Efficient Electrocatalysis of Overall Water Splitting by Ultrasmall $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ Coupled Ni_3S_2 Nanosheet Arrays

Yuanyuan Wu,^a Yipu Liu,^a Guo-Dong Li,^a Xu Zou,^a Xinran Lian,^a Dejun Wang,^{a,d} Lei Sun,^c Tewodros
Asefa,^{*,b} and Xiaoxin Zou^{*,a}

^a *State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China*

^b *Department of Chemistry and Chemical Biology & Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, United States*

^c *State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, P. R. China*

^d *Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China*

*Corresponding author. E-mail: xxzou@jlu.edu.cn (X. Zou); tasefa@rci.rutgers.edu (T. Asefa)

Abstract

The overall water splitting into hydrogen and oxygen is one of the most promising ways to store intermittent solar and wind energy in the form of chemical fuels. However, this process is quite thermodynamically uphill, and thus needs to be mediated simultaneously by efficient hydrogen evolving and oxygen evolving catalysts to get any feasible output from it. Herein, we report the synthesis of such a catalyst comprising ultrasmall $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ -decorated Ni_3S_2 nanosheet arrays supported on nickel foam (NF) *via* a partial cation exchange reaction between NF-supported Ni_3S_2 nanosheet arrays and cobalt(II) ions. We show that the as-prepared material, denoted as $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$, can serve as a self-standing, noble metal-free, highly active and stable, bifunctional electrocatalyst for the two half reactions involved in the overall water splitting: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). Furthermore, we demonstrate that a high-performance electrolyzer for the overall water splitting reaction can be assembled by using $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ as the electrocatalyst at both the cathode and the anode sides of the electrolyzer. This electrolyzer delivers water-splitting current densities of 10 and 100 mA/cm^2 at applied potentials of 1.53 and 1.80 V, respectively, with remarkable stability for >200 h in both cases. The electrolyzer's performance is much better than the performances of electrolyzers assembled from many types of other bifunctional electrocatalysts as catalyst couple. Moreover, the overall performance of the electrolyzer is comparable with the performances of electrolyzers containing two different, benchmark, monofunctional HER and OER electrocatalyst couple (*i.e.*, Pt/C-IrO₂).

Keywords: Water splitting · Nickel sulfide · Cobalt sulfide · Electrocatalysis · Composite material

1. Introduction

Due to the intermittent nature of wind and solar energy, the hunt has long been on to find suitable energy generating and storage methods that may allow the utilization of the massive amounts of energy given off by these two renewable energy sources. One of the most promising methods to do so is by electrolyzing water (or the water splitting reaction) using these two energy sources, and producing the green energy carrier hydrogen, along with oxygen as a by-product.¹⁻⁴ However, splitting water is thermodynamically an unfavorable and energetically an uphill process. The reaction is further complicated by the high intrinsic activation barriers inherent to the two half reactions involved in water splitting, *i.e.*, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER).⁵⁻⁷ In order to improve the efficiency of the electrocatalytic water splitting reaction, efficient hydrogen evolution and oxygen evolution electrocatalysts, preferably based on earth-abundant elements, are thus critically needed.

Thanks to past efforts by researchers working in this area, there are now a large number of such noble metal-free materials that are electrocatalytically active for either HER⁸⁻¹⁰ or OER.¹¹⁻¹⁴ By comparison, bifunctional electrocatalysts that can operate effectively for both HER and OER, which are more preferable for electrocatalysis of overall water splitting, are less common.¹⁵⁻³³ Such bifunctional electrocatalysts are highly desired because: (i) they can be more easily integrated into a single water splitting device, (ii) their catalytic performances for HER and OER can be optimized simultaneously under similar conditions, and (iii) they can significantly reduce the cost of water splitting electrolyzers since they eliminate the need for different parameters and reaction conditions, which have to otherwise be adjusted separately to optimize the HER and OER catalysts' activities in a given electrolyzer.

Up to now, some cobalt, nickel, iron or molybdenum-based materials have been found to have electrocatalytic activities for both HER and OER.¹⁵⁻³³ They include mainly metal (hydro)oxides (*e.g.*, Ni-Fe-LDH),¹⁵⁻²⁰ nitrides (*e.g.*, Ni₃FeN),^{21,22} phosphides (*e.g.*, NiP),²³⁻²⁸ selenides (*e.g.*, NiSe),^{29,30} etc. However, when coupled within electrolyzers, most of them give much lower electrocatalytic output in the overall water splitting reaction than the noble-metal-based, benchmark Pt and IrO₂-based catalytic

couples do. Ideally catalytic couples that can generate a water-splitting current density of 10 mA/cm² or more at a small potential of ~1.5 V are required,¹⁹ something that many of the previously reported non-noble metal-based materials cannot do. Moreover, many of them lack long-term stability during the overall water splitting reaction.

We have recently shown that a nickel foam (NF)-supported Ni₃S₂ nanosheet array (Ni₃S₂/NF) can serve as a very promising bifunctional electrocatalyst for both HER and OER.³³ Moreover, the material has an intrinsically metallic/conductive property, and can thus operate as a self-standing electrode (without binders or underlying substrates) while remaining stable during electrocatalysis. However, its electrocatalytic activity toward the overall water splitting reaction—giving an output of 10 mA/cm² at a potential of ~1.7 V while serving as electrocatalyst simultaneously at both the anode and the cathode sides of an electrolyzer—is still lower than what is ideally needed. Thus, we have explored suitable chemical modification strategies that can make this otherwise interesting electrocatalyst to have a higher catalytic activity for an overall water splitting reaction, or an activity that rivals that of the benchmark Pt-IrO₂ catalytic couple.

Herein we report, for the first time, a material that meets this goal, or an efficient composite bifunctional HER and OER nanoelectrocatalyst comprising NF-supported Ni₃S₂ nanosheet arrays containing ultrasmall Ni_xCo_{3-x}S₄ nanoparticles. The synthesis of this material, which is named Ni_xCo_{3-x}S₄/Ni₃S₂/NF, is achieved *via* a facile, two-step synthetic procedure consisting of the synthesis of Ni₃S₂/NF, followed by controlled, partial cation exchange reaction between the Ni₃S₂/NF and Co(II) ions. Interestingly, when used as electrocatalyst at both electrodes to catalyze HER and OER in an alkaline electrolyzer, this nanostructured electrocatalyst gives a water-splitting current density of 10 mA/cm² at an applied potential of as low as 1.53 V while also showing an excellent stability for, at least, 200 h. The activity of this electrolyzer, which contains Ni_xCo_{3-x}S₄/Ni₃S₂/NF as electrocatalyst at both electrodes, is *ca.* 7.6 times higher than that of the corresponding one containing Ni₃S₂/NF.

2. Experimental Section

2.1. Synthesis of $\text{Ni}_3\text{S}_2/\text{NF}$

The synthesis of $\text{Ni}_3\text{S}_2/\text{NF}$ was carried out according to our previously reported method.³³ Typically, a piece of NF (1 cm x 3 cm) was immersed into a 25 mL Teflon-lined stainless autoclave containing 10 mL of aqueous thiourea solution (1.445 mmol/L). The autoclave was then sealed and kept at 150 °C for 5 h. The material was taken out and washed with ethanol three times and dried in vacuum at room temperature, giving the $\text{Ni}_3\text{S}_2/\text{NF}$ material as product.

2.2. Synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$

$\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ was synthesized *via* a facile cation exchange reaction between $\text{Ni}_3\text{S}_2/\text{NF}$ and Co(II) ions. In a typical synthesis, a piece of $\text{Ni}_3\text{S}_2/\text{NF}$ was immersed into a mixture solution containing cobaltous acetate tetrahydrate (0.622 g) and ethylene glycol (30 mL) in a 50 mL Teflon-lined stainless autoclave. The autoclave was then sealed and maintained at 200 °C for 12 h. The resulting material was washed with water and ethanol several times and dried at room temperature, giving the $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ material.

2.3. Synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$

In a typical synthesis, a piece of $\text{Ni}_3\text{S}_2/\text{NF}$ was immersed into a solution containing cobaltous acetate tetrahydrate (0.622 g) and ethylene glycol (30 mL) in a 50 mL Teflon-lined stainless autoclave. The autoclave was then sealed and kept at 200 °C for 72 h. The material was taken out and washed with water and ethanol several times and dried at room temperature, giving the $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ material.

2.4. Electrochemical measurements

All electrochemical measurements were performed with a three-electrode system using a CH Instrument (Model 650E), in which $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ or $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ was used directly as the working electrode. A plastic cell with a diameter of 3 cm and a height of 5 cm was used as the

electrochemical cell. The working surface area of the electrode was maintained as 0.09 cm^2 , by sealing the rest of the electrode with a modified acrylate adhesive. The current densities are then all normalized with the electrodes' geometric surface areas. A Hg/HgO electrode and a carbon rod were used as reference and counter electrodes, respectively. The Hg/HgO reference electrode was calibrated according to the method published by Asefa and co-workers before.³⁹ 1 M KOH was used as the electrolyte during the electrocatalytic reactions. In order to fabricate the working electrodes of Pt/C, IrO₂ and RuO₂, they were drop-casted on Ni foam in such a way that their loading amount is 0.56 mg/cm^2 and the working electrode's surface area is 0.09 cm^2 , which are the same values as those of Ni_xCo_{3-x}S₄/Ni₃S₂/NF. This was followed by deposition of a conductive polymer binder (deposited from 0.3 % Nafion solution) over the films. A scanning rate of 0.1 mV/s was used for linear sweep voltammetry measurements. In order to get the Tafel plots, steady-state current density as a function of potential was measured with a dwell time of 5 min. Experimental details on how the effective electrode surface area, electrochemical impedance, and Faradaic yields of the electrocatalysts are determined are provided in SI.

3. Results and Discussion

To synthesize the efficient bifunctional electrocatalyst Ni_xCo_{3-x}S₄/Ni₃S₂/NF, a simple controlled cation exchange reaction between Ni₃S₂/NF and Co(II) ions was conducted (see Figure 1 and Experimental section for details). Although cation exchange synthetic methods have been proven to be versatile in producing various sulfide nanomaterials,³⁴⁻³⁶ there has been no study involving a cation exchange reaction between nanostructured Ni₃S₂ and any cations, especially for the purpose of making efficient electrocatalysts. Here, first Ni₃S₂/NF with exposed {210} facets is synthesized according to our previously reported method,³³ where its detailed characterization results can also be found. Additionally, its SEM images are provided in Figure S1 in Supporting Information (SI) of this report. By using two different reaction times for the cation exchange reaction, two cation-exchanged products are synthesized. By using a reaction time of 12 h, a partially cation-exchanged product, denoted as

$\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$, which has some underlying Ni_3S_2 and which shows the highest electrocatalytic activity (see below), is obtained. However, upon using a reaction time of 72 h, a completely cation-exchanged product, which is named as $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and which has less catalytic activity, is obtained.

The typical scanning electron microscopy (SEM) images of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ (Figures 2A and 2B) reveal that the material has a three-dimensional macroporous foam-like structure, and its surface is covered uniformly with a mass of vertically oriented nanosheets with a thickness of *ca.* 20 nm. The presence of vertically grown nanosheets is further supported by transmission electron microscopy (TEM, Figure 2C). These results suggest that, after the controlled cation exchange reaction between $\text{Ni}_3\text{S}_2/\text{NF}$ and Co(II) ions, the product $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ maintains the morphology of the underlying $\text{Ni}_3\text{S}_2/\text{NF}$ (Figure S1 in SI). A closer observation of the nanosheets of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ by high-resolution TEM (HRTEM) reveals that the nanosheets contain a lot of monodispersed nanoparticles with 3-5 nm in size on them (Figure 2D). Additional HRTEM images (Figures 2E and 2F) further reveal that these nanoparticles have two sets of lattice fringes with the same interplanar spacing of 0.235 nm corresponding to the (400) crystallographic planes of cubic $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ phase. The angle between them is found to be 90° , which is in good agreement with the theoretical value for such a structure. These results also imply that the exposed facet in the $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ nanoparticles is {001}. The selected-area electron diffraction (SAED) pattern (Figure 2G) reveals a set of diffraction rings that are characteristic of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ nanocrystals, confirming the presence of such nanocrystals on the nanosheets of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. Elemental mapping of the material (Figure S2 in SI) shows that all the elements that are expected to be present in the material, *i.e.*, Ni, Co and S, are there and are homogeneously distributed at nanoscale over the entire nanosheets of the material. When combined with the results obtained from HRTEM image in Figure 2D, the elemental mapping result further provides a strong evidence for the existence of uniformly distributed $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ nanocrystals on the Ni_3S_2 nanosheets of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. On the other hand, results obtained by X-ray photoelectron spectroscopy (XPS, Figure S3 in SI) suggest that there is no strong electronic interaction between $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ and Ni_3S_2 .

The powder X-ray diffraction (XRD) pattern of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ (Figure S4 in SI) shows that the material contains crystalline Ni_3S_2 and metallic nickel. The presence of crystalline Ni_3S_2 in $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is also confirmed by additional TEM images (Figure S5 in SI). The XRD peaks of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ in the XRD pattern is not quite observable possibly because of their ultrasmall size as well as their low density in the material, causing them to barely able to diffract in XRD. However, the transformation of $\text{Ni}_3\text{S}_2/\text{NF}$ to $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ by the cation exchange reaction is confirmed by Raman spectroscopy (Figure 2H). The Raman spectra can be divided into two parts: a spectrum below 450 cm^{-1} and a spectrum above 450 cm^{-1} . In the Raman spectrum of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$, a set of weak Raman bands in wavenumber region below 450 cm^{-1} that can be attributed to Ni_3S_2 and a set of Raman bands in the wavenumber region above 450 cm^{-1} that can be ascribed to $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ are observed.^{37,38} This result clearly demonstrates that the as-obtained material contains $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ and Ni_3S_2 . On the other hand, Raman bands related to Ni_3S_2 are not observed in the Raman spectrum of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$, indicating the complete conversion of $\text{Ni}_3\text{S}_2/\text{NF}$ to $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ in this particular material. Additionally, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ (the material that contains no underlying Ni_3S_2) is characterized by various analytical methods (Figure S6 in SI), including energy dispersive X-ray spectroscopy (EDS), SEM, HRTEM and STEM imaging, and elemental mapping. The results suggest that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ is composed of NF-supported $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ nanosheet arrays with a similar morphology as the original Ni_3S_2 and contains a Ni-to-Co atomic ratio of 1.6 : 100.

The electrocatalytic activity of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ for HER and OER was studied using a typical three-electrode electrochemical cell in 1 M KOH solution, in which $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ was directly used as the working electrode (see details in Experimental Section). For comparative purposes, the electrocatalytic activities of $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ were also studied under the same conditions. In addition, the electrocatalytic activity of 20 wt. % Pt/C, a benchmark noble-metal based electrocatalyst for HER, and the electrocatalytic activities of IrO_2 and RuO_2 , benchmark catalysts for OER, were also measured. As commercial Pt/C, IrO_2 and RuO_2 come in powdered forms, their working electrodes were prepared by dispersing them in isopropanol, then drop-casting their dispersions onto NF,

and finally coating the dried samples with a conductive polymer binder (Nafion[®]). Although this procedure of working electrode preparation for powdered electrocatalysts is widely used, it is not an ideal method as it inevitably makes some of the catalytic active sites (*e.g.*, Pt/C) to be buried, and thus experience insufficient electron transport processes from the current collector (*i.e.*, NF). In contrast to this, the self-standing, three-dimensional, integrated electrode materials (*i.e.*, Ni_xCo_{3-x}S₄/Ni₃S₂/NF and Ni_xCo_{3-x}S₄/NF) developed here have well-exposed catalytic active sites and thus experience facile electron transfer processes. In other words, the kind of self-standing electrodes developed here have apparent advantages over powdered materials for electrocatalysis, besides, of course, being more convenient to use.

Figure 3A shows the comparison of the electrocatalytic activity of Ni₃S₂/NF, Ni_xCo_{3-x}S₄/NF, Ni_xCo_{3-x}S₄/Ni₃S₂/NF and 20 wt. % Pt/C toward HER. As expected, Pt/C is found to be the most active electrocatalyst for HER, especially at small current densities (<300 mA/cm²). But, Ni₃S₂/NF, Ni_xCo_{3-x}S₄/NF and Ni_xCo_{3-x}S₄/Ni₃S₂/NF also exhibit good electrocatalytic activity for HER, with their catalytic activity increasing in the order of Ni₃S₂/NF < Ni_xCo_{3-x}S₄/NF < Ni_xCo_{3-x}S₄/Ni₃S₂/NF. For instance, at -0.5 V *vs.* RHE, the current densities (which measure electrocatalytic activity) of Ni₃S₂/NF, Ni_xCo_{3-x}S₄/NF and Ni_xCo_{3-x}S₄/Ni₃S₂/NF are 122, 271 and 719 mA/cm², respectively. Thus, the electrocatalytic activity of Ni_xCo_{3-x}S₄/Ni₃S₂/NF toward HER can be said to be ~6 times higher than that of Ni₃S₂/NF. This result shows that the introduction of Ni_xCo_{3-x}S₄ nanoparticles on NF-supported Ni₃S₂ nanosheets by cation exchange reaction improves the catalytic activity of the latter toward HER. The Tafel slopes of Ni₃S₂/NF, Ni_xCo_{3-x}S₄/NF and Ni_xCo_{3-x}S₄/Ni₃S₂/NF are found to be 188, 156 and 107 mV/decade, respectively (Figure S7 in SI). This also suggests that Ni_xCo_{3-x}S₄/Ni₃S₂/NF has a better electrocatalytic activity toward HER than the former two. Furthermore, Ni_xCo_{3-x}S₄/Ni₃S₂/NF produces current densities of 10, 100, 200 and 500 mA/cm² at overpotentials of 136, 258, 318 and 432 mV, respectively. These values make it among the most efficient non-precious electrocatalysts for HER in basic media.⁸⁻¹⁰

In Figure 3B the amount of hydrogen evolved experimentally from a 140 min-long electrocatalytic HER in the presence of Ni_xCo_{3-x}S₄/Ni₃S₂/NF versus the amount expected from the reaction based on

theoretical considerations are compared (see details in SI). The result reveals that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ gives a stable rate of hydrogen evolution, with values very close to the one expected theoretically. This further implies that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ affords a Faradaic efficiency of $\sim 100\%$ in HER in basic media.

To evaluate the electrocatalytic stability of the material during HER, a multi-step chronoamperometric curve with $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is first obtained (Figure 3C). The result reveals that the current density remains quite stable at each potential or overpotential in the entire test range, from 50 mV to 550 mV with an increment of 50 mV. This means the material is highly stable during electrocatalysis of HER in a wide current density range ($0\text{--}900\text{ mA/cm}^2$). Furthermore, the result of current density versus time ($I\text{--}t$) recorded for $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ -catalyzed HER over longer reaction time (Figure 3D) shows once again that the material retains its electrocatalytic activity, besides its morphology (Figure S8 in SI), for at least 50 h. So, based on the above results, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ can be said to be not only an excellent but also a highly stable electrocatalyst for HER.

To try to determine the reasons that contribute to $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$'s excellent catalytic activity toward HER, the material as well as its corresponding control materials are further analyzed by electrochemical impedance spectroscopy (EIS), and their effective electrode surface areas are measured. Figure 3E shows the Nyquist plots for $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. Based on their fitting equivalent circuit model, the values of charge transfer resistance in these three materials are found to be 83.7, 32.7 and 26.1 Ω , respectively. This result indicates that the electron transfer process in HER over $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is much faster than those over $\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$. In addition, the effective electrode surface areas of these three materials are measured, and the values are compared with one another (Figure 3F). The effective electrode surface areas of $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ are found to be 187.5, 192.5 and 350.5 cm^2 , respectively (see the calculation in detail in SI). Comparison of the results, once again, indicates that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ has a better or larger electrocatalytically active area than the former two.

To further correlate the microstructures of the materials with their catalytic activities for HER, density functional theory (DFT) calculations are performed (see Figures S9-S13, Tables S1-S3 in SI,

and the accompanying detailed discussions in the SI section). The theoretical studies have allowed us to specifically determine as to: (i) where the hydrogen-evolution catalytic sites on the surfaces of Ni_3S_2 and Co_3S_4 are, (ii) what the influence of Ni-doping on the HER activity of Co_3S_4 is, and (iii) how the catalytic activity at the interface between Ni_3S_2 and Co_3S_4 fares with respect to the other parts of the materials.

To answer the first question, structural models of $(\bar{2}10)$ surface of Ni_3S_2 and (001) surface of Co_3S_4 are constructed, based on the experimental characterization results obtained earlier. Then, the adsorption free energy of H^* ($\Delta G(\text{H}^*)$) for some possible adsorption sites of H^* on the two surfaces are determined (Figures S8 and S9 in SI). The value of $\Delta G(\text{H}^*)$ of a given catalytic site serves as a good metric for the catalytic activity of the site for HER, where a site possessing a smaller $\Delta G(\text{H}^*)$ absolute value is generally expected to show a better activity.^{1a,c} The DFT calculation reveals that, in the case of both Ni_3S_2 and Co_3S_4 , the coordinatively unsaturated surface S site has a much smaller $\Delta G(\text{H}^*)$ value than the metal (Ni or Co) site, indicating that the S sites on both Ni_3S_2 and Co_3S_4 's surfaces should be more catalytically active for HER (Figures 4A and 4B). Furthermore, the calculation also indicates that the $\Delta G(\text{H}^*)$ value of a S site in Co_3S_4 (0.228 eV) is smaller than that of a S site in Ni_3S_2 (0.348 eV) (Tables S1 and S2 in SI). This result suggests that Co_3S_4 would possess a relatively higher intrinsic catalytic activity for HER than Ni_3S_2 would.

After determining the catalytic sites responsible for HER on Ni_3S_2 and Co_3S_4 , the effect of Ni-doping of Co_3S_4 on the catalytic activity of the material in HER is examined. Given that HER takes place only on the catalyst's surface, the Ni-substitution sites that might strongly influence the catalytic activity of Co_3S_4 in HER should be the Ni sites that are exposed either on the surface or bonded to the surface unsaturated S sites. Hence, three possible structural models of the Ni-doped Co_3S_4 surfaces (denoted as Ni1, Ni2 and Ni3) were constructed. Figures 4C-4E illustrate the most stable/active H^* adsorption configurations for the three models of Ni-doped Co_3S_4 surfaces. Comparison of the $\Delta G(\text{H}^*)$ values obtained for these three configurations show that the Ni-doping at Ni2 significantly enhances the catalytic activity of the adjacent S site in Co_3S_4 for HER, while the Ni-doping at Ni1 and Ni3 sites

slightly decreases the catalytic activity of the sites in comparison with those in pristine Co_3S_4 (Table S3 in SI). Even though the Ni-substitution in some cases compromise Co_3S_4 's catalytic activity for HER, all of the Ni-doped Co_3S_4 surfaces still exhibit better catalytic activity toward HER than the Ni_3S_2 surface. This result is also in good agreement with the experimental findings above, which has indicated that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ has significantly better electrocatalytic activity than $\text{Ni}_3\text{S}_2/\text{NF}$ for HER (Figure 3A).

Since our experimental results clearly show that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ has a large proportion of heterojunction interfaces between Ni_3S_2 and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ domains and that it exhibits a higher HER activity than $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_3\text{S}_2/\text{NF}$, it is important to examine the possible roles played by this interface with respect to $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$'s electrocatalytic activity. In order to simplify the problem, interface models for Ni_3S_2 and Co_3S_4 are constructed, while ignoring the effect of Ni-substitution on the materials' electrocatalytic activity. Figure 4F presents the optimized H^* adsorption configuration at the interface between Ni_3S_2 and Co_3S_4 . The computed results reveal that the $\Delta G(\text{H}^*)$ value of 0.167 eV corresponding to the S site at the interface is much smaller than those of the active sites in Ni_3S_2 and Co_3S_4 (Figure 4G). This suggests that the former may have more efficient catalytic activity for HER.

The above experimental results and theoretical calculations indicate that the significantly higher catalytic performance toward HER exhibited by $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ compared with that by $\text{Ni}_3\text{S}_2/\text{NF}$ can be rationally interpreted as follows: (i) $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ is intrinsically a better electrocatalyst for HER than Ni_3S_2 , (ii) the heterojunction interfaces in $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ contain some highly catalytic active sites, and (iii) both Ni_3S_2 and Co_3S_4 possess metallic or conductive property, as revealed by the fact that their density of state (DOS) crossing the Fermi level (Figure 4H). These properties, together with the self-supported nature of the $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ material, thus make the catalytic active sites in this material to be readily accessible to the electrons coming from the electrode during the electrocatalysis or make this material a superefficient electrocatalyst.

Besides their electrocatalytic properties for HER, the electrocatalytic activity of $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ toward OER is investigated. As shown in Figure 5A, $\text{Ni}_3\text{S}_2/\text{NF}$,

$\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ all exhibit a considerable electrocatalytic activity for OER as well, with their activity following a trend of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF} > \text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF} > \text{Ni}_3\text{S}_2/\text{NF}$. For example, at 1.8 V, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_3\text{S}_2/\text{NF}$, give current densities of 752, 437 and 321 mA/cm^2 , respectively. This means, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ shows 2.3 times higher catalytic activity than $\text{Ni}_3\text{S}_2/\text{NF}$ for OER. Further experiments reveal that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ gives current densities of 10, 100, 200 and 500 mA/cm^2 at small overpotentials of 160, 320, 370 and 475 mV, respectively, in the OER. Not surprisingly, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ also gives a smaller (or a better) Tafel slope (95 mV/decade) compared with $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ (109 mV/decade) and $\text{Ni}_3\text{S}_2/\text{NF}$ (124 mV/decade) (Figure 5B). Finally, it is worth adding here that all the three materials ($\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$) afford much better catalytic activity for OER than NF-supported IrO_2 and RuO_2 (or the highly active, benchmark noble metal-based OER electrocatalysts) at the same catalyst loading.

During the OER, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is found to give $\sim 100\%$ Faradaic yield as well, based on the amount of O_2 determined experimentally and expected theoretically (Figure 5C). The material is also highly stable in OER, retaining its activity and morphology even after 30 hour-long electrocatalytic OER (Figures 5D and S14). The above results overall demonstrate that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is an excellent electrocatalyst for OER. In fact, based on these results the material can be said to be one of the most efficient, non-noble metal electrocatalysts for OER, and better than several recently reported, highly efficient OER electrocatalysts.¹¹⁻¹⁴ For example, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ can give a current density of 10 mA/cm^2 at an overpotential of ~ 160 mV, whereas an Fe-Co-W hydroxide catalyst, the best OER electrocatalyst recently reported by Zhang *et al.*,¹² can produce the same current density only at a higher overpotential of ~ 190 mV. In addition, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ exhibits better catalytic activity than some highly active nonprecious Ni-Fe (hydro)oxide-based oxygen-evolution electrocatalysts recently reported in the literature (see Table S5, SI).

It is worth noting here that the $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is slightly oxidized (or undergoes slight desulfurization) during the electrocatalytic OER, without losing its activity and structural integrity (see XPS and TEM characterization results in Figures S15-17, SI). The combined results suggest that

ultrasmall $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ nanoparticles in the composite material are totally transformed into hydroxides during OER, but the underlying crystalline Ni_3S_2 nanosheets remains unchanged. The *in situ* generated surface hydroxides and oxyhydroxides on the catalyst are most likely the actual catalytic active sites on it for OER, because such surface hydroxides and oxyhydroxides are widely reported to be the active catalytic species for OER in several non-(hydro)oxide-based oxygen-evolving electrocatalysts.^{21,23,24,29} Nevertheless, even though the formation of a small amount of metal hydroxides on the material may not be avoided, the catalytic activity of the material reported herein is much better than that of relevant, intentionally prepared Ni- and Co-containing (hydro)oxide catalysts, which generally afford a current density of 10 mA/cm^2 only at much higher overpotential of >300 mV (Table S4 in SI). Thus, the oxidation alone does not seem to fully account for $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$'s better catalytic activity compared with many Ni-Co oxide and hydroxide catalysts. This means, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$'s efficient catalytic activity can only be explained by its overall composition. The low electrical conductivity of Ni-Co (hydro)oxide catalysts is one of their major reasons behind their intrinsically low electrocatalytic activity. On the other hand, the higher conductivity of the underlying chalcogenide of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ may be, at least, partly responsible for its better catalytic activity. In other words, the conductivity of the underlying chalcogenide of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ can facilitate the accessibility of its surface active sites during OER, albeit the material is slightly oxidized.

Given $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$'s remarkable electrocatalytic activity toward both HER and OER, an electrolyzer, whose anode and cathode both consist of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$, is assembled, and its electrochemical output is evaluated. This electrolyzer affords current densities of 10 and 100 mA/cm^2 at 1.53 and 1.80 V, respectively (Figure 6A). More importantly, this electrolyzer can retain its catalytic activity at both current densities for >200 h (Figure 6B), demonstrating the stability of the material as electrocatalyst on both electrodes simultaneously. On the other hand, the electrolyzers based exclusively on $\text{Ni}_3\text{S}_2/\text{NF}$ or $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ electrocatalysts give much lower water-splitting current densities of 13.2 and 25.2 mA/cm^2 at 1.80 V, respectively (Figure 6A). This means, the catalytic output of the electrolyzer assembled with $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is about 7.6 and 4.0 times higher than the catalytic

output of the electrolyzers based on $\text{Ni}_3\text{S}_2/\text{NF}$ or $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$, respectively. Furthermore, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is also found to be a much better electrocatalyst than metallic Ni, a material known to be a good benchmark electrocatalyst for alkaline electrolyzers. More specifically, the catalytic output of the electrolyzer assembled with $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ is *ca.* 13.2 times higher than that of the electrolyzer containing exclusively Ni foam at its cathode and anode (Figure 6). It is worth adding here that $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ shows better electrocatalytic performances than most of previously reported bifunctional electrocatalysts for overall water splitting as well (see Table S6, SI).¹⁵⁻³³

4. Conclusions

In conclusion, nickel foam (NF)-supported Ni_3S_2 nanosheet arrays decorated with ultrasmall $\text{Ni}_x\text{Co}_{3-x}\text{S}_4$ have been synthesized *via* a partial cation exchange reaction between NF-supported Ni_3S_2 nanosheet arrays and Co(II) ions. The resulting material has been found to be a highly efficient and ultrastable electrocatalyst for both HER and OER. Furthermore, a high-performance electrolyzer that contains $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ as a bifunctional electrocatalyst at both anode and cathode has been demonstrated for the overall water splitting reaction. The results presented herein could help paving the way towards the development of high-efficiency water splitting electrochemical devices.

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Biosketches and Pictures of Authors

Yuanyuan Wu is currently a Ph.D. candidate under the supervision of Prof. Xiaoxin Zou at State Key Laboratory of Inorganic Synthesis and Preparative Chemistry in Jilin University. She obtained her bachelor degree from Anyang Normal University. Her present research interest focuses on the design of 3D nanomaterials for electrocatalytic overall water splitting.

Yipu Liu received her bachelor's degree in 2014 from Jilin University, Changchun, PR China. She is currently working toward her PhD degree at State Key Laboratory of Inorganic Synthesis and Preparative Chemistry at Jilin University. Her main research interest is the development of active electrocatalytic materials for water splitting.

Guo-Dong Li received his Ph. D. from Jilin University in 2001. He then worked as a visiting scholar at Hong Kong University of Science and Technology for nearly 2 years from 1999-2001. In 2001, he joined in Jilin University as a staff. He is currently a professor in the College of Chemistry at Jilin University. His research interests include chemical sensors, electrochemical and photoelectrochemical water splitting and lithium ion batteries.

Xu Zou is currently a M.S. under the supervision of Prof. Xiaoxin Zou at State Key Laboratory of Inorganic Synthesis and Preparative Chemistry in Jilin University. She obtained her bachelor's degree from Taiyuan Normal University. Her present research interests focus on the synthesis of large current-density water-splitting electrocatalysts.

Xinran Lian is currently a junior student in Department of Chemistry, School of Science at the University of Tokyo. She was an undergraduate student at Jilin University starting in 2014, and she is participating in Global Science Course Program at the University of Tokyo since 2016.

De-jun Wang received his Ph. D. from Jilin University in 1989. He then worked as a Postdoctoral researcher at Kyoto University for 1 year since 1989-1990. In 1992, he joined Jilin University as a staff. He is currently a Professor in the College of Chemistry, Jilin University. His research interests include surface photovoltage technology, photoelectric sensors, photoelectrochemical water splitting and solar cells.

Lei Sun received his Ph. D. from Jilin University in 2011. He then worked at Dalian Institute of Chemical Physics as a Postdoctoral Fellow for 2 years from 2011-2013. He is currently an associate professor of State Key Laboratory of Molecular Reaction Dynamics at Dalian Institute of Chemical Physics. His research interests include microporous materials for gas capture and photovoltaic application.

Tewodros (Teddy) Asefa is currently a Professor in the Department of Chemistry and Chemical Biology & the Department of Chemical and Biochemical Engineering at Rutgers University at New Brunswick, USA. He got his BSc from Addis Ababa University, MSc from the State University of New York at Buffalo, PhD from the University of Toronto. He then did a Post-doctoral stint for 2 years at McGill University. His group is involved in the development of synthetic methods to an array of functional nanomaterials and investigation of their potential applications in catalysis, electrocatalysis, cancer treatment and nanomedicine, solar-cells, and environmental remediation.

Xiaoxin Zou was awarded a PhD degree in Inorganic Chemistry from Jilin University (China) in June 2011. He then moved to the University of California, Riverside and Rutgers, The State University of New Jersey, as a Postdoctoral Scholar from July 2011 to October 2013. He is currently an Associate Professor in State Key Laboratory of Inorganic Synthesis and Preparative Chemistry at Jilin University. His research interests focus on the design and synthesis of noble metal-free, nanostructured and nanoporous materials for water splitting and renewable energy applications.

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Table of Contents (ToC) Figure

Figure Captions

Figure 1. Schematic illustration of the synthesis of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ by cation exchange reaction between $\text{Ni}_3\text{S}_2/\text{NF}$ and Co(II) ions. The two different materials are obtained simply by varying the reaction times. Note that NF is not shown in the illustration for clarity.

Figure 2. (A,B) SEM images, (C,D) TEM images, (E,F) HRTEM images, and (G) SAED pattern of $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. (H) Raman spectra of $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$.

Figure 3. (A) Steady-state current density as a function of applied potential during HER in 1 M KOH solution over NF, $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ and Pt/C (20 wt %). (B) Electrocatalytic efficiency of hydrogen evolution over $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ at a current density of 25 mA/cm^2 for 140 min. (C) Multi-step chronoamperometric curves of HER over $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ in 1 M KOH solution. The overpotential starts at 50 mV and ends at 550 mV with an increment of 50 mV every 500 s. (D) Current density versus time (I - t) curve obtained for $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ at an overpotential of 136 mV over 50 hour-long electrocatalytic HER. (E) Electrochemical impedance spectroscopy (EIS) Nyquist plots of $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. The inset of (E) shows an electrical equivalent circuit model, in which CPE , R_{ct} , and R_s stand for constant phase angle element, charge transfer resistance and series resistance, respectively. (F) Plots of the difference in current density (J) between the anodic and cathodic sweeps ($J_{\text{anodic}} - J_{\text{cathodic}}$) at 0.15 V vs. RHE against the scan rate is plotted. The slope of the fitted line on the data points is then used to determine the double-layer capacitance (C_{dl}), and finally to estimate the electrochemical surface area (ECSA), of $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. Note that the current density is normalized with the geometric surface area of the electrode in each case.

Figure 4. (A-F) The most active adsorption sites of H^* on the Ni_3S_2 , the Co_3S_4 and the Ni-doped Co_3S_4 surfaces with three different Ni-substitution sites, and at the interface between Ni_3S_2 and Co_3S_4 . (G) The

calculated free-energy diagram of HER at equilibrium potential for the most catalytically active sites shown in (A-F). (H) Computed density of states (DOS) of Co_3S_4 and Ni_3S_2 . The Fermi level is set at 0 eV.

Figure 5. (A) Steady-state current density as a function of applied potential during OER in 1 M KOH solution over NF, $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$, IrO_2 and RuO_2 . (B) Tafel plots for OER over $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ and $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$. (C) Electrocatalytic efficiency of oxygen evolution over $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ at current densities of 10 and 30 mA/cm^2 . (D) Current density versus time (I - t) curve obtained with $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ at an overpotential of 160 mV over 30 hour-long electrocatalytic OER. The current density is normalized with the electrode's geometric surface area.

Figure 6. (A) Steady-state current density as a function of applied potential in 1 M KOH at 25 °C for electrolyzers whose anode and cathode both contain $\text{Ni}_3\text{S}_2/\text{NF}$, $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{NF}$ or $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ as electrocatalysts. For comparison, steady-state current density as a function of applied potential in 1 M KOH at 25 °C for electrolyzers containing a NF-NF catalytic couple is also included. (B) I - t curves at applied potentials of 1.53 and 1.80 V for an electrolyzer whose anode and cathode both are constituted with $\text{Ni}_x\text{Co}_{3-x}\text{S}_4/\text{Ni}_3\text{S}_2/\text{NF}$ electrocatalyst. For comparison, I - t curve at an applied potential of 1.53 V for electrolyzers containing a NF-NF catalytic couple is also included. The current density is normalized with the electrode's geometric surface area in each case.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.