FMRI RET 2015-Characterizations Of Iron-Based Metal-Organic Frameworks

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Abstract

The need for cost-effective and efficient alternative energy systems has encouraged research in polymer exchange membrane fuel cells. Platinum group metals (PGM) are the conventional electrocatalysts at the cathode of PEMFCs. The high cost and limited availability of these metals has led to investigations in efficient non-PGM electrocatalysts. Metal-Organic Frameworks (MOFs), a family of porous crystalline materials have been used as a sacrificial species in an attempt to reduce the need for PGM catalysts. This three part study will examine the effects of transition metal content in a modified Metal-Organic framework (ZIF-7) as a self-sacrificing precursor for an ORR catalyst. The first phase of the study examined cobalt based MOF. During this phase, an iron based MOF will be characterized.

Background

Clean renewable energy is a vital and growing need in the global economy. Polymer Exchange Membrane Fuel Cells (PEMFCs) are an effective alternative energy source that has been available for decades. Their use is severely limited by their high cost in comparison to other options. Thus, research into optimizing their performance and lowering their cost is ongoing. One area of research is to replace the significantly higher levels of platinum at the cathode (5-10 times greater than at the anode) and improve the oxygen reduction reaction (ORR). [1] Previous research has demonstrated the potential of MOFs that have undergone post-synthetic modification (PSM).[2,3]

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs that exhibit better thermal and chemical stability than MOFs in general. Metal exchange (ME), a type of PSM, will be used to replace the zinc atoms within the structure with various transition metals. Previously, in the first part of the study, samples of cobalt substituted for zinc in ZIF-7 were created but with limited success and reproducibility. In this phase of the study, iron was chosen as the substitution metal as previous research has shown the great potential of iron-carbon composites.[4] Once these samples were synthesized, characterization of their structures could begin. Ultimately, the goal is to better understand the mechanism behind the ORR. A systematic study of the ORR activity of these transition metals can further knowledge and understanding of the factors that contribute to catalytic activity and directly lead to better design of efficient and inexpensive catalysts.

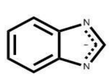
$Zn(NO_3)_2 \cdot 6H_2O$ $Co(NO_3)_2 \cdot 6H_2O$	+		+	*N,N*-dimethylformamide
0.75	:	1	:	150

Fig 1. Synthesis schematic of ZIF-7

Objectives

- Synthesis of iron based MOF
- Characterization of ME samples using Powder X-ray diffraction (PXRD), Energy Dispersive X-ray Spectroscopy (EDS), and Scanning Electron Microscopy (SEM)

Approach

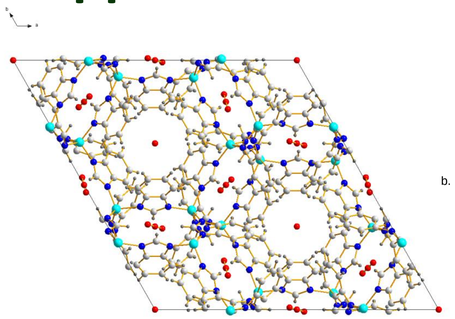


Fig 2. Crystal structure of ZIF-7

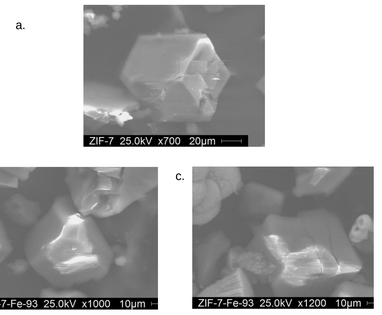


Fig 3. SEM images of a) ZIF-7 b) ZIF-7-Fe

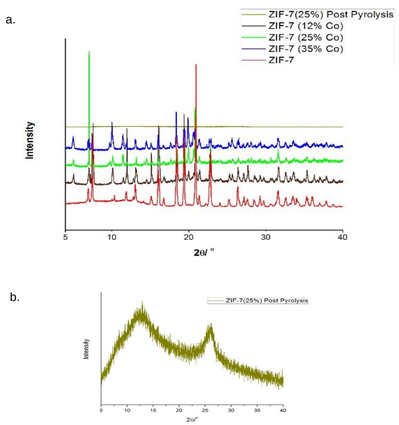


Fig 4. a) PXRD comparison of cobalt analogs. b) ZIF-7 (25%) Co post pyrolysis

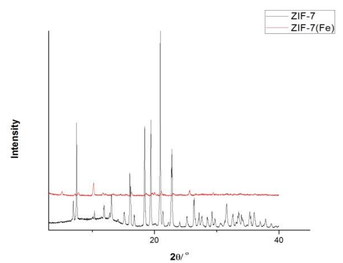


Fig 5. PXRD comparison to parent ZIF-7 to ZIF-7 Fe (30%)

Fe content by mass (%)	
ZIF-7(Zn)	30
	47
	62
	93

Table 1. Fe content by mass compared to Zn

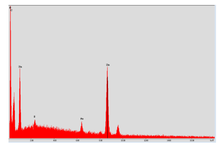


Fig 6. EDS spectrum of ZIF-7

Conclusions and Future Work

Analysis of the samples demonstrated the successful synthesis of the Iron MOF. Therefore catalysis studies can commence. We will be using a rotating ring disk electrode to determine the onset potentials and electron transfer numbers for the ORR.

Referenced Resources

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For more information about the program visit: http://fmri-ret.eng.usf.edu/. The Research Experience for Teachers (RET) at the Functional Materials Research Institute at USF is funded by the National Science Foundation under award number 1301054.