

Multi-Component Fe–Ni Hydroxide Nanocatalyst for Oxygen Evolution and Methanol Oxidation Reactions under Alkaline Conditions

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Supporting Information



ABSTRACT: Iron-incorporated nickel-based materials show promise as catalysts for the oxygen evolution reaction (OER) halfreaction of water electrolysis. Nickel has also exhibited high catalytic activity for methanol oxidation, particularly when in the form of a bimetallic catalyst. In this work, bimetallic iron–nickel nanoparticles were synthesized using a multistep procedure in water under ambient conditions. When compared to monometallic iron and nickel nanoparticles, Fe–Ni nanoparticles show enhanced catalytic activity for both OER and methanol oxidation under alkaline conditions. At 1 mA/cm², the overpotential for monometallic iron and nickel nanoparticles was 421 and 476 mV, respectively, while the bimetallic Fe–Ni nanoparticles had a greatly reduced overpotential of 256 mV. At 10 mA/cm², bimetallic Fe–Ni nanoparticles had an overpotential of 311 mV. Spectroscopy characterization suggests that the primary phase of nickel in Fe–Ni nanoparticles is the more disordered alpha phase of nickel hydroxide.

KEYWORDS: electrocatalyst, nonprecious metal, core-shell nanoparticles, oxygen evolution reaction, alcohol oxidation, fuel cell

INTRODUCTION

Sustainable energy conversion and storage continues to be a key driver for the development of nanostructured electrocatalysts. In particular, hydrogen has received a great deal of attention as a renewable source of clean energy,^{1–5} and therefore, sustainable hydrogen generation remains a critical need. H₂ fuel is often considered to be a promising candidate for energy conversion technologies such as fuel cells due to its high specific energy density and for processes such as ammonia synthesis that currently use environmentally harmful methods of hydrogen production.^{6,7} The most common source of H_2 fuel is produced through steam reforming, where fossil-fuel-derived coal or methane is reacted with steam to produce H_2 . Due to worldwide dependence on fossil fuel-based H_2

Received:September 6, 2016Revised:November 22, 2016Published:November 29, 2016

production, the ammonia synthesis industry alone contributes between 0.8 and 6.4% of worldwide CO_2 per year^{8,9} (equivalent to 0.3–2.2 Gt CO_2 in 2013)¹⁰ to greenhouse gas emissions, while the ammonia-based fertilizer industry contributes 9 trillion grams (Tg) of NO_x per year.¹¹ In addition to its use in agriculture, ammonia is now considered as a potential storage molecule for H_2 ,^{12,13} as well as a potential alternative fuel source,¹⁴ making both direct H_2 production and NH_3 production with H_2 critical to energy conversion and storage. With a smaller environmental impact, potentially lower cost, and purity of the final product, water splitting through electrolysis provides an attractive alternative to produce H_2 for multiple industries worldwide.^{15,16}

Water splitting can be separated into two half-reactions: the oxygen evolution reaction (OER) (eq 1) and the hydrogen evolution reaction (HER) (eq 2). The efficiency of water splitting is limited by the slow kinetics of OER, which require a four-proton-coupled electron-transfer reaction under alkaline conditions:^{17,18}

$$4OH^- \to O_2 + 2H_2O + 4e^-$$
 (1)

$$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$$
(2)

To accelerate the reaction rate and decrease the overpotential, electrocatalysts are used. The best-performing catalysts are often noble metals or noble metal oxides, such as platinum, iridium oxide, or ruthenium oxide.^{19–21} However, the high cost and limited availability of these materials make widespread application difficult. As such, it is essential to find low cost and earth-abundant catalytic materials for OER.

Catalytic materials containing only first-row transition-metal oxides and oxyhydroxides, including those based on manganese, iron, cobalt, or nickel, have demonstrated high OER activity.²²⁻²⁷ In particular, nickel-based catalysts have been shown to be among the most active under alkaline conditions,²⁸ and these materials remain the most common catalytic material for anodic water splitting in commercial applications.^{17,22} Recent findings have shown that the most highly active nickelbased catalysts for OER are nickel (oxy)hydroxides that contain iron within their layered structure.^{17,22,23,28-34} Trotochaud et al. found that incidental incorporation of iron impurities from alkaline electrolytes into Ni(OH)₂/NiOOH thin films can lead to lower overpotential, while iron-free NiOOH actually exhibits poor catalytic activity.³² While the iron significantly increases the conductivity of Ni(OH)₂/NiOOH, the authors also conclude that the incorporated iron leads to partial charge transfer, which activates the nickel centers within the film.³² For mixed metal Ni-Fe oxide films, OER activity was shown to be highest for samples containing 40% iron,³¹ and for Ni-Fe oxyhydroxide films, maximum OER activity was observed between 17% and 25% iron.³⁰

An alternative to utilizing H_2 in fuel cells is the use of liquid carbon-based fuels, such as ethanol or methanol. These liquid fuels exhibit much higher energy densities (15 MJ/L and 24 MJ/L, respectively) than H_2 (4 MJ/L to 6 MJ/L), and as liquids at room temperature, ethanol or methanol can be easier to handle than compressed H_2 . Additionally, these fuels may be produced from renewable resources, such as biomass feedstocks.^{35,36} Of particular interest is methanol, which can undergo a 6 e⁻ oxidation to CO₂. However, like OER, the slow kinetics of methanol (and ethanol) electrooxidation require the use of an electrooxidation under alkaline conditions contain precious metals, often platinum or palladium.^{37,38} Similar to OER, the alkaline environment in a direct alcohol fuel cell enables nonprecious-metal-based catalysts to remain stable and active during electrocatalysis. While some examples do exist showing electrocatalytic fuel oxidation with purely nonprecious metal catalysts,^{39–46} more research is needed to make these materials competitive with their precious metal counterparts.

In this work, core-shell iron-nickel nanoparticles were prepared using a multistep aqueous-based synthesis technique and then characterized as an electrocatalyst for both OER and methanol oxidation under alkaline conditions. High-resolution transmission electron microscopy, X-ray absorption finestructure spectroscopy, high-energy X-ray diffraction coupled to atomic pair distribution function analysis, and X-ray photoelectron spectroscopy are used to characterize these materials. When compared to monometallic nanoparticles composed of either iron only or nickel only, the bimetallic iron-nickel nanoparticles show significantly higher catalytic activity for OER and methanol oxidation as well as a much lower overpotential. Results demonstrate the ability to create bimetallic electrocatalytic nanomaterials from nonprecious metals using a scalable aqueous synthetic technique. The synthesized Fe-Ni nanoparticle catalyst can be used to catalyze two separate electrochemical reactions with enhanced activity; these results illustrate the potential of the synthesized catalyst for economical and efficient energy conversion applications.

EXPERIMENTAL SECTION

Materials. All chemicals were American Chemical Society grade and used as received without further purification, except where noted. Deionized water was obtained from an in-house filtration system (18 M Ω). Iron sulfate heptahydrate (FeSO₄*7H₂O), sodium borohydride (NaBH₄), nickel chloride hexahydrate (NiCl₂*6H₂O), 99.999% nickel nitrate hexahydrate (Ni(NO₃)₂*6H₂O), amino tris(methylene phosphonate) (ATMP, molecular weight = 298 g/mol), polyvinylpyrrolidone (PVP₄₀, molecular weight = 40 000 g/mol), sodium hydroxide, concentrated nitric acid, concentrated sulfuric acid, and methanol were purchased from commercial suppliers. A quaternary amine-based block copolymer was used as an alkaline exchange ionomer for electrochemical testing.⁴⁷ Specific synthesis details for the ionomer are provided in the Supporting Information.

Nanoparticle Synthesis. Core-shell iron-nickel nanoparticles ("Fe-Ni NPs") were synthesized using a multistep procedure performed in water under ambient conditions. First, zerovalent iron (ZVI) nanoparticle cores were synthesized at a concentration of 1 g/L following a previously reported procedure.⁴⁸⁻⁵¹ Briefly, aqueous solutions of iron sulfate heptahydrate and the ligand stabilizer amino tris(methylene phosphonic acid) (ATMP) were combined in a 250 mL threeneck flask with a ratio of 0.05 mol ATMP:mol Fe. The ATMPstabilized iron solution was mixed using an orbital shaker for 15 min while bubbling argon to remove dissolved O2. This is performed to hinder uncontrolled oxidation of the iron nanoparticles. Next, a freshly prepared aqueous solution of sodium borohydride in a ratio of 2.2 mol BH4:mol Fe was added dropwise by syringe at approximately 2 mL/min while mixing by hand to reduce the stabilized Fe²⁺ to ZVI nanoparticles. This molar ratio was chosen so as to provide 2 mol of BH_4^- per mol of Fe^{2+} for complete reduction of all Fe^{2+} atoms, with an additional 10% excess to account for the side

reaction of BH_4^- with water.⁵² The solution was stirred with an orbital shaker for 30 min to allow for complete reaction and held under vacuum to draw out evolving hydrogen gas.

A nickel shell was added to the ZVI nanoparticles cores through electroless deposition with a ratio of 1 mol Ni:mol Fe. First, an aqueous solution of nickel chloride hexahydrate (100 g/L) was mixed with the stabilizer polyvinylpyrrolidone $(PVP_{40}; M_W = 40\,000)$ in a ratio of 0.005 mol PVP_{40} :mol Ni. The PVP₄₀-stabilized nickel was then added dropwise by syringe to the ZVI nanoparticle suspension while mixing by hand after exposing the flask to air to release the vacuum from the previous step. Next, the solution was mixed on an orbital shaker while holding under vacuum for 15 min to allow for complete deposition of the nickel shell. The resulting ironnickel nanoparticles were centrifuged, the supernatant was removed by pipet, and the nanoparticles were resuspended in methanol to achieve a final concentration of 2 g/L.53 For comparison with the bimetallic nanoparticles, monometallic iron and nickel nanoparticles were also synthesized at a concentration of 1 g/L. Iron nanoparticles ("Fe NPs") were synthesized following the same procedure used to make the ZVI nanoparticle cores. Due to the magnetic nature of the resulting nanoparticles, a strong magnet was used to pelletize the nanoparticles instead of centrifugation. Nickel nanoparticles ("Ni NPs") were synthesized following the same general procedure, but using PVP₄₀ as the stabilizer instead of ATMP. Glassware used to synthesize Ni NPs was rinsed with 1 M H₂SO₄ prior to synthesis to remove iron impurities that could incorporate into the nanoparticles.³² Both iron and nickel nanoparticles were resuspended in methanol at a concentration of 2 g/L after removing the supernatant. At least three batches of each sample (Fe-Ni NPs, Fe NPs, and Ni NPs) were synthesized to ensure repeatability.

Characterization. All imaging and elemental analysis were performed on a spherical aberration corrected JEOL-ARM 200F transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV. The microscope was operated in scanning mode (STEM), and all images shown are bright field (BF) STEM images. Images were acquired in Digital Micrograph with an image size of 1024 pixels \times 1024 pixels, a 25 μ s dwell time, and a spot size of 7C. Energy-dispersive Xray spectroscopy (EDS) was performed in STEM mode using an Olympus silicon drift detector with a STEM spot size of 5C. Analysis and quantification of the EDS line scans and maps were performed in the Olympus Aztec acquisition and processing software. Nanoparticle samples were dispersed on TEM grids consisting of ultrathin carbon supported by lacey carbon (01824, Ted Pella, U.S.A.). To prepare TEM samples, nanoparticles suspended in methanol at a concentration of 2 g/ L were diluted by a factor of 50 with methanol. A 3 μ L aliquot was drop cast and allowed to dry on the TEM grid. The samples were prepared immediately prior to imaging to avoid oxidation of the nanoparticles. The TEM grid was plasma cleaned immediately prior to imaging in pure argon plasma for 45 s (Fischione 1070 plasma cleaner).

Inductively coupled plasma mass spectrometry (ICP-MS) experiments were performed on Fe–Ni NPs to determine bimetallic stoichiometry. The nanoparticles were digested in 5% nitric acid in a 1:20 dilution from a 1 g/L nanoparticle suspension. Experiments were performed at the Laboratory for Environmental and Geological Studies at the University of Colorado at Boulder using a Perkin-Elmer SCIEX instrument. The detection limits were 0.014 ppm for iron and 0.018 ppm

for nickel. Three aliquots were measured from each sample, and the resulting concentrations were averaged. Reported values have been adjusted for the dilution with nitric acid.

X-ray photoelectron spectroscopy (XPS) was performed by Rocky Mountain Laboratories, Inc. Samples were drop cast onto silicon wafers and allowed to dry in air prior to measurements. Analyses were performed with an Al K α X-ray source. The sampling depth was less than 10 nm, and the analysis area was approximately 500 μ m in diameter. The nominal detection limit for elemental analysis is approximately 0.1 atomic %, but spectral interferences may prohibit the detection of some elements in relatively low concentrations. Charge neutralization of the sample surface was achieved with the use of a low-energy electron flood gun. Energy scales of the spectra are referenced to the C 1s C–C/C–H signal at 284.5 eV.

X-ray absorption fine-structure spectroscopy (XAFS) was performed the Advanced Photon Source at Argonne National Laboratory at the 12-BM beamline. The nanoparticle samples were drop cast in methanol on to Kapton tape and measured from 150 eV below the K-edge absorption of Fe (7.11 keV) or Ni (8.33 keV) to 800 eV above the respective absorption edges. Metal foils of either Fe or Ni were used to calibrate E_0 and served as reference material for subsequent linear combination fitting of the X-ray absorption near-edge structure (XANES). Additional standards implemented into the linear combination fitting of Fe-XANES and Ni-XANES, which included metal oxide and phosphide powders purchased from commercial sources, were ground into a fine powder by mortar and pestle and spread across tape for XAFS measurements. All data processing and linear combination fitting was performed using the software program Athena.⁵⁴

High energy X-ray diffraction (HE-XRD) experiments were performed at the 11-ID-C beamline of the Advanced Photon Source at Argonne National Laboratory. Lyophilized powders were loaded into 2 mm quartz capillaries to obtain diffraction patterns at very high Q (~4.5 nm⁻¹) using 115 keV irradiation. HE-XRD patterns were converted into atomic pair distribution functions (PDFs) using the software program RAD.⁵⁵ Briefly, HE-XRD patterns were background subtracted and converted into structure functions via:

$$S(Q) = 1 + \frac{I^{\text{coh}}(Q) - \sum c_i |f_i(Q)|^2}{|\sum c_{i}f_i(Q)|}$$
(3)

where $I^{\text{coh}}(Q)$ is the coherent part of the HE-XRD pattern and c_i and $f_i(Q)$ are the atomic concentration and X-ray scattering factors, respectively, for the atomic species *i*. The atomic pair distribution functions, G(r), were obtained from the Fourier transform of Q[S(Q) - 1] via:

$$G(r) = \left(\frac{2}{\pi}\right) \int_{Q=0}^{Q_{\text{max}}} Q[S(Q) - 1]\sin(Qr) dQ$$
(4)

where G(r) is defined as $G(r) = 4\pi r [\rho(r) - \rho_0]$, wherein $\rho(r)$ is the atomic density at distance r, and ρ_0 is the average atomic density in the sample.

Electrochemical Measurements. Catalyst inks were prepared by combining equal parts 2 g/L nanoparticles suspended in methanol with a 0.035 wt % solution of alkaline exchange membrane ionomer in methanol to give a mass ratio of 6:1. The ink was sonicated in a cold water bath for at least 10 min to ensure complete mixing. Two microliters of ink was

then drop cast immediately on a clean glassy carbon electrode (surface area = 0.07 cm^2) and allowed to dry in air at room temperature. Electrocatalytic performance of the nanoparticles for both OER and methanol oxidation was measured using a three-electrode setup with Ag/AgCl in 3 M KCl as the reference electrode and a graphite rod as the counter electrode. Prior to measurements, the 1 M NaOH electrolyte was bubbled with nitrogen gas for 30 min to remove dissolved oxygen, after which continuous nitrogen flow remained in the headspace above the electrolyte. The Ag/AgCl reference electrode was placed in a salt bridge containing 3 M NaCl for all experiments to prevent AgO formation from NaOH exposure. Cyclic voltammograms (CVs) were taken using a voltage window of 0 to 0.8 V versus the reference electrode. CVs were first taken of the clean glassy carbon electrode to obtain a background measurement, which was then subtracted from all subsequent measurements. For OER measurements, CVs of the nanoparticles were performed in 1 M NaOH until the response stabilized, which was typically 30 cycles. Subsequently, methanol oxidation measurements were taken by adding 0.2 M, 1 M, and 2 M methanol. Samples were cycled for 10 cycles at each concentration for general measurements and 20 cycles each for detailed measurements. For comparison, ethanol oxidation was also measured at the same three concentrations. For Ni NPs, the electrolyte was purified to remove Fe impurities prior to use following a procedure outlined in the literature.³² Briefly, the electrolyte, 1 M NaOH, was purified by mixing with high-purity particulate $Ni(OH)_2$ for 4 h, where the Ni(OH)₂ was precipitated from 99.999% nickel nitrate hexahydrate and NaOH. The purified electrolyte was stored in sulfuric acid-rinsed 50 mL tubes. The electrolyte for Fe-Ni NPs and Fe NPs measurements was not purified because iron at much higher concentrations is already present in the nanoparticles, and additional iron is not expected to have a noticeable impact on electrochemical performance. The scan rate was 20 mV/s for all measurements. The measured potential vs Ag/AgCl was converted to potential vs the reversible hydrogen electrode (RHE) E_{RHE} using the following equation:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059^{*} \rm pH + E_{\rm Ag/AgCl}^{0}$$
(5)

where $E_{Ag/AgCl}$ is the measured potential versus Ag/AgCl, pH is measured to be 12.6 for the 1 M NaOH electrolyte, and $E^{0}_{Ag/AgCl}$ is 0.21 V for the Ag/AgCl reference electrode in 3 M NaCl according to the manufacturer's Web site. All electrochemical data was also adjusted using an iR_{u} correction, where *i* is the current and $R_{\rm u}$ is the uncompensated series resistance. $R_{\rm u}$ was determined by potentiostatic electrochemical impedance spectroscopy. Values were read at a frequency of 100 kHz. The calculated value of iR_u was subtracted from the measured potential vs RHE for all cyclic voltammetry measurements. The overpotential at a given current density²⁶ is calculated by subtracting 1.23 V from the measured potential versus RHE after the onset of OER. The values reported here are averages taken from separate measurements on three freshly synthesized nanoparticle batches for each of the samples (Fe-Ni NPs, Fe NPs, Ni NPs). A discussion of the associated error analysis can be found in the Supporting Information.

RESULTS AND DISCUSSION

Composition and Structural Characterization. Brightfield STEM images of Fe-Ni NPs show nanoparticles with diameters ranging from approximately 50 to 150 nm (Figure 1). As can be seen in the image at lower magnification (Figure 1a),



Figure 1. Bright-field STEM images of Fe–Ni nanoparticles. (a) Lowmagnification image of an aggregate of Fe–Ni NPs. (b) Highermagnification image of single iron-rich nanoparticle showing the nanocrystalline grain structure. Individual grains are approximately 5 to 10 nm in size. (c) Image of organic globules containing predominantly nickel and phosphorus.

the nanoparticles tended to agglomerate or form chains. Two types of nanoparticles were observed during imaging: dense nanoparticles (Figure 1b) and low-density organic globules (Figure 1c). The nanoparticle population consisted of approximately equal parts of these two types of nanoparticles. The dense nanoparticles were composed of nanocrystalline regions with a crystallite size of approximately 5 to 10 nm. This internal morphology is similar to that previously observed for ZVI nanoparticles synthesized with the same synthesis procedure.⁵⁰ Each nanoparticle had a low-contrast shell approximately 5 nm in thickness, which was either organic stabilizer or a thin oxide layer. Low-contrast voids inside the nanoparticles suggest that there was also internal porosity. The low contrast of the globules indicated that they were much less dense than the nanocrystalline particles (Figure 1c); for example, the low-contrast particles on the upper right of the aggregate in Figure 1a can be compared to the high-contrast particles on the lower right of the aggregate. The size of the organic globules was approximately the same as the denser nanocrystalline nanoparticles. The globules sustained electron beam damage in the form of bubbling after only a few seconds of irradiation with a stationary electron probe, suggesting that they consisted mostly of organic material and were not metallic or oxides. TEM images for the iron only and nickel only nanoparticles can be found in the Supporting Information (Figure S1).

The relative spatial distribution of elements in Fe–Ni NPs was determined by EDS (Figure 2). It is important to note that the resulting elemental maps are qualitative and do not necessarily indicate quantitative spatial distribution of the elements. However, these elemental maps can provide insight into the relative concentration of each element at different locations. Figure 2a shows elemental maps for iron, oxygen, nickel, and phosphorus for the nanoparticle shown in Figure 1b. The EDS signal for phosphorus was mapped because it provided an elemental signature, likely originating from the



Figure 2. EDS mapping of Fe–Ni NPs. (a) Individual elemental maps for the nanoparticle in Figure 1b. (b) Overlay of all elemental maps on a bright field STEM image of the nanoparticle. (c) Representative plot of the atomic percent of each element in (a) as a function of position for a line scan across the nanoparticle in (b).

stabilizer ATMP used during synthesis of the iron core. The EDS maps reveal that each target element was present throughout the entire nanoparticle. The iron EDS map had a higher signal at the center of the nanoparticle due to increased thickness of the spherical particle at that location. The nickel map showed a signal in the interior of the nanoparticle as well as an increased signal on the nanoparticle surface, and the nickel signal extended farther from the center of the nanoparticle than the iron signal. The oxygen and phosphorus maps showed a relatively homogeneous EDS signal over the entire nanoparticle. An overlay of the iron and nickel signal with the BF STEM image demonstrates the core—shell structure of the Fe—Ni nanoparticle (Figure 2b).

An EDS line scan was performed on the same nanoparticle to estimate the relative atomic concentrations in the core and shell of the nanoparticle (Figure 2c). The core of the nanoparticle (position near 80 nm) was predominantly oxygen and iron at an approximate ratio of 3:2. Oxygen was likely introduced during synthesis, possibly when the iron core nanoparticles are exposed to air before the addition of nickel precursor and PVP and/or after nickel addition during postsynthesis processing of the nanoparticles. There was approximately 5 atomic % phosphorus in the center of the nanoparticle and no detectable nickel signal. The iron concentration decreased and oxygen content increased toward the edges of the nanoparticle. The phosphorus and nickel signals also slightly increased to approximately 7 atomic % at the nanoparticle edges. Although the Fe-Ni nanoparticles were synthesized with a 1:1 molar ratio of Fe:Ni based on the concentrations of precursor metal salts, the discrepancy between the molar ratio of Fe:Ni in the precursors salts and the nickel atomic % measured by EDS suggests that the majority of the nickel did not reduce onto the surface of the iron nanoparticles during electroless deposition. The excess nickel may have remained in solution as Ni²⁺, and it is likely that the nickel cation bound to excess ATMP in solution, forming the nickel globules (Figure 1a,c). EDS mapping showed that these globules consisted predominantly

of nickel, oxygen, and phosphorus, consistent with nickel bound to ATMP (Supporting Information, Figure S3).

To determine the concentrations of iron and nickel in the nanoparticles, ICP-MS was used. A table summarizing the results for each of the three nanoparticle samples is shown in the Supporting Information (Table S1). Of particular interest is the ratio of iron to nickel in Fe-Ni NPs, but measurements were taken for Fe NPs and Ni NPs as well for use as controls. As expected, Fe NPs contained no trace of nickel. There was a very small amount of phosphorus detected (7 ppm), but it was less than 1% of the amount of iron detected. Ni NPs also contained a very similar concentration of phosphorus (6 ppm). However, no phosphorus-containing molecules (e.g., ATMP) are used in the synthesis of Ni NPs, so it is believed that the phosphorus detected in Ni NPs and Fe NPs is due to impurities. While excess ATMP might have been a source of phosphorus in Fe NPs, the equal amounts of phosphorus found in both Fe NPs and Ni NPs suggest that any excess ATMP is washed away during postsynthesis processing. Likewise, Ni NPs contained a trace amount of iron (0.4 ppm). However, the amount detected was on the same order of magnitude as that detected in the nitric acid used to digest the samples for measurements. Therefore, the iron in Ni NPs is likely a result of ICP-MS sample preparation.

For Fe–Ni NPs, ICP-MS results show that there is approximately 3 times the concentration of iron as nickel in this sample. While these nanoparticles were synthesized in a ratio of 1 mol Fe:mol Ni, EDS showed that there was significantly less nickel in the core–shell nanoparticles than expected. The nickel concentration as measured by ICP-MS is higher than that seen for EDS because the measurement includes nickel from both the core–shell nanoparticles and the nickel-rich organic globules. Interestingly, the phosphorus signal for Fe–Ni NPs is approximately 1 order of magnitude higher than for Fe NPs and Ni NPs, which can be attributed to ATMP phosphorus being retained as part of the nickel-rich organic globules as well as some incorporating into the core– shell nanoparticles (Figure 1).

The surface composition and oxidation state of Fe–Ni NPs, Fe NPs, and Ni NPs was measured by XPS. Survey spectra (Figures S4, S5, and S6 in Supporting Information) were used to determine the relative elemental compositions for each of the nanoparticle samples (Table 1). Due to the inhomogeneity

Table 1. Relative Elemental Concentration of Samples As Determined by XPS in Atomic $\%^a$

sample	Fe	Ni	0	С	Р	balance
Fe only	24	-	51	18	0.7	5.9
Ni only	-	29	45	22	-	4.3
Fe–Ni NPs	11	14	45	23	3.3	3.8

^{*a*}All nanoparticles have a significant amount of oxygen, either in the form of metallic oxides or oxygen binding to nanoparticle stabilizers. Fe–Ni NPs show approximately equal amounts of iron and nickel.

of the samples, the values in the table are only used to provide a relative comparison of the samples and do not necessarily represent exact compositions. Additionally, elements that are present in smaller amounts may not be discernible from the background and therefore may not be identified. The monometallic nanoparticles (Fe NPs and Ni NPs) contained similar atomic % of their respective metals, along with oxygen contents that are nearly 50% for each sample.



Figure 3. High-resolution XPS scans. (a) Fe 2p signal for Fe NPs, (b) Fe 2p signal for Fe–Ni NPs, (c) Ni 2p signal for Ni NPs, and (d) Ni 2p signal for Fe–Ni NPs.

While it is likely that much of this oxygen is in the form of metallic oxides, some of the oxygen signal may be from the ATMP and PVP₄₀ stabilizers, as well as possible contamination from exposure to the ambient environment. Fe-Ni NPs show approximately the same atomic % of oxygen as the monometallic nanoparticles, and nearly equal amounts of both iron and nickel. The slightly higher nickel content is due to XPS being a surface specific technique and the small sampling depth. As discussed earlier, EDS measurements show that there is a higher concentration of nickel on the surface of Fe-Ni NPs, which helps to explain the higher concentration of nickel measured by XPS. Fe NPs and Fe-Ni NPs both exhibit a small amount of phosphorus. Each sample also has a considerable amount of carbon, which is attributed to the ATMP and PVP₄₀ stabilizers still present in the samples. The balance for Fe-Ni NPs, Fe NPs, and Ni NPs are elements that remain in the samples despite rinsing with methanol at the end of the synthesis procedures and originate from the precursors used during synthesis of the nanoparticles. A more detailed discussion of each of these trace contaminants is presented in the Supporting Information. It is possible that some of these contaminant elements could influence the electrocatalytic performance of the nanoparticles. In particular, both chloride and sulfur have been shown to be poisoning species for electrocatalysts.⁵⁶⁻⁵⁹ However, for the results presented here, it is assumed that each sample will experience equivalent negative impacts on the electrocatalytic activity because contaminants are present in all of the samples.

It is important to note that both iron and nickel are measured by XPS near the surface of Fe-Ni NPs even though the synthesis procedure creates a core-shell morphology as confirmed by STEM/EDS. In addition, the ratio of Fe:Ni is slightly less than 1 despite the presence of both iron-rich and low-density organic globule nanoparticle morphologies (Figure 1) in the XPS sample. EDS measurements found that little to no iron is present in the low-density ATMP-nickel oxide globules (Supporting Information, Figure S3). These results suggest a relatively high iron content in the shell of the coreshell Fe-Ni NPs. It is known that metal atoms can migrate within an initial multimetallic core-shell structure.⁶⁰⁻⁶² The tendency of certain atoms to exhibit a preference for either the core or shell of a nanoparticle is phenomenon referred to as surface segregation. Research by Wang and Johnson attributed this behavior to two separate factors: cohesive energy and the Wigner-Seitz radius of an atom.^{63,64} The less negative segregation energy for nanoparticles with iron cores and nickel shells (-0.10 eV) as compared to nanoparticles with nickel cores and iron shells (-2.02 eV) suggests that the former configuration is preferable. However, the difference in Wigner-Seitz radius helps to explain the presence of iron in the shell of the Fe-Ni NPs. The radius of iron (1.41 Å) is slightly larger than that of nickel (1.38 Å), suggesting that iron will migrate to the shell in order to relieve compressive strain in the core.^{63,65} Recent research has also found that iron easily incorporates into the nickel hydroxide crystal structure, 32,66 which further supports the presence of iron in the nickel shell. In addition, the integration of oxygen into the core-shell nanoparticles can

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Figure 4. XANES at the (a) Fe K-edge and (b) Ni K-edge for Fe–Ni NPs, with associated LCF (red lines) and resulting composition output from each fit. Tables S3 and S4 in the Supporting Information provide a complete breakdown of the LCF results.

be attributed to the electroless deposition process, where nickel cations deposit onto the iron core nanoparticle surface, occurs through a two-electron transfer from Fe⁰ to Ni²⁺ as a result of the difference in the standard reduction potentials of Fe^{2+} and $Ni^{2+} (E^{0}_{Fe2+} = -0.44 \text{ V}; E^{0}_{Ni2+} = -0.25 \text{ V})$. The products of this electron transfer reaction are Ni⁰ and Fe²⁺. Because the synthesis is performed in water with some oxygen exposure, both the deposited Ni⁰ and the Fe²⁺ may form oxides and/or hydroxides during the synthesis procedure. Oxygen may also migrate through the nickel shell and iron core. $^{67-69}$ All of these mechanisms are likely occurring in concert to produce the overall core-shell structure, with a significant oxygen content in the iron core, a significant iron content in the nickel shell, and an iron-nickel oxide/hvdroxide in the shell. While complicated, this synthesis procedure and the resulting nanoparticle morphology provide an opportunity for future exploration of the bimetallic iron-nickel mixture, as well as control of the synthesis method to obtain specific spatial morphology and phases.

To determine the specific oxidation states of the metals in the samples, high-resolution XPS scans were performed at the Fe 2p and Ni 2p regions (Figure 3). The Fe 2p signal for Fe NPs exhibits $2p^{1/2}$ and $2p^{3/2}$ peaks at 724.1 and 710.5 eV, respectively. Fe 2p spectra suggest the presence of iron hydroxide and iron oxide species (Figure 3a).^{30,66,70,71} For Ni NPs, $2p^{1/2}$ and $2p^{3/2}$ peaks at 869.8 and 852.2 eV, respectively, are from metallic nickel.^{71,72} The larger peaks at 873.3 and 855.7 eV can be assigned to Ni(OH)₂ (Figure 3c),^{66,71} with a possible small contribution from NiOOH, where nickel is in the 3+ oxidation state.⁷² As expected, the Fe-Ni NPs are more complicated. Similar to Fe NPs, the $2p^{3/2}$ peak of iron in Fe–Ni NPs is centered at 710.4 eV, suggesting the presence of iron hydroxide and oxide species, perhaps with a smaller fraction of oxides as compared to Fe NPs (Figure 3b). However, the Ni 2p signal shows that none of the nickel in Fe-Ni NPs is metallic (Figure 3d). Rather, there appear to be several different nickel species present, and there may be a mixture of both 2+ and 3+ oxidation states. Peaks at 873.1 and 855.6 eV can be assigned to Ni(OH)₂. However, NiOOH in either the gamma or beta phase can also be attributed to the 855.6 eV peak.⁷² It is interesting to note that peaks located at 874.7 and 857.1 eV are both shifted to higher energies than the peaks assigned by Klaus et al. to either NiO (873.5 and 856.0 eV) or NiOOH (874.0 and 856.3 eV). However, possible differences in peak position between γ -NiOOH and β -NiOOH were not discussed.⁶⁶ Overall, the similarity of the Ni 2p peaks of the Fe-Ni NPs sample to the Ni 2p peaks of the Ni NPs sample, as well as the

broad shape of the satellite peaks, suggest that the nickel phase is primarily $Ni(OH)_2$.

Grosvenor et al. demonstrated successful interpretation of nickel hydroxide and nickel oxyhydroxide XPS spectra through an analysis that allowed multiple binding energies and contributions from both the Ni²⁺ and Ni³⁺ oxidation states.⁷ In their analysis of samples of Ni(OH)₂, γ -NiOOH, and β -NiOOH, Ni(OH)₂ had contributions to the XPS spectra from only Ni²⁺ and γ -NiOOH had contributions from only Ni³⁺, but β -NiOOH had contributions from both Ni²⁺ and Ni^{3+,73} Biesinger et al. also distinguished between γ -NiOOH and β -NiOOH, where again, γ -NiOOH only had contributions from Ni³⁺, but β -NiOOH had contributions from Ni²⁺ and Ni³⁺. In their analysis, the 2+ contribution to β -NiOOH causes an increase in peak position from 855.7 to 857.7 eV,⁷² which is similar to the increase in peak position observed in the data presented here. It should be noted that differences between the alpha and beta phases of Ni(OH)₂ were not identified in these studies.^{72,73} Similarly, the data presented in Figure 3 also demonstrate an increase in peak position for the Ni 2p spectra when Ni NPs are compared to Fe-Ni NPs. These results, in conjunction with the previously detailed studies on Ni 2p spectra and chemical species assignment,^{72,73} suggest that a portion of the nickel in Fe–Ni NPs was present as β -NiOOH, with $Ni(OH)_2$ as a primary phase.

To further understand the atom-specific chemistry and local structural environment of both iron and nickel in the nanoparticles, X-ray absorption fine-structure spectroscopy (XAFS) was performed. Fe-Ni NPs, along with a series of iron and nickel standards, were probed around the iron and nickel K-edge X-ray absorption transitions to identify the local structure near each element. Using X-ray absorption near edge structure (XANES) data from Fe-Ni NPs and appropriate standards, linear combination fitting (LCF) was performed to identify the stoichiometry of each of the iron- and nickelcontaining species. The Fe-XANES and Ni-XANES spectra for Fe-Ni NPs are shown in Figure 4a,b, respectively. The XANES data and LCF demonstrate the variety of metal speciation in Fe-Ni NPs. Probing Fe atoms in Fe-Ni NPs, the best LCF to the Fe-XANES data yields $50.3\% \pm 0.9\%$ bulk zerovalent Fe, $27.9\% \pm 0.6\%$ Fe(OH)₃, 18.1% $\pm 0.5\%$ Fe₂O₃, and 4.0% \pm 0.4% Fe₃O₄. Of the 156 possible combinations of standards, the top 5 fitting combinations all exhibited approximately 50% monometallic Fe and 25% to 30% $Fe(OH)_3$, with the remaining contribution to the LCF being a mixture of two other oxidized Fe species (Table S3 in the Supporting Information). Given the complexity of possible combinations

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Figure 5. (a) Fe K-edge EXAFS data for Fe-Ni NPs, Fe NPs, and the standard materials that resulted in the best LCF of the Fe-Ni NPs Fe-XANES data. (b) Ni K-edge EXAFS data for Fe-Ni NPs, Ni NPs, and the standard materials that resulted in the best LCF of the Fe-Ni NPs Ni-XANES data.

of oxidized Fe species, this outcome is to be expected. It is worth noting that there is no meaningful contribution to Fe²⁺ chelated to ATMP in the Fe-Ni NPs, indicating a potential displacement of ATMP from Fe to Ni during synthesis. The amount of oxidized iron is consistent with EDS mapping, while the amount of iron and nickel oxide interactions suggest significant incorporation of iron into the nickel-heavy exterior of Fe-Ni NPs. This result is also consistent with the XPS and EDS results, where both iron and nickel were identified in the surface of the nanoparticles. In general, discrepancies between these data and the data from XPS can be attributed to XPS being a surface technique while X-ray absorption spectroscopy is a bulk measurement of the entire nanoparticle sample. Because XANES measurements provide local structural and chemical information over the entire system, the combined XPS and XANES results suggest that iron atoms near the surface are in the form of oxides, while some metallic iron remains near the center of the nanoparticle core.

Similar analysis can be performed on the Ni-XANES data to better understand Ni speciation in the Fe-Ni NPs. LCF of the Ni-XANES data indicates that all nickel species are oxidized. The best LCF produced 85.5% \pm 1.6% α -Ni(OH)₂, 10.7% \pm 1.8% Ni²⁺ chelated to ATMP, and 3.4% \pm 0.6% β -NiOOH. The top 5 LCFs consisted of greater than 80% α -Ni(OH)₂ and approximately 10% Ni²⁺ chelated to ATMP (Table S4). The minimal contribution by a third and fourth Ni species are used to complete the fit, which did not drastically influence the goodness of fit. It should be noted that when metallic nickel is forced into the LCF, values for E_0 become unrealistic, which further indicates a complete absence of zerovalent nickel in these materials. These data correlate well with the results from XPS, showing that the nickel in Fe-Ni NPs is completely oxidized and not in the form of metallic nickel. While the XPS results suggest some β -NiOOH may be present, XANES LCF results suggest that most of the nickel is in the alpha hydroxide form. Because the LCF analysis was performed with known alpha and beta $Ni(OH)_2$ standards, the XANES analysis is likely more representative of the nickel phases present. The complementary results between XPS and Ni-XANES further indicate that the nickel is predominately on the surface. Additionally, the presence of Ni²⁺ chelated to ATMP confirms that the globular materials from STEM analysis are indeed Ni²⁺ bound to ATMP.

The monometallic nanoparticles (XANES edges shown in Figure S7) were analyzed using LCF as well. For Fe NPs, the best LCF resulted in 48.0% \pm 0.9% Fe(OH)₃, 36.1% \pm 1.5% metallic Fe, 8.5% \pm 0.5% Fe²⁺ chelated to ATMP, and 5.2% \pm

0.4% Fe₃O₄. The top LCF all exhibited metallic Fe and Fe(OH)₃ as major components, with minor contributions from Fe²⁺ chelated to ATMP and oxidized iron species (Table S5). The best LCF of Ni NPs resulted in a composition of 55.8% ± 0.8% metallic nickel, 32.7% ± 0.2% β-NiOOH, 9.9% ± 0.4% α-Ni(OH)₂, and 5.7% ± 0.2% β-Ni(OH)₂. This fit is substantially improved over the next top LCF (Table S6) and clearly reflects the complex oxide character in these nanomaterials.

After background subtraction and edge-step normalization, the extended XAFS (EXAFS) data were converted to k-space and k^2 -weighted (Supporting Information, Figure S8) and then Fourier transformed to r-space. Figure 5a shows Fe-EXAFS results for Fe-Ni NPs, monometallic Fe NPs, and the standard materials that resulted in the best LCF of the Fe-Ni NPs Fe-XANES data. For Fe-Ni NPs, the main feature is positioned 2.2 Å and is aligned with the Fe foil reference. Both peaks are at shorter distances than the known Fe-Fe nearest-neighbor distance of 2.48 Å in bcc Fe, which is expected due to uncorrected photoelectron phase shift, yet the alignment of these features suggests that a majority of the iron atoms are metallic (i.e., zerovalent). However, differentiation between Fe-Fe and Fe-Ni is difficult because the nearest-neighbor distances in metallic nickel are very similarly spaced. Nevertheless, the EXAFS observations for Fe-Ni NPs corroborate the LCF results that indicate that a significant fraction of the iron atoms are metallic. The lower-r features at 1.6 Å and 1.1 Å in Fe-Ni NPs are due to expected iron oxidation, which was also observed in the LCF analysis of Fe-XANES. Interestingly, Fe NPs exhibit EXAFS features at shorter metallic distances, which is often observed in disordered nanoparticles." Examination of the Ni K-edge EXAFS data for Fe-Ni NPs illustrates the lack of zerovalent nickel (Figure 5b). The main Ni-EXAFS feature for Fe-Ni NPs is positioned at 1.5 Å and essentially matches the Ni-EXAFS of α -Ni(OH)₂. This observation is quantitatively confirmed with the LCF in the previous section. Conversely, Ni NPs appear largely metallic from the EXAFS data, exhibiting a main feature that is shifted to smaller distances as compared to the bulk Ni foil (2.0 Å vs 2.1 Å). This slight shift in nearest-neighbor distances is frequently observed in EXAFS.74-76

While XAFS provides detailed local structure and chemical information in an element specific fashion, structural information past the nearest-neighbor distances is difficult to obtain for nanoscale materials. Atomic-scale structural information over longer length scales is desirable to help ascertain overall structural composition and long-range order, particularly for heterogeneous multicomponent materials such



Figure 6. Pair distribution function (PDF) analysis calculated from high energy X-ray diffraction measurements of Fe–Ni NPs, Fe NPs, and Ni NPs, showing (a) short-range order and (b) long-range order.



Figure 7. (a) OER cyclic voltammograms for Fe–Ni NPs, Fe NPs, and Ni NPs taken at 20 mV/s in 1 M NaOH. Each sample was cycled 30 times to allow the CV to stabilize. The CVs shown here are from the 31st cycle. (b) An enlarged view of the CVs near the OER onset potential showing redox features.

as Fe-Ni NPs. This knowledge can then be used to understand structure/function relationships to describe catalytic properties. As such, HE-XRD coupled to PDF analysis was performed on the bimetallic and monometallic nanoparticles to obtain longrange structural information at sub-Angstrom resolution. In atomic PDF analysis, diffraction patterns taken at sufficiently high energy are Fourier transformed over the entire diffraction pattern to provide atomic-scale structural information.^{77,78} As the Fourier transform accounts for both Bragg and diffuse features in the diffraction pattern, atomic PDF analysis is ideal for detailed structural determination of materials lacking long-range structural order,^{79–82} including nanomaterials.^{83–88} HE-XRD patterns were taken at 115 keV (Supporting Information, Figure S9a), converted into total structure functions (Figure S9b), and Fourier transformed to their corresponding atomic PDFs (Figure 6). The atomic PDF, $G(r) = 4\pi r [\rho(r) - \rho_0]$, exhibits peaks as a function of atomic pair distances when the local atomic density, $\rho(r)$, exceeds the average atomic density, ρ_0 . Interestingly, Fe–Ni NPs, Fe NPs, and Ni NPs all exhibit limited long-range order, with peaks in the atomic PDFs oscillating to zero at distances much shorter than the size of the nanoparticles. Moreover, the peaks in the PDFs do not correspond to traditional spacing of a bcc Fe or fcc Ni lattice. These observations, in conjunction with the nanoparticle sizes observed in the STEM analysis, indicate that the synthetic methods used to prepare the nanoparticles are inducing a

significant degree of structural disorder in these materials. This structural disorder likely has a direct impact on the resulting catalytic properties, as more disordered nanoparticles have been shown to be highly reactive.⁸⁹⁻⁹⁴ The first peaks in the atomic PDF represent the first coordination spheres in the material (i.e., bond lengths). Fe-Ni NPs exhibits an atomic pair distance at 2.50 Å, which is slightly larger than the 2.47 Å seen in metallic iron. There is a notable absence of a peak at 2.86 Å in the PDF for Fe-Ni NPs, which arises from known Fe-Fe distances along the edge of the bcc unit cell, which further suggests deviation from a regular metallic structure. A peak at 2.0 Å in Fe-Ni NPs corresponds to expected oxidized species and best reflects the Ni–O bond length in α -Ni(OH)₂ (as supported by Ni-XANES LCF). A shoulder positioned at 3.0 Å in the Fe-Ni nanoparticles does not correspond to any known crystalline iron or nickel metal distance, and it likely reflects the substantial disorder in these materials and/or possible longerrange Fe-O distances.95 Monometallic Fe NPs and Ni NPs display metallic bond lengths at 2.54 Å and 2.50 Å, respectively, which are longer than observed in their bulk metallic counterparts. Taken together, the atomic PDF analysis emphatically demonstrates the lack of order in these nanoparticles, which could have profound effects on their corresponding catalytic properties.

Electrochemistry. Electrocatalytic OER and methanol oxidation for the nanoparticle samples were performed using

Table 2. E	lectrochemical	Performance	Normalized	l to	Catal	yst Mass	for	Both	OER	and MeOH	í Oxid	lation"
						/						

_		OER	MeOH				
sample	OvP @ 10 mA/mg (mV)	maximum current density (mA/mg @ 1.58 V vs RHE)	OnP (V vs RHE)	maximum current density (mA/mg @ 1.58 V vs RHE)			
Fe NPs	408	82	1.56	31			
Ni NPs	421	39	1.34	213			
FeNi NPs	237	1795	1.40	1709			
^a Overpotentia	al (OvP) values for O	ER are reported at 10 mA/mg, onset potential	(OnP) values for	r MeOH are reported vs RHE, and maximum			

current density values are reported to reported at 10 million single single potential (0 m) values for the reported vs ferill, and ma current density values are reported for all three nanoparticle samples. Catalyst mass tested was 2 μ g.

cyclic voltammetry. Electrochemical measurements were made on three separate batches per sample (Fe-Ni NPs, Fe NPs, and Ni NPs) to ensure repeatability. Representative cyclic voltammograms (CVs) comparing the OER activity of Fe-Ni NPs to Fe NPs and Ni NPs in 1 M NaOH electrolyte are shown in Figure 7. Fe-Ni NPs shows a significant increase in response at higher potentials, while both Fe NPs and Ni NPs exhibit only a modest increase in current density over the entire voltage window, suggesting the bimetallic nanoparticles have higher activity for OER than the monometallic nanoparticles. Until recently, many studies concluded that β -Ni(OH)₂ was much more active for OER than α -Ni(OH)₂.^{32,96-98} However, Trotochaud et al. confirmed through the intentional incorporation of iron into α -Ni(OH)₂ and evaluation of iron-free α - $Ni(OH)_2$ catalysts that it is in fact iron incorporation into the Ni(OH)₂ phase that enables increased OER activity with aging in base and/or with repeat CVs.³² Prior studies evaluating the increase in performance of β -Ni(OH)₂ with age were likely studying iron-incorporated β -Ni(OH)₂. Furthermore, both Trotochaud et al. and Gao et al. demonstrated that iron-free α -Ni(OH)₂ is more active than iron-free β -Ni(OH)₂.^{32,99} While the XPS results reported here suggest a mixture of Ni(OH)₂ (of undetermined phase) and possibly both gamma and beta forms of NiOOH, XANES measurement interpretation suggests that the majority of nickel in bimetallic Fe-Ni NPs is in the form of α -Ni(OH)₂ with no observed contribution from β -Ni(OH)₂. The underlying iron core in Fe-Ni NPs also allows for iron incorporation into α -Ni(OH)₂. Though the results presented herein are complex due to the nanoparticle morphology and the heterogeneous nature of the sample, it appears overall that the synthesis method allows for the formation of iron-incorporated α -Ni(OH)₂ with possible γ/β -NiOOH phases present, and this phase structure enables significant OER activity. In contrast, Ni NPs contain much less $Ni(OH)_2$ (in both the alpha and beta form) than Fe-Ni NPs, and the purified electrolyte does not contain iron impurities. This combination of a lesser amount of catalytically active nickel species and lack of iron incorporation into that active species leads to the much lower performance of Ni NPs as compared to Fe-Ni NPs.

The overpotential for the bimetallic nanoparticles is also considerably lower than for each of the monometallic nanoparticles. At 10 mA/cm², Fe–Ni NPs had an overpotential of 311 mV. Neither Fe NPs nor Ni NPs reached a current density of 10 mA/cm² within the measured voltage window, further illustrating the superior performance of the bimetallic nanoparticles for OER. In order to quantitatively compare the bimetallic and monometallic nanoparticles, the overpotential for all three samples was measured at 1 mA/cm². Fe NPs and Ni NPs had an overpotential of 421 and 476 mV, respectively, while Fe–Ni NPs was significantly lower at 256 mV. Additionally, overpotential and maximum current density were calculated on a per catalyst mass basis (Table 2). All electrochemical experiments were performed on an asdeposited catalyst mass of 2 μ g and a mass loading of 29 μ g/ cm², based on nanoparticle concentration in the synthesized nanoparticle solution. The mass-normalized maximum current density (mA/mg, Figure S18) is significantly higher than the geometric surface area normalized current density (mA/cm²; Figure 7), and the current density of Fe–Ni NPs is a factor of 22× higher than the Fe NPs and a factor of 46× higher than the Ni NPs. The increase in mass-normalized current density illustrates the advantage of higher surface area to mass ratio for nanoparticle catalysts, where the measured current density for the Fe–Ni NPs (1795 mA/mg @ 1.58 V vs RHE) is one of the highest reported results thus far, as compared with other recently reported nanostructured and thin film catalysts.^{32,99–105}

An enlarged view of the features that appear near the onset potential demonstrate the differences in electrochemical behavior of the monometallic and bimetallic nanoparticles (Figure 6b). Ni NPs exhibit redox peaks consistent with the Ni(OH)₂/NiOOH transition in alkaline electrolytes. In contrast, Fe NPs do not give any indication of redox peaks, which is to be expected as the oxidation of iron to Fe^{2+}/Fe^{3+} occurs at negative potentials versus Ag/AgCl.³¹ However, as can be seen with Fe-Ni NPs, the incorporation of iron within nickel hydroxide causes the redox peaks to shift to slightly higher potentials, and there is a decrease in total peak area, which is consistent with that reported in other studies.^{22,31,32} This shift in the redox peaks is attributed to iron suppressing the transformation of Ni(OH)₂ to NiOOH.³¹ However, unlike some other reports,^{31,32} the oxidation peak height increases for Fe-Ni NPs. This result may due to the higher content of Ni(OH)₂ in Fe-Ni NPs as compared to Ni NPs (which contains a significant amount of metallic nickel) and/or an increase in the number of active sites available for nickel oxidation due to the incorporation of iron. The shape of the peaks also changes for the bimetallic nanoparticles. Ni NPs show two anodic peaks, the first of which may be an artifact of the oxidation of metallic nickel and the second peak being the oxidation of Ni²⁺ to Ni³⁺. In contrast, Fe-Ni NPs show only one oxidation peak. This oxidation peak is partially obscured by the rapid increase in current density due to OER. For both Ni NPs and Fe-Ni NPs, the ratio of the peak current densities (i.e., the current measured at the peak of the anodic sweep divided by the current measured at the peak of the cathodic sweep) is not equal to 1, indicating that for the conditions tested, the nickel redox reaction is not reversible. This irreversible behavior may be due to mechanisms including mass transport limitations and the phase transition between Ni(OH)₂, which is an insulator, and NiOOH, which is conductive.¹⁰⁶ Peak current densities, i_p , were measured at 1.40 V for the anodic sweep and 1.25 V for the cathodic sweep



Figure 8. Cyclic stability of (a) Fe NPs, (b) Ni NPs, and (c,d) Fe–Ni NPs in 1 M NaOH taken at a scan rate of 20 mV/s. The OER response remains nearly consistent during cycling for Fe–Ni NPs, while the redox peaks corresponding to Ni^{2+}/Ni^{3+} increase height with cycling. However, no further increase is observed after 30 cycles.



Figure 9. (a) Cyclic voltammograms of Fe-Ni NPs, Fe NPs, and Ni NPs in 1 M NaOH with 1 M methanol at a scan rate of 20 mV/s. CVs shown are after samples stabilized. (b) An enlarged view of the CVs near the OER onset potential showing features attributed to methanol oxidation.

for Ni NPs, and at 1.42 V for the anodic sweep and 1.33 V for the cathodic sweep for Fe–Ni NPs.

Electrochemical cycling has a pronounced effect on each of the three nanoparticle samples (Figure 8). Both monometallic nanoparticle samples show a noticeable decrease in OER activity with cycling (Figure 8a,b). This may be due a decrease in the number of active sites with cycling either from poisoning effects or changes in structure and composition. Fe NPs are particularly susceptible to uncontrolled oxidation when exposed to aqueous solutions, often transforming in color from black prior to electrochemical measurements to the brown color of rust after cycling. Several previous reports have shown an increase in OER activity with aging for nickel oxide catalysts, often attributed to the transformation of α -Ni(OH)₂ to β -Ni(OH)₂.³¹ However, as discussed previously, it is more likely that the increase in OER activity was actually a result of iron impurities from the electrolyte incorporating into Ni-(OH)₂.^{28,32,66} In purified electrolyte, decreased OER activity



Figure 10. (a,b) CVs of Fe-Ni NPs in the absence and presence of 1 M methanol. (c,d) CVs of Fe-Ni NPs with 0.2 M, 1 M, and 2 M methanol added to the electrolyte.

with aging has been observed and is attributed to a decrease in the number of active defect sites or reduced OH⁻/O₂ transport rates within the layered structure of β -Ni(OH)₂.³² Here, Ni NPs were cycled in purified NaOH electrolyte to avoid possible contributions from iron impurities. With cycling, there is a significant decrease in OER activity as well as changes to the anodic peak assigned to the Ni(OH)₂/NiOOH transformation. While the metallic nickel oxidation peak seems to remain unchanged, the Ni²⁺/Ni³⁺ peak decreases in intensity and shifts to higher potentials, suggesting the formation of β -Ni(OH)₂ with cycling. The changes to the Ni²⁺/Ni³⁺ anodic peak corresponding to the decreasing OER activity suggests that Ni(OH)₂/NiOOH is indeed the active species in these nanoparticles, with metallic nickel contributing very little to the OER activity.

In contrast to the monometallic nanoparticles, Fe–Ni NPs exhibit very stable OER activity with cycling (Figure 8c,d). Additionally, the redox peaks prior to the onset of OER experience increased activity with cycling up to 30 cycles, as well as a shift toward lower potential. This suggests an increase in the number of the active sites with cycling until the sample stabilizes, and the shift toward lower potential could indicate further incorporation of iron into the nickel hydroxide shell upon cycling. Above 30 cycles, no further increase is observed. Thus, incorporating iron and nickel into a single nanoparticle benefits the catalytic performance of each metal individually. The deposition of a nickel shell protects the iron core nanoparticle from uncontrolled oxidation, which leads to better retention of OER activity as compared to Fe NPs. At the same time, the nickel shell benefits from the incorporation of iron into its structure and iron-directed formation of more active nickel species.

CVs of Fe-Ni NPs, Fe NPs, and Ni NPs in 1 M NaOH after 1 M methanol was added show the electrochemical activity of each of the samples (Figure 9). Onset potentials (vs RHE) and maximum measured current densities (mA/mg) are reported in Table 2. Again, Fe NPs show very little catalytic activity. A slight increase in the current density remains at higher voltages due to oxygen evolution, but the maximum current density decreased slightly when methanol was added to the electrolyte. The opposite behavior is seen for Ni NPs. With the addition of methanol, the maximum current density increases. Additionally, a new anodic peak appears that has a significantly higher current density than what was seen for Ni NPs in purified 1 M NaOH. This new peak has a lower onset potential and is shifted toward a lower potential as compared to the Ni²⁺/Ni³⁺ redox peak. As such, the new peak can be attributed to methanol oxidation. During the reverse cycle, methanol oxidation continues to take place, which is believed to be a result of the regeneration of active adsorption sites on the catalyst from the removal of adsorbed intermediates and products.^{39,107} A cathodic peak remains at the same potential as seen for pure 1 M NaOH, but the intensity has been dampened (Figure S10b in Supporting Information). For Fe-Ni NPs, there are also new anodic peaks due to methanol oxidation. A comparison of Fe-Ni NPs in both the absence and presence of methanol illustrate these differences in electrochemical behavior (Figure 10a,b). The peaks are less well-defined because of the overlap with the

significant increase in current density from OER. Similar to the CVs measured without methanol (Figure 7), the oxidation peak for Fe–Ni NPs has a higher onset potential than Ni NPs. The peak current density is also higher, demonstrating the superior catalytic activity of the bimetallic nanoparticles toward methanol oxidation as well as OER.

Changing the methanol concentration in the electrolyte has a noticeable effect on the electrochemical properties of the bimetallic nanoparticles (Figure 10c,d). As the concentration of methanol in the electrolyte increases from 0.2 to 2 M, the methanol oxidation peak increases. However, the increase in current density from methanol oxidation is not linear with increasing methanol concentration. Above 2 M methanol, there was a more modest change in the anodic peak current. It has been observed that at lower methanol concentrations, methanol oxidation is a diffusion-controlled process.^{39,107-109'} At higher concentrations, methanol oxidation is limited by the kinetics of the reaction and no longer depends on the amount of methanol available.^{108,109} The maximum current density due to OER also decreases slightly with the addition of methanol for Fe-Ni NPs and continues to decrease with increasing concentrations of methanol. The increasing methanol concentration may lead to higher surface coverage of the nanoparticles with methanol and the reaction intermediates. This will block OH⁻ from accessing reactive sites on the catalyst, limiting the oxygen evolution reaction and leading to a decrease in the maximum current density.¹⁰⁹ For comparison, Fe-Ni NPs were also measured for ethanol oxidation at concentrations of 0.2 M, 1 M, and 2 M ethanol (Supporting Information, Figure S13). Similar to the behavior observed with methanol, an anodic peak appears prior to the increase in current density due to OER. The peak height increases with ethanol concentration, but at the same time, the OER activity decreases.

CONCLUSIONS

Multicomponent iron-nickel nanoparticles were prepared using a simple, multistep synthesis procedure in water under ambient conditions. For comparison, monometallic iron and nickel nanoparticles were also prepared. The iron-nickel nanoparticles exhibit a core-shell structure, with an iron/iron hydroxide core composed of nanoscale grains surrounded by a thin iron-incorporated nickel hydroxide shell. Similar to the monometallic iron nanoparticles, a portion of the iron in the bimetallic nanoparticles is in the form of iron oxides and iron hydroxides. The nickel shell in the bimetallic nanoparticles is completely oxidized, most of which is in the form of α -Ni(OH)₂ with a small contribution from β -NiOOH. In contrast, the nickel hydroxide in the monometallic nickel nanoparticles is in the form of α -Ni(OH)₂ and β -Ni(OH)₂, with a considerable amount of metallic nickel present as well. Electrochemical measurements clearly show the significant effects of these differences for the three nanoparticles samples. The iron-nickel nanoparticles exhibit significantly higher activity toward the oxygen evolution reaction and much lower overpotential when compared to the monometallic iron and nickel nanoparticles. At 1 mA/cm², the overpotential for the monometallic iron and nickel nanoparticles was 421 mV and 476 mV, respectively, while the bimetallic Fe-Ni nanoparticles had a greatly reduced overpotential of only 256 mV. At 10 mA/cm², bimetallic Fe-Ni nanoparticles had an overpotential of 311 mV. While the β -Ni(OH)₂ found in the nickel nanoparticles was historically thought to be more reactive than the α -Ni(OH)₂ found in the iron-nickel

nanoparticles, our results are consistent with recent findings that α -Ni(OH)₂ is more active than β -Ni(OH)₂ and that iron incorporation enables high activity of Ni(OH)₂/NiOOH. For methanol oxidation, the iron–nickel nanoparticles again outperform both of the monometallic nanoparticle samples. These results show the superior performance of the prepared iron–nickel nanoparticles as catalysts for both OER and methanol oxidation and thus leads to the opportunity for further development of nonprecious metal catalysts for a variety of alkaline electrochemical applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b02552.

TEM images of Fe NPs and Ni NPs; elemental analysis of Ni-rich particles; ICP results for Fe NPs, Ni NPs, and Fe–Ni NPs; XPS survey spectra and detailed composition results; details of XANES LCF analysis; XANES results for Fe NPs and Ni NPs; EXAFS results for Fe NPs and Ni NPs; HE-XRD patterns for Fe NPs, Ni NPs, and Fe–Ni NPs; additional electrochemistry results; experimental details for ionomer synthesis; error analysis of electrochemistry results; and current density data based on nanoparticle mass for OER and methanol oxidation (PDF)

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The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Funding for this research was provided by the NIST Nanomanufacturing Initiative through the NIST Nanoparticle Manufacturing Program. The authors would like to acknowledge Roy H. Geiss for TEM images of Fe NPs and Ni NPs (Supporting Information, Figure S1). ICP-MS measurements were performed at the Laboratory for Environmental and Geological Studies at the University of Colorado at Boulder. XPS measurements were performed by Rocky Mountain Laboratory, Inc. in Golden, CO. XAFS and HE-XRD measurements were performed in 12-BM and 11-ID-C beamlines at the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract DE-AC02-06CH11357. N.S. acknowledges National Science Foundation award number DMR-1063150, REU Site: Research Experiences for Undergraduates in Renewable Energy. The authors also acknowledge Army Research Office MURI award W911NF-11-1-0462.

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