3-D Printed NiFeMn Alloy as a Bifunctional Catalyst for Oxygen Evolution Reaction and Oxygen Reduction Reaction

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*Wet lab experiments conducted before COVID-19; data analysis and simulations done remotely

Abstract

Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are critical to many important technologies such as fuel cells, electrolysis, and many other energy conversion and storage devices. A material that can catalyze both OER and ORR would allow for the advent of new technologies, such as reversible fuel cells and rechargeable metal-air batteries. Currently, most catalysts are only capable of catalyzing either OER or ORR, but not both. There are few bifunctional catalysts which catalyze both OER and ORR, but the ones that do exist, such as iridium oxide, are too expensive or scarce. The purpose of this project is to create a low-cost bifunctional catalyst that can catalyze both OER and ORR. Our work with nickel-iron-manganese alloys has demonstrated that it is possible to create a bifunctional catalyst from non-precious metals, but further work must be done to determine the optimal ratio of Ni, Fe and Mn that allows for both OER and ORR catalytic activity.

Background

Oxygen Evolution and Reduction Reactions

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ [1]

Equation 1, also referred to as the oxygen evolution reaction (OER), is the half reaction that occurs at the anode during electrochemical splitting of water. Most catalysts that show good activity for OER are expensive and rare, such as iridium.

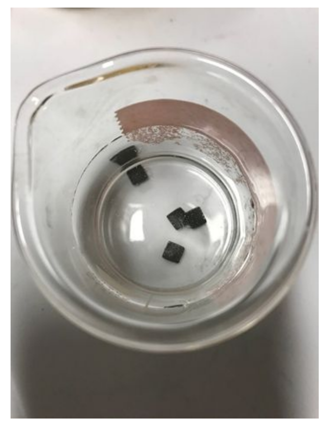
The oxygen reduction reaction (ORR) in an aqueous solution can reduce oxygen to either H_2O or H_2O_2 depending on the pathway taken. ORR is useful for reversible fuel cells and rechargeable metal-air batteries. Currently, the best catalyst for ORR is platinum, which is rare and costly.

NiFeMn Alloys

Dr. Detsi's previous research has demonstrated that nickel-iron (NiFe) alloys have displayed catalytic activity for oxygen evolution reaction.[1] This nickel-iron alloy had nanoscale porosity, giving it increased surface area for enhanced catalytic activity. Unexpectedly, adding in manganese to the alloy gave it an additional capacity for ORR catalytic activity. This result suggests that a unique composition of NiFeMn with the correct ratio of elements could yield both ORR and OER activity.

Methods and Techniques

Dealloy NiFeMn Samples in $(NH_4)_2SO_4$



Dealloying removes some manganese from the alloy, leaving behind a nanoporous material

Perform Energy Dispersive X-ray Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) on samples

Make Slurry for Cyclic Voltammetry (CV) Testing

70% NiFeMn (5 grams)
20% carbon (1.5 grams)
10% PVDF Binder (0.0179 mL)

Grind all of this together and spread out on carbon paper. Place in vacuum oven at 90 Celsius to dry overnight.

Repeat same procedure, but without the 5 grams of NiFeMn, to create a reference to compare to

Run CV Tests to Determine OER and ORR Catalytic Activity

Working electrode: Slurry

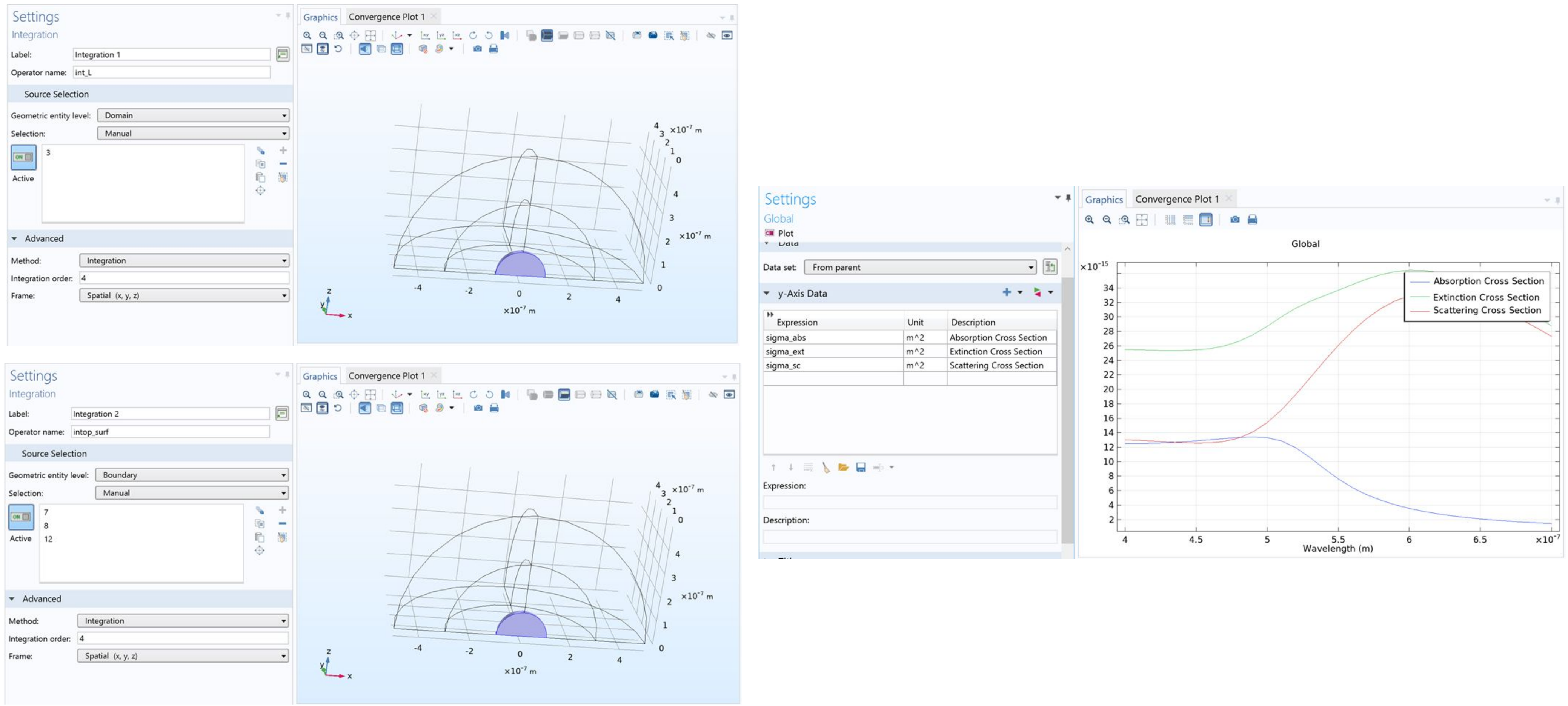
Counter electrode: Platinum

Reference Electrode: Hg/HgO in 1M KOH

Electrolyte: N_2-saturated 1M NaOH

Electrodes are connected to the potentiostat, where the data can be analyzed remotely.

Run Simulations to Examine Nanoparticle Interactions with Light



Results and Future Direction

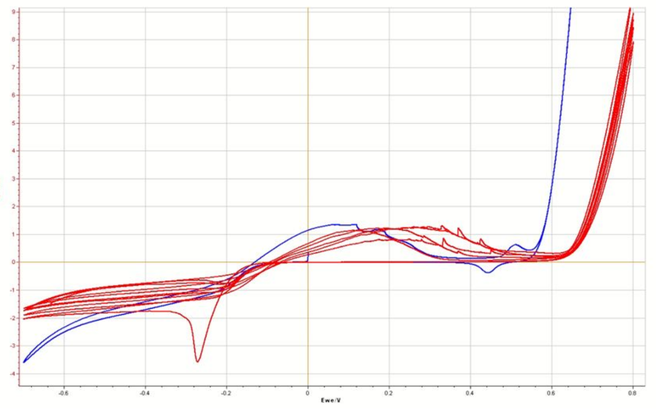
EDS of Samples

	Ni (at.%)	Fe (at.%)	Mn (at.%)
Sample 1	60.3	23.9	15.8
Sample 2	65.0	22.7	12.6
Sample 3 (Not dealloyed, at.% estimated)	15	15	70

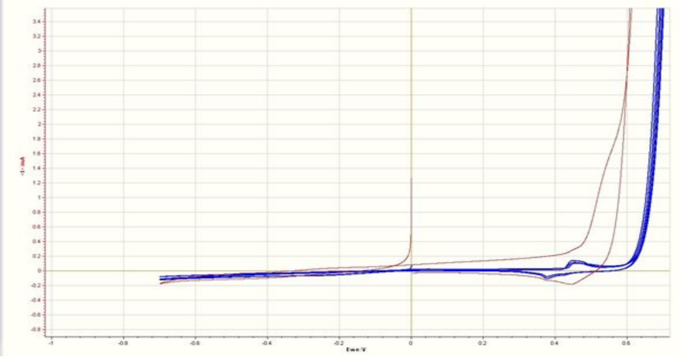
CV Curves

Blue curves represent the reference material, red curves represent the slurry with the NiFeMn alloy

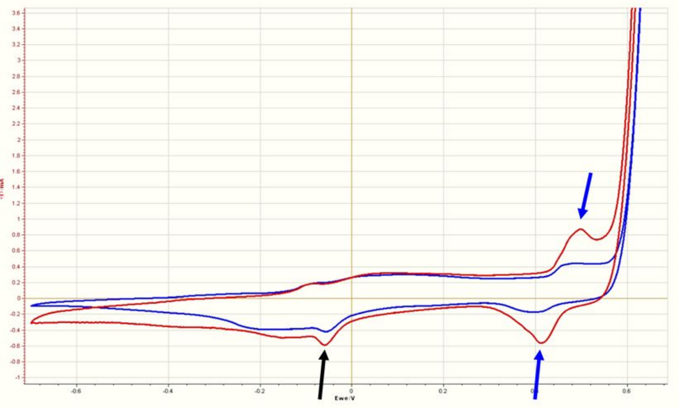
Sample 1:



Sample 2:



Sample 3:



Sample 1 showed both OER and ORR activity. Sample 2 showed OER activity but minimal ORR activity. Sample 3 showed OER activity, but the reduction peak (black arrow) cannot be conclusively determined to be ORR until the test is done again in a nitrogen saturated environment. It seems that dealloying for too long, as in the case of Sample 2, removes too much manganese and reduces the ORR activity. The future step is to dealloy a series of samples with residual Mn content varying from minimal to pristine and test them under nitrogen saturated environments.

Simulation: The model successfully determined the absorption, scattering, and extinction cross sections for nanoparticles. The next step is to apply the same model to a nanoporous geometry, simulating a material like the nanoporous NiFeMn alloy created.

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1. ***Energy Environ. Sci.***, 2016,**9**, 540-549