

PRF #: 57330-DN17

**Project Title:** Influence of Metal Incorporation on the Organizational Structure of Sulfonated Block Copolymers in Solution

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### Progress of Research

The focus this research thus far has been a fundamental investigation of how organic charged polymers and small molecule chelator-type ligands impact the physical and chemical properties of metallic and metal oxide nanoparticles. The suite of ligands and polymers discussed herein are either produced through petroleum refining to fine chemicals processes or are under consideration and research for use in petroleum extraction processes. For example, carboxymethylcellulose materials have been studied as a hydraulic fracturing fluid additive to control viscosity. The aminophosphonic acid ligands used are common scale inhibitors in oil field operations and are produced via reactions that involve petrochemicals such as formaldehyde. The physical interactions of these polymers and ligands with metal/metal oxide surfaces are critical for a range of applications in the petroleum industry, from hydraulic fracturing to petroleum processing, scale inhibition, and catalytic chemical processes. Over the past year, we have continued our research on specific organic ligands in the coordination of metals, moving into the study of precipitation of monometallic and bimetallic oxide nanoparticles and focusing specifically on the ligand aminotrimethylene phosphonate (ATMP).

ATMP was used as a ligand stabilizer during the formation of iron-nickel oxide nanoparticles, where the composition of iron and nickel were varied, and the nanoparticles were then evaluated with electrochemistry to understand current-voltage behavior.

In Figure 1a, results show that the iron content of the nanoparticles causes an increase in the current density produced, but at iron percentages above 50%, the current decreases. Further, the iron content of the nanoparticles also has a direct impact on the voltage at which nickel redox chemistry occurs. In Figure 1b, the nickel redox peak, where  $\text{Ni}^{2+}$  transitions to  $\text{Ni}^{3+/4+}$ , shifts from an overpotential of 150 mV at 0% Fe to as high as 260 mV for an iron content of 50% Fe. The increase in current density and the shift in nickel redox voltage are largely correlated, where an increase in current density produced also results in an increase in the nickel redox peak voltage. These results have implications for the role that iron plays in controlling nickel electrochemistry, which could impact a range of energy-related technologies from water electrolysis to batteries and fuel cells, where petroleum-based polymers play critical roles as ligands, binders, and membrane materials. Overpotentials are calculated based on the theoretical potential for the oxidation of water to oxygen, 1.23 V.

We have performed a full suite of characterization on the ligand-stabilized iron-nickel oxide nanoparticles, including transmission electron microscopy, x-ray diffraction, and x-ray photoelectron spectroscopy (XPS). XPS results are shown in Figure 2, where these data are representative of the surface chemistry of the as-synthesized nanoparticles. Results show that the relative composition

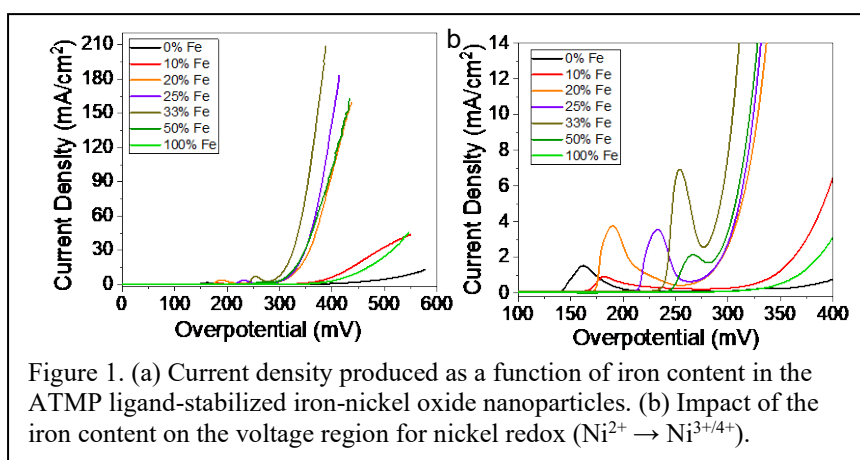


Figure 1. (a) Current density produced as a function of iron content in the ATMP ligand-stabilized iron-nickel oxide nanoparticles. (b) Impact of the iron content on the voltage region for nickel redox ( $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+/4+}$ ).

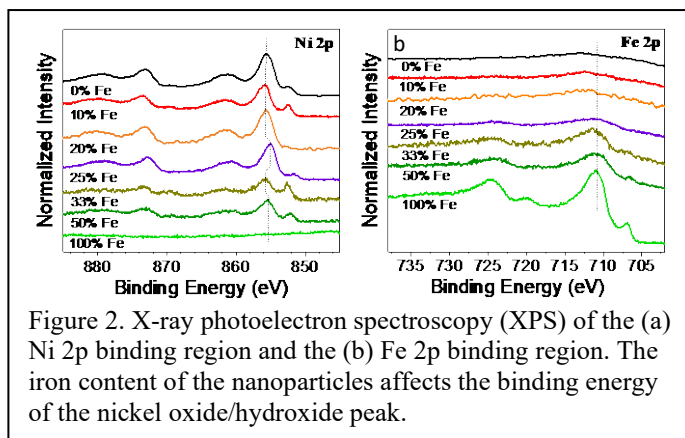


Figure 2. X-ray photoelectron spectroscopy (XPS) of the (a) Ni 2p binding region and the (b) Fe 2p binding region. The iron content of the nanoparticles affects the binding energy of the nickel oxide/hydroxide peak.

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of the iron and the nickel varies at the surface of the nanoparticles as a function of theoretical iron-nickel content used during synthesis. In addition, the peak position (855 eV) of the primary oxide/hydroxide peak in the Ni 2p binding region shifts with changing Fe content. This result may indicate changes in oxide vs hydroxide surface chemistry. In addition, a small metallic peak at 852 eV is observed, suggesting that the as-synthesized nanoparticles have both nickel metal and nickel oxide/hydroxide species. Similarly, both iron oxide and iron metal contributions are observed for higher Fe content samples in the Fe 2p binding region.

We have used our custom-designed in situ cell to perform a full suite of Raman spectroscopy measurements in liquid and electrochemical environments. The purpose of designing and using this cell is to be able to probe metal/metal oxide materials and their dynamic chemistry in aqueous, solvent, and humid environments, as well as when the experimental materials are held under an applied potential. All measurements were performed in an aqueous electrolyte solution of 1 M NaOH. In Figure 3, we observe that as the nickel content in the nanoparticles decreases, the emergence of nickel oxyhydroxide features (peaks at 478 and 559  $\text{cm}^{-1}$ ) shifts to higher voltages. This shift to higher voltages continues to increase as iron content increases, from 10% Fe to 50% Fe. This shift to higher voltages mirrors the positive shift in the nickel redox peak observed in Figure 1b with increasing iron content. The in situ Raman spectroscopy results thus confirm the inferred nickel redox behavior from the electrochemistry experiments and demonstrate that in situ electrochemical spectroscopy techniques are critical for understanding how chemistry influences electrochemical response and how surface chemistry changes in the aqueous and electrochemical environments.

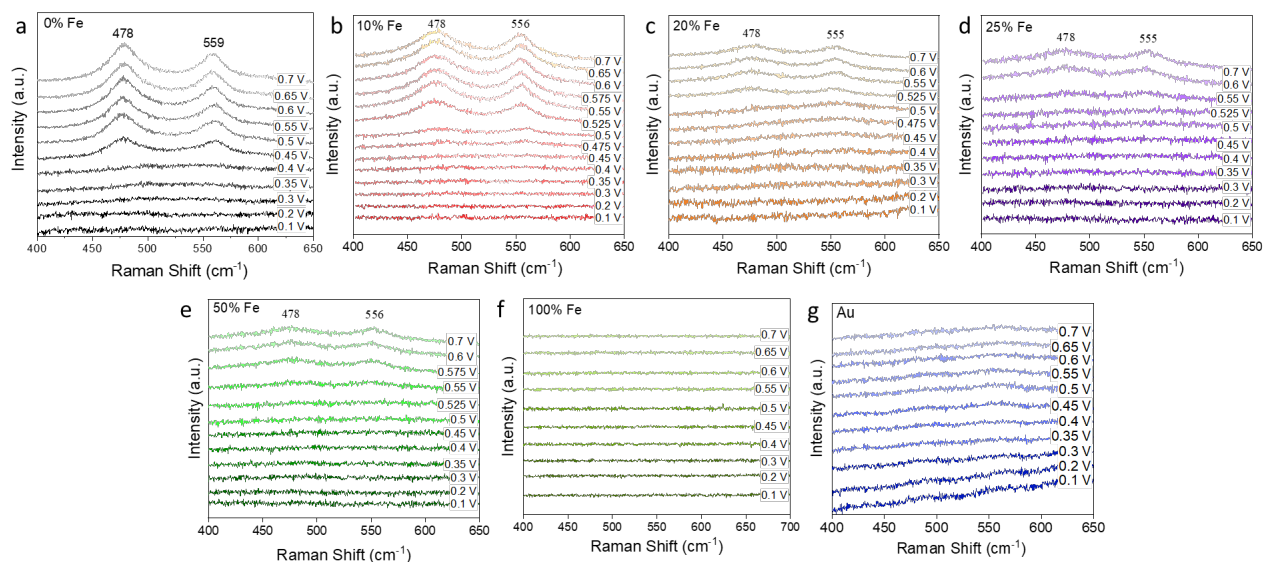


Figure 3. In situ electrochemical Raman spectroscopy characterization of iron-nickel oxide nanoparticles as a function of iron content: (a) 0% Fe, (b) 10% Fe, (c) 20% Fe, (d) 25% Fe, (e) 50% Fe, (f) 100% Fe, and (g) the gold (Au) substrate used as the support for all nanoparticle experiments.

### Impact on the Careers of the PI and Students

This grant has enabled the PI's research group to develop several in situ measurement techniques, including QCM, Raman spectroscopy, and more recently, Fourier transform infrared spectroscopy (FTIR). We have spent two years developing custom-designed cells and are now using both in situ Raman spectroscopy and in situ FTIR throughout the research projects in the group. These techniques and knowledge that has been gained as a result of the ACS PRF grant will have a lasting impact across all of our research activities into the future. The grant has supported a significant effort to develop these techniques and the cells and setups required, and it is expected that the PI's research group will continue to use these techniques across all projects to conduct fundamental research on metal/metal oxide materials and ligand-metal interactions, as well as on future materials systems. The postdoc who was been funded has expanded her expertise to new fields, such as electrochemistry, and will have several high impact publications from this work. In addition, she was successfully recruited into an industrial research position this past year and is now working full time as a Ph.D.-level scientist. In addition to a postdoctoral researcher, this grant also involved two undergraduate researchers and two Ph.D. students in the research group. All of the students involved have learned a diverse set of skills and have been involved collaboratively in this research, which will have a positive impact on their careers.