed and kept at 120 °C for 6 h with a heating rate of 3 °C min⁻¹. The resulting samples were then washed with water under sonication and dried in a vacuum oven at 60 °C for 6 h. NiFe-OH was synthesized using the same procedure but without adding NH₄F.

2.3. Characterization

Crystallographic information was obtained by XRD (Siemens D500 X-ray diffractometer) using Cu Kα radiation. The morphology and structure of the materials were studied using a FEI Quanta 250 field-emission scanning electron microscope (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 1253.7 eV radiation to determine the composition of the materials.

2.4. Electrochemical measurements

All electrochemical measurements were conducted using a Gamry Interface 1000 potentiostat in a three-electrode setup using the electrocatalyst 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). Long-term stability tests were carried out using chronopotentiometric measurements. The loading masses of NiFe-OH-F and NiFe-OH on nickel foam are about 3.3 mg/cm² and 2.1 mg/cm², respectively. The current densities were calculated using the geometrical 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) were fabricated on 3D Ni foam frameworks by a one-step hydrothermal method at 120 °C. The inset side-view image in Fig. 1b shows the thickness of the NiFe-OH-F layer, which is about 2 μm. The lattice spacing of 0.27 nm in the inset HR-STEM image in Fig. 1c indexes to the (101) plane of NiFe hydroxide [14]. XRD measurements were conducted on NiFe-OH and NiFe-OH-F to confirm their crystalline nature. Except for the three peaks of the Ni substrate, all the other peaks in Fig. 1d can be indexed to 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 affect the original structure of NiFe-OH. Energy-dispersive X-ray (EDX) spectroscopy was then employed to characterize 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 mapping images suggest the homogeneous distribution of these elements. The iridium (Ir) peaks in the inset EDX spectra originate from

the Ir layer coated on the sample surface before SEM characterization. The molar ratio of Ni: Fe: F is about 8.0: 3.4: 5.2, and was estimated by inductively coupled plasma emission spectrometry (ICP-MS) and EDX.

XPS was used to further probe the chemical composition and the effect of incorporating F⁻ in NiFe hydroxide. All the XPS high-resolution spectra were calibrated using C1s. The high-resolution Ni 2p₃/₂ spectra (Fig. 2a) of NiFe-OH-F and NiFe-OH were fitted by two peaks corresponding to Ni²⁺ (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 2p₃/₂ peaks in NiFe-OH-F compared to NiFe-OH were generated by incorporation of F⁻. The positive binding energy shifts of 0.35 eV for Ni²⁺ and 0.55 eV for 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 713.5 eV are indexed to Fe 2p₃/₂ [20]. As both NiFe-OH-F and NiFe-OH show a hydroxide structure, we also analyzed the O 1s spectrum. The high-intensity peaks of O 1s at 530.92 to 530.97 eV can be assigned to –OH groups [18,21]. This detailed analysis therefore further confirmed the hydroxide nature of NiFe-OH-F and NiFe-OH. Moreover, the XPS F 1s spectrum in Fig. 2d demonstrates the successful incorporation of F⁻ into NiFe-OH-F [22]. Overall, the XPS analysis and the above XRD characterization of NiFe-OH-F are consistent with our previous report [13].

The electrocatalytic performance of NiFe-OH-F, NiFe-OH, and Ni foam toward HER was evaluated in argon-saturated 1 M KOH solution using a three-electrode system. Note that a graphite rod was used as the counter-electrode rather than the conventional Pt to avoid the oxidation-dissolution of Pt influencing the HER activity of the samples [23]. Fig. 3a shows the iR-corrected polarization curves of various electrodes at a scan rate of 5 mV/s. Compared to NiFe-OH, NiFe-OH-F needs a ∼91 mV lower overpotential of −206 mV to drive a typical current density of −10 mA/cm². This performance is comparable to the recently reported non-noble metal-based HER compounds, including exfoliated NiFe hydroxide/defective graphene ($\eta_{\text{-10 mA/cm}^2}$ = −210 mV) [24], CoSe/NiFe hydroxide/Ni foam ($\eta_{\text{-10 mA/cm}^2}$ = −260 mV) [25], Janus Co/CoP ($\eta_{\text{-10 mA/cm}^2}$ = −193 mV) [26], MA-MoS₂ ($\eta_{\text{-0.9 mA/cm}^2}$ = −200 mV) [27], NiSe₂/CNT ($\eta_{\text{-35.6 mA/cm}^2}$ = −250 mV) [28], and NiCo₂S₄ NWS/Ni foam ($\eta_{\text{-10 mA/cm}^2}$ = −210 mV) [29]. Ni foam shows poor HER activity and the performance of NiFe-OH is actually slightly worse than Ni foam for current densities < 20 mA/cm², indicating that the active sites on the Ni foam surface might be partially blocked by the NiFe-OH layer.

To gain more insight into the HER reaction kinetics, 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). The 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 the 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 resistances. We can observe that the R_Ω of NiFe-OH-F is smaller than that of NiFe-OH, indicating that the NiFe-OH-F electrode has higher electrical conductivity than the NiFe-OH electrode. In summary, we can conclude that the incorporation of F⁻ enhances charge transfer during HER and enhances the conductivity of NiFe-OH-F. These beneficial effects of fluoride incorporation result in 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/cm². The electrode maintained a steady potential for over 12 h (Fig. 3c) and exhibited good stability. When the stability measurement was complete, the sample was again characterized by SEM and XRD. As shown in the inset images in Fig. 3c, both the morphology and typical XRD peaks of the post-HER sample were the same as for the original sample. It can be deduced that the NiFe-OH-F electrode has good durability for HER under alkaline conditions.