Iron disulfide (FeS₂) promises an earth-abundant, low-cost alternative to platinum group metals for the hydrogen evolution reaction (HER), but its performance is currently limited by reactivity of active sites and poor electrical conductivity. Here we employ Ketjenblack (KB) as a support to create an Fe-based electrocatalyst with high-electrical conductivity and maximal active sites. Moreover, a systematic study on the role of cobalt (Co) dopant was carried out. Electrochemical results show enhancements in HER activity of Co-doped FeS₂ [FeₓCo₁₋ₓS₂], atomic content of Fe (x = 0.98–0.32) in comparison to un-doped FeS₂ in acidic electrolyte (pH = 0). The overpotential necessary to drive a current density of 10 mA/cm² is −0.150 V and only decreases by 1 mV after 500 cycles of a durability test (cycling the potential between 0.0 and −0.15 V), indicating a long-term durability in acidic environment. This work suggests that FeₓCo₁₋ₓS₂ offers a viable approach to improve the activity and durability of transition metal-sulfide electrocatalysts.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0761704jes] All rights reserved.

Manuscript submitted November 18, 2016; revised manuscript received January 24, 2017. Published February 3, 2017.

Advanced materials for the electrochemical hydrogen evolution reaction (HER) are keys to the utilization and storage of renewable energy. Currently, the most effective electrocatalysts for the HER are platinum group metals (PGM). However, platinum is expensive and is unsuitable for large-scale use in HER cells. It remains a challenge to develop highly active catalysts based on materials that are abundant and at low cost. Researchers have been investigating the electrocatalytic properties of transition metal sulfides including, but not limited to, molybdenum disulfide (MoS₂), iron disulfide (FeS₂), cobalt disulfide (CoS₂), and nickel disulfide (NiS₂). Among these materials, two-dimensional layered MoS₂ received great attention. Moreover, MoS₂ is the first earth abundant compound to be studied as an HER catalyst, and its catalytic activity has been significantly boosted over the last decade, but beyond the scope of the present investigation.

Cubic FeS₂, pyrite, is the most common sulfide mineral; it has a NaCl-type cubic structure with the S₂− groups situated at the cube center and midpoints of the cube edges, and the low-spin Fe²⁺ atoms located at the corners and face centers. FeS₂ has many appealing properties such as a bandgap in the range of 0.8–0.95 eV, a large optical absorption coefficient (λ ≥ 700 nm, α ≥ 5 × 10⁵ cm⁻¹), high-carrier mobility (for single crystals), non-toxicity, and environmental compatibility. Therefore, FeS₂ has attracted particular interest as a material for energy-conversion applications such as electrodes for dye-sensitized solar cells (DSSCs), lithium-ion batteries (LIBs), thermal batteries, photocapacitors and electrocatalyst. More specifically, the overpotential required to attain 10 mA/cm² decreased by only 1 mV (from −0.150 to −0.151 V) after a cycling test.

Experimental

Material.—Regent grade iron acetate [Fe(C₂H₃O₂)₂], cobalt acetate [Co(C₂H₃O₂)₂], and sodium sulfide (Na₂S) were obtained from Sigma-Aldrich. Ethylene glycol and sulfuric acid were purchased from BDH Chemicals. A commercial carbon black Ketjenblack EC-300J (AkzoNobel) with surface area of 800 m²/g was used as a support.

Modification of carbon support.—A chemical oxidation method was used to modify the surface of the carbon support using nitric acid (21 and 10 N) as oxidant. In a typical procedure, the carbon (1 g) was refluxed in 50 mL of acid solution at 70 °C for 24 h. The functionalized carbon was filtered, washed with copious amount of deionized water, and dried at 110 °C. The acid-treated carbons are designated as KB-21N and KB-10N, in which 21N and 10N denote the concentration of nitric acid initially in the reflux solution. Pristine (non-functionalized) carbon is designated as KB-0N.

Synthesis of carbon-supported metal sulfide electrocatalysts (30 wt% FeₓCo₁₋ₓS₂/KB).—Supported metal sulfide electrocatalysts (FeₓCo₁₋ₓS₂/KB, x indicates atomic content of Fe and KB indicates pristine or modified carbon supports) with various Fe-to-Co ratios were prepared by wet-chemical sulfidization of metal precursors using hydrogen sulfide (H₂S). In the synthesis, Na₂S was slowly added to

---

Co1−xS2/KB, x indicates atomic content of Fe and KB indicates pristine or modified carbon supports.)
a stirred solution containing metal acetate precursors ([Fe(C₂H₃O₂)₂] and/or [Co(C₂H₃O₂)₂]), ethylene glycol, and carbon support with an intended metal sulfide loading of 30 wt%. Sulfurization was initiated by adding 0.5 M H₂SO₄ dropwise until the solution reached a pH of 6.0, and then the solution was heated to 165°C for 1 h. After cooling, the electrocatalyst was vacuum filtered, washed, and dried.

**Material characterization.**—The structure and composition of the carbon supports and metal sulfide electrocatalysts were characterized by inductively-coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Catalyst compositions were analyzed using a Perkin Elmer 8000 DV ICP-OES. Surface analysis of the carbon supports and metal sulfides was investigated using a FEI Verios 460L high-resolution field emission scanning electron microscope. TEM was carried out using a JEOL-2010F microscope equipped with a field emission electron gun source and operated at 200 kV. Raman spectra were collected on a Renishaw-1000 Raman spectrometer with an excitation wavelength of 514.5 nm. XRD analysis was performed using a Rigaku SmartLab X-ray diffractometer at a tube voltage of 40 kV and a current of 44 mA were used. XPS was performed on a SPECS XPS with PHOIBOS 150 analyzer using a Mg Kα X-ray source. The binding energy (BE) scale was calibrated using the C 1s (284.5 eV) signal. The XPSPEAK software Version 4.1 was used and Shirley baselines. Linearity of the BE scale of the detector was assured using four Au peaks, namely Au 4f7/2 (84.0 eV), Au 4d5/2 (284.5 eV), Au 4p3/2 (546.4 eV), and Au 4s (762.2 eV).

**Electrochemical characterization.**—The electrochemical properties of the carbon supports and electrocatalysts were characterized via cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. All electrochemical studies were performed in 0.5 M H₂SO₄ using a Bio-Logic potentiostat (VMP3), a Pt-mesh counter electrode, a saturated calomel reference electrode [SCE, 0.265 V vs. reversible hydrogen electrode (RHE)], and a glassy carbon working electrode (0.196 cm²). The catalyst ink was prepared by blending the electrocatalyst powder (4.2 mg) with 0.3 mL H₂O and 1.2 mL Nafion solution (0.25 wt%) in an ultrasonic bath. The required amount of the catalyst ink was deposited onto the glassy carbon disk using a micropipette. After drying, 7 μL of Nafion solution was placed on top of the disk to improve adhesion to the glassy carbon electrode. The series resistance (Rₛ) and charge-transfer resistance (Rₓ) of the electrocatalysts were characterized using electrochemical impedance spectroscopy (EIS) and fitting the results with a simplified Randles equivalent circuit. The AC impedance measurement was performed at −0.15 V using a frequency range of 10⁵ to 0.2 Hz with a perturbation voltage amplitude of 5 mV. All potentials reported are referred to the RHE.

**Stability test for electrocatalysts.**—The electrochemical stability and performance of metal sulfide electrocatalysts were examined by continuously cycling the potential at 50 mV/s between 0.0 and −0.15 V with periodic measurements of impedance and catalytic activity. The lower voltage limit (−0.15 V) was chosen since this is the potential at which the FeₓCo₁−ₓS₂ drives approximately a cathodic current density of 10 mA/cm², a value that roughly corresponds to a 10% solar-to-hydrogen conversion efficiency in a solar water splitting device. The potential cycling was carried out for 500 cycles in 0.5 M H₂SO₄. Nitrogen gas was bubbled into the electrolyte throughout the experiment. Under the potential cycling conditions, the deterioration of the catalysts was accelerated.

**Results and Discussion**

**Pristine and modified carbon supports.**—Figure S1 shows SEM images of the pristine and modified carbon supports resulting from the catalyst-ink process. The KB-0N and KB-10N carbons displayed surfaces containing pores with diameters > 100 nm. On the other hand, the KB-21N was less porous than the other two carbons and displayed significant agglomeration, as shown in Figure S1 c. The TEM images in Figure S2 indicate that refluxing KB in HNO₃ changed the average size of the carbon support; the average sizes were 32, 40, and 63 nm for KB-0N, KB-10N, and KB-21N, respectively. Moreno-Castilla and coworkers reported that carbon modification using concentrated HNO₃ significantly decreased the Brunauer-Emmett-Teller (BET) surface area and the porosity of the carbon black. It is anticipated that metal sulfides may not benefit from using KB-21N as support because of its reduced surface area. We further assess surface areas of the carbon supports using an electrochemical technique, as reported later in this section.

Figure S3 shows Raman spectra collected from the pristine and modified KB carbons. Results exhibited typical Raman spectra of carbon black, namely D (or A₁g, breathing mode) and G (or E₂g, vibrational mode) bands. The D band (1340–1352 cm⁻¹) is observed in sp² carbons containing impurities or other symmetry-breaking defects. The G band (1587–1599 cm⁻¹) is related to the vibrations in sp² carbon materials. All spectra were normalized with respect to the G-band intensity for comparison purposes. The intensity ratio I_D/I_G was used to estimate the defect density of carbon materials: the smaller ratio indicates fewer defects and therefore higher structural quality than a larger ratio. The Raman characteristics are summarized in Table SII. The pristine KB-0N and KB-10N carbons had I_D/I_G ratios ~1.20, which indicates low degree of crystallinity. Interestingly, the I_D/I_G
ratio of the functionalized KB using the highest concentration of nitric acid (21 N) decreased to 0.93. Nevertheless, the mechanism that caused the decrease in \( i_{p}/i_{g} \) ratio for KB-21N is unclear to date.

In order to compare the active surface area (ASA) of the carbon supports, we measured the capacitive current associated with electrochemical double-layer charging. This double-layer charging current \( (i) \) is proportional to both the scan rate \( (\nu) \) and ASA of the electrode:

\[
i \propto \nu \times ASA \tag{1}
\]

The capacitive currents for the pristine and HNO\(_3\)-modified KB carbons were measured as a function of scan rate (Figure 1a and S4). The ratio of the currents for the modified and pristine KB were taken as the relative area factor:

\[
\text{relative area factor} = \frac{i_{KB,HNO_3}}{i_{KB}} = \frac{ASA \text{ of modified KB}}{ASA \text{ of pristine KB}} \tag{2}
\]

The results indicated that the KB-10N carbon had 1.4 times higher ASA than pristine KB–0N. However, a decrease in ASA was observed after modification with concentrated (21 N) HNO\(_3\). The KB-0N and KB-10N carbons were selected for further electrochemical studies due to results of these preliminary characterizations.

**Characterization of metal sulfides electrocatalysts.**—Figure 2 shows XRD patterns of various Fe\(_{x}\)Co\(_{1-x}\)S\(_2/KB-0N\) electrocatalysts. XRD patterns may be divided into four groups: (1) Cubic FeS\(_2\) with particle sizes ranging from 22 to 30 nm were found at iron atomic contents from 1.00 to 0.50; (2) Electro-catalyst with an iron content of 0.32 showed diffraction peaks of multi-phases including metal sulfides [FeS\(_2\), and CoS\(_x\) (CoS, Co\(_9\)S\(_8\), and Co\(_3\)S\(_4\)) and metal sulfates (FeSO\(_4\) and/or CoSO\(_4\)]; (3) Further decrease in iron content \((x = 0.18)\) caused disappearance of FeS\(_2\) diffraction peaks; and (4) Fe\(_{0.00}\)Co\(_{1.00}\)S\(_2/KB-0N\) with \(x = 0\) and 0.09 only showed diffraction peaks of CoS\(_x\). An average particle size of 5 nm was calculated using Debye–Scherrer equation for Fe\(_{0.00}\)Co\(_{1.00}\)S\(_2/KB-0N\).

The surface morphology and elemental composition of the Fe\(_{x}\)Co\(_{1-x}\)S\(_2/KB-0N\) electrocatalysts were investigated using SEM and energy dispersive X-ray spectrometer (EDS). Fe\(_{1.00}\)Co\(_{0.00}\)S\(_2/KB-0N\) (Figure S5a) displayed a porous surface similar to KB-0N. Since no distinct difference in surface morphology was found, the area shown in Figure S5a was imaged using a concentric backscatter detector to locate the FeS\(_2\) particles. The bright spots shown in Figure S5b confirmed the presence of FeS\(_2\) particles. As indicated in Figure S5c, most of the FeS\(_2\) particles are covered by the carbon support. Moreover, the Fe\(_{1.00}\)Co\(_{0.00}\)S\(_2/KB-0N\) contained 17 and 13 wt% of Fe and S, respectively, as indicated by EDS analysis. The 17:13 weight ratio is greater than that expected from the FeS\(_2\) stoichiometry (14:16) which suggests possible formation of an amorphous impurity such as FeSO\(_4\). Figure S6 shows SEM images of the Fe\(_{0.00}\)Co\(_{1.00}\)S\(_2/KB-0N\). The particle sizes of CoS\(_x\) are in the sub-micrometer range. The apparent discrepancy in particle size between XRD (Figure 2) and SEM (Figure S6) results is most likely due to undesired fluorescence from cobalt-rich samples caused by Cu radiation used for XRD analysis; consequently, cobalt samples usually yield XRD patterns with high background noise and little signal.

The SEM images of the Fe\(_{0.00}\)Co\(_{0.00}\)S\(_2/KB-0N\) electrocatalyst in Figure S7 reveal successful deposition of the metal sulfide particles onto the carbon supports by wet-chemical sulfurization. Most importantly, the metal sulfide particles were uniformly distributed on the carbon supports (Figure S7b and S7c). Similar morphology is seen for the Fe\(_{0.50}\)Co\(_{0.50}\)S\(_2/KB-10N\) electrocatalyst (Figure 3b). The rectangular region in Figure 3b is enlarged to further examine the particle

---

**Figure 2.** XRD patterns of the 30 wt% Fe\(_{x}\)Co\(_{1-x}\)S\(_2/KB-0N\): (a) Fe\(_{1.00}\)Co\(_{0.00}\)S\(_2\); (b) Fe\(_{0.68}\)Co\(_{0.32}\)S\(_2\); (c) Fe\(_{0.32}\)Co\(_{0.68}\)S\(_2\); (d) Fe\(_{0.18}\)Co\(_{0.82}\)S\(_2\); (e) Fe\(_{0.09}\)Co\(_{0.91}\)S\(_2\); and (f) Fe\(_{0.00}\)Co\(_{1.00}\)S\(_2\). Note: Electro-catalysts with iron atomic contents \((x)\) from 1.00 to 0.50 show diffraction peaks from cubic FeS\(_2\) only.

**Figure 3.** SEM images of the (a) KB-10N, (b) and (c) Fe\(_{0.50}\)Co\(_{0.50}\)S\(_2/KB-10N\). Figure 3c is an enlarged view of the rectangular region marked in Figure 3b.
morphism. Figure 3c shows agglomerations of the Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2} particles, which is why SEM images show larger particle size (75 to 200 nm) than XRD-based calculations (20 to 30 nm). It is well known that the number of active sites is crucial for an electrochemical reaction and significantly increases when the particle size is reduced to less than 10 nm.\textsuperscript{49} Therefore, reducing particle size and preventing aggregation of the Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2} nanoparticles may be a key to an electrocatalyst with excellent HER activity.

To further assess the chemical state and elemental composition of the Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2} electrocatalysts, XPS was performed on the Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2}/KB-0N electrocatalysts. The survey scan shows the electrocatalyst contained 11.8, 6.1, and 6.0 wt% of S, Fe, and Co, respectively, which indicates different chemical states: CoS\textsubscript{x} and CoSO\textsubscript{4}.\textsuperscript{42} Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2}/KB-10N electrocatalyst. The survey scan shows the Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2} nanoparticles may be a key to an electrocatalyst with excellent HER activity.

Effect of carbon support and preparation method on the HER activity.—The electrocatalytic performance of FeS\textsubscript{2} strongly depends on two factors: (1) support surface area and (2) interaction between FeS\textsubscript{2} particles and carbon support. Figure S10 shows the voltammograms of three FeS\textsubscript{2} electrocatalysts toward HER. The unsupported FeS\textsubscript{2} showed a large onset potential of −0.225 V and a poor activity which required more than −0.275 V overpotential to attain 0.3 mA/cm\textsuperscript{2}. An increase in HER activity can be achieved by using high-surface area carbon as support. The potentials required to drive 5 mA/cm\textsuperscript{2} were −0.218 and −0.250 V for the FeS\textsubscript{2}/KB-0N and FeS\textsubscript{2}+KB-0N electrocatalysts, respectively, with the latter being a physical mixture of FeS\textsubscript{2} and KB-0N. For the mixture of the two particulates, it is reasonable to anticipate that only a portion of FeS\textsubscript{2} benefits by interaction with the carbon support due to agglomeration of the FeS\textsubscript{2} nanoparticles. In the case of FeS\textsubscript{2}/KB-0N, the FeS\textsubscript{2} was synthesized in the presence of the carbon support. The KB-0N provided a novel substrate for the nucleation and subsequent growth of FeS\textsubscript{2}. Therefore, a substantial improvement in the catalytic activity of the FeS\textsubscript{2}/KB-0N electrocatalyst may be attributed to the interactions between functional groups on carbon and FeS\textsubscript{2}.\textsuperscript{4} The polarization results of bare GC and KB-0N electrodes are also reported in Figure S10. In contrast to the FeS\textsubscript{2}, the bare GC and KB-0N showed no HER activity in the investigated potential region.

In order to compare the effect of Co-dopant on electrochemical performance, the HER was performed on various Fe\textsubscript{0.50}Co\textsubscript{1−x}S\textsubscript{x}/KB-0N electrocatalysts. Figure 5 shows the polarization curves and the corresponding Tafel plots of the Fe\textsubscript{0.50}Co\textsubscript{1−x}S\textsubscript{x}/KB-0N for ten values of x. (The Tafel plots reported here were derived from LSV.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** X-ray photoelectron spectra of the Fe\textsubscript{0.50}Co\textsubscript{0.50}S\textsubscript{2}/KB-10N electrocatalyst from (a) S 2p, (b) Fe 2p, and (c) Co 2p.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** (a) Polarization curves of the Fe\textsubscript{0.50}Co\textsubscript{1−x}S\textsubscript{x}/KB−0N electrocatalysts measured in a 0.5 M H\textsubscript{2}SO\textsubscript{4} solution at a scan rate of 5 mV/s. Catalyst loading was 150 \textmu g/cm\textsuperscript{2} and all voltages are corrected for ohmic loss; (b) corresponding Tafel plots obtained from Figure 5a; and (c) effect of Co substitution on charge-transfer resistance at −0.15 V. Data are from fit of Nyquist plots.
Tafel slopes of the Fe-doping atoms combine to generate H2 gas, whereas in the Heyrovsky surface. Then, the reaction could proceed either via the Tafel reaction exhibited good activity, achieving a cathodic current density of 10 mV/decade. Usually, Tafel slopes ranging from 40 to 120 mV/decade.11,43–45 desirable to drive a large current at low overpotential, and metal sulfides the lowest Rct of 23 mV/decade, showing relatively fast kinetics to drive the HER. On the contrary, electrocatalysts with low iron content as the Nyquist plots (Figure S11) for the Fe3S2 displayed in Figure 5b, reveal different Tafel slopes among the Fe3Co0.5S2, which are summarized in Table I. The Tafel slopes of the Fe2Co1−xS2 with x between 1.00 and 0.32 are in the range 50 to 60 mV/decade, showing relatively fast kinetics to drive the HER. On the contrary, electrocatalysts with low iron content (0 ≤ x ≤ 0.18) showed poor HER activity and Tafel slopes from 70 to 124 mV/decade.

The mechanism of HER in an acidic environment typically involves three steps.15 The first is called the Volmer or discharge reaction step, generating an adsorbed hydrogen atom (Hads) on the electrode surface. Then, the reaction could proceed either via the Tafel reaction or the Heyrovsky reaction. In the Tafel reaction, two adsorbed hydrogen atoms combine to generate H2 gas, whereas in the Heyrovsky reaction, another electron reacts with an adsorbed hydrogen atom and another proton from the solution to yield H2. A small Tafel slope is desirable to drive a large current at low overpotential, and metal sulfides usually exhibit Tafel slopes ranging from 40 to 120 mV/decade.11,43–45

The enhanced catalytic capability was confirmed by the EIS results, as the Nyquist plots (Figure S11) for the Fe3Co1−xS2 (x = 0.98 to 0.32) exhibited substantially reduced charge-transfer resistance (Rct) as compared to the Fe3Co1−xS2 (Figure S1c). Among the Fe3Co1−xS2, the lowest Rct of 23 Ω was obtained at x = 0.68.

According to DFT calculations reported by Wang and coworkers,30 sulfur on the edges of Fe3S2 are the HER active sites. The calculated energy barrier for hydrogen atom adsorption (Hads + Hads) on the Fe3Co1−xS2 (x = 0.9) was significantly lower than that on Fe3S2. The authors also showed the bond length of H-S on a S site of Fe3S2 was shorter than on a S site of Fe3Co1−xS2. The longer bond length of H–S (weaker H-S bond) on the Fe3Co1−xS2 means a hydrogen atom could approach the active site to form a H–H bond more effectively. Similar effects have been reported by Long et al. for iron-doped nickel sulfide.45 Therefore, the enhanced HER activity observed in Figure 5 may be attributed to the lowered kinetic energy barrier for hydrogen atom adsorption and subsequently H2 formation via Volmer-Heyrovsky mechanism46 due to the Co dopant.

To study the HER activity of the Fe3Co1−xS2 affected by carbon support, the HER on Fe3Co1−xS2/KB-10N was measured (Figure S13) and compared with that on the Fe3Co1−xS2/KB-0N electrocatalysts (Figure 5a). The HER activity of the Fe3Co1−xS2/KB-10N was improved over that of Fe3Co1−xS2/KB-0N (Figure 6a and Table I) at x = 0.91 to 0.32. These results indicate that the enhancement of electrocatalytic HER activity strongly depends on the carbon materials.47,48 Bond formation between the electrocatalyst and the underlying carbon support may change the chemical bonding environment for carbon, oxygen, and metal atoms in the supported catalyst, resulting in enhanced catalytic activity.49 Our results suggest that the advantages of the Fe3Co1−xS2/KB-10N are the effects of (1) functional groups and defects needed for nucleation and growth of catalyst particles, (2) high

| Catalyst Composition* | Tafel slope (mV/decade) | j∞ (A/cm²) | Rct (Ω) | Potential (V) |
|------------------------|-------------------------|------------|---------|--------------|
| Fe0.00Co1.00S2         | 62                      | 2.17 × 10⁻⁶ | 274     | −0.229       |
| Fe0.99Co0.01S2         | 61                      | 4.33 × 10⁻⁶ | 136     | −0.206       |
| Fe0.91Co0.09S2         | 56                      | 4.21 × 10⁻⁶ | 75      | −0.187       |
| Fe0.82Co1.18S2         | 52                      | 3.41 × 10⁻⁶ | 48      | −0.180       |
| Fe0.68Co1.32S2         | 51                      | 5.14 × 10⁻⁶ | 23      | −0.166       |
| Fe0.50Co1.50S2         | 52                      | 4.79 × 10⁻⁶ | 36      | −0.173       |
| Fe0.32Co0.68S2         | 51                      | 1.36 × 10⁻⁶ | 101     | −0.199       |
| Fe0.18Co0.82S2         | 73                      | 2.83 × 10⁻⁶ | 1890    | −0.270       |
| Fe0.09Co0.91S2         | 72                      | 1.65 × 10⁻⁶ | 2210    | NA           |
| Fe0.00Co1.00S2         | 124                     | 3.16 × 10⁻⁶ | 4930    | NA           |

*From XRD; j∞: Exchange current density; Rct: Charge-transfer resistance at −0.15 V.

The table shows the summary of various iron-cobalt sulfide electrocatalysts: 30 wt% Fe3Co1−xS2/KB-10N. Electrochemical data were obtained using a catalyst loading of 150 μg/cm².

Figure 6. (a) Comparison of potentials at 10 mA/cm² for the Fe3Co1−xS2/KB-0N and Fe3Co1−xS2/KB-10N electrocatalysts. (b) Comparison of HER stability for the Fe3Co1−xS2/KB-0N and Fe3Co1−xS2/KB-10N. All voltages are corrected for ohmic loss.
electrical conductivity, and (3) increased ASA of the HNO₃ modified carbon support.

Stability is an important criterion for an electrocatalyst. The electrochemical stability of supported Fe₉₋ₓCoₓS₂ electrocatalysts was examined using a short-term cycling experiment.⁴,⁵ The potential cycling was carried out for 20 cycles for the Fe₉₋ₓCoₓS₂/KB-0N electrocatalyst and 100 cycles for the Fe₉₋ₓCoₓS₂/KB-10N electrocatalyst (Figure 6b). As shown in Table SIII, the potential at 10 mA/cm² decreased by only 0.173 to −0.181 in only 20 cycles. These results provide evidence that the modified carbon support not only improves the HER performance but also stability of the Fe₉₋ₓCoₓS₂.

Figure 7 shows the polarization curves of the Fe₉₋ₓCoₓS₂/KB-10N electrocatalyst for a stability test of 500 cycles. Summary of the electrochemical data of the Fe₉₋ₓCoₓS₂/KB-10N electrocatalyst are examined using a short-term cycling experiment.⁴,⁵ The potential at 10 mA/cm²; C₀Sₓ; C₀S, C₀9S₈, and C₀3S₄.

Conclusions

In this study, we synthesized and investigated cobalt-doped iron sulfides (Fe₉₋ₓCoₓS₂) as electrocatalysts for hydrogen evolution. A chemical oxidation method was used to increase the active surface area of the carbon support. SEM images of the Fe₉₋ₓCoₓS₂/KB (Ketjenblack) revealed deposition of metal sulfide particles onto the carbon supports by the wet-chemical sulfuration process. XRD results showed cubic FeS₂, with particle size ranging from 22 to 30 nm, was formed at iron atomic content from 1.00 to 0.50. An increase in HER activity was evident by a decrease of the overpotential at a current density of 10 mA/cm²; the potential dropped from −0.229 V for un-doped FeS₂ to −0.166 V with a 32% Co-doping (Fe₀.₆₈Co₀.₃₂S₂/KB-0N). The electrocatalytic performance was further improved by using a Ketjenblack support oxidized with 10 N nitric acid. Among the electrocatalysts examined, the Fe₀.₆₈Co₀.₃₂S₂/KB-10N exhibited highest HER activity (an overpotential of −0.150 V at 10 mA/cm² and a loading of 300 μg/cm² with a Tafel slope of 52 mV/decade) and promising long-term durability in acidic environment. Electrocatalysts synthesized in this study may be looked at as prospective replacements to precious metal catalysts for the HER.

Acknowledgments

The authors thank Dr. Linyou Cao for the use of the Raman spectrometer. Material characterization work was performed in part at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (award number ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI). Chemical composition analysis of the electrocatalysts by ICP-OES was performed at the Environmental and Agricultural Testing Service laboratory (EATS), Department of Crop and Soil Sciences, at North Carolina State University.

Table II. Summary of various iron-cobalt sulfide electrocatalysts: 30 wt% FeₓCo₁₋ₓS₂/KB–10N. Electrochemical data were obtained using a catalyst loading of 150 μg/cm².

| Catalyst Composition         | Tafel slope (mV/decade) | j₀ (A/cm²) | Rct (Ω) | Potential (V) |
|-----------------------------|-------------------------|------------|---------|---------------|
| Fe₀.₃₂Co₀.₆₈S₂/KB-0N        | 52                      | 8.58 × 10⁻⁶ | 26      | −0.168        |
| Fe₀.₅₀Co₀.₅₀S₂/KB-10N       | 50                      | 4.48 × 10⁻⁶ | 27      | −0.168        |

*From XRD; j₀: Exchange current density; Rct: Charge-transfer resistance at −0.15 V.

1. J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, and S. Pandelov, *J. Electrochem. Soc.*, **152**, J23 (2005).
2. W. C. Sheng, H. A. Gasteiger, and Y. Shao-Horn, *J. Electrochem. Soc.*, **157**, B1529 (2010).
3. D. V. Esposito, S. T. Hunt, A. L. Stottlemyer, K. D. Dobson, B. E. McCandless, R. W. Birkmire, and J. G. G. Chen, *Angew. Chem., Int. Ed.*, **49**, 9859 (2010).
4. Y. G. Li, H. L. Wang, L. M. Xie, Y. Y. Liang, G. S. Hong, and H. J. Dai, *J. Am. Chem. Soc.*, **133**, 7296 (2011).
5. T. F. Jaramillo, K. P. Jorgensen, J. Bonde, J. H. Nielsen, S. Horch, and I. Chorkendorff, *Science*, **317**, 100 (2007).
6. M. L. Helm, M. P. Stewart, R. M. Bullock, M. R. DuBois, and D. L. DuBois, *Science*, **335**, 863 (2011).
7. J. R. McKone, E. L. Warren, M. J. Bierman, S. W. Boettcher, B. S. Brunschwig, N. S. Lewis, and H. B. Gray, *Energy Environ. Sci.*, **4**, 3573 (2011).
8. M. Zeng and Y. G. Li, *Journal of Materials Chemistry A*, A, 14942 (2015).
9. M. S. Faber and S. Jin, *Energy Environ. Sci.*, **7**, 3519 (2014).

References
