FMRI RET 2014-Exploration in Transmetalation of Co-ZIFs as Precursors for Oxygen Reduction Reaction Electrocatalysts in Polymer Exchange Membrane Fuel Cells

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Abstract

The potential of fuel cells as a component of alternative energy systems has encouraged research in optimizing their performance and cost-effectiveness. Platinum group metals are currently the most widely used electrocatalysts for the oxygen reduction reaction (ORR) at the cathode in polymer exchange membrane fuel cells (PEMFCs). Since reserves of platinum group metals are limited and expensive, explorations into alternative materials have been at the forefront of fuel cell research. In this study, a zinc based Metal-Organic framework (ZIF-7) will be modified as a self-sacrificing precursor for an ORR catalyst. To determine the effect on the catalytic activity and potentially gain an understanding of the mechanism behind the ORR reaction in this system, zinc will be exchanged with varying amounts of cobalt.

Background

The growing need for clean, renewable energy is an issue of global concern that is being addressed in a variety of ways. PEMFCs are of particular interest and their use in alternative energy systems could be expanded if their performance could be optimized and their cost-effectiveness increased. One of the main concerns with increased PEMFC use is the cost of the platinum catalyst. The ORR at the cathode is significantly slower than the oxidation of H_2 at the anode and requires 5-10 times the amount of platinum.[1] Potentially, MOFs could be a lower cost, more readily available solution.[2,3]

Zeolitic imidazolate frameworks (ZIFs) are a subclass of metal organic frameworks (MOFs) that generally exhibit better thermal and chemical stability than other MOFs. Metal exchange (ME), a type of post-synthetic modification (PSM) will be used to decorate ZIFs with varying metal nodes. Previously, in Approach 1, samples of 10%, 25%, and 35% substitution of cobalt for zinc in ZIF-7 were created by co-synthesis. A second approach for creating high percentage ME is being investigated. If these samples can be synthesized, they could be used 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.

Objectives

- Create protocol for ME using PSM (Approach 2)
- Characterization of ME samples using powder X-ray diffraction (PXRD)
- Comparison of methods used in Approaches 1 and 2

Approach 1

Samples were synthesized solvothermally with benzimidazole, *N,N*-dimethylformamide, and varying amounts of zinc nitrate and cobalt nitrate. PXRD analysis confirmed the retention of crystallinity, and ICP-MS studies were used to determine cobalt concentrations in the frameworks.

Figure 1. ME on ZIF-7 using Approach 1 (co-synthesis). Solutions range from 100% to 10% zinc to cobalt.

Approach 2

ZIF-7 was submerged in metal salt solutions of varying concentrations and temperatures which allowed the metal ions of the framework to be replaced by the metal ions of the salt.

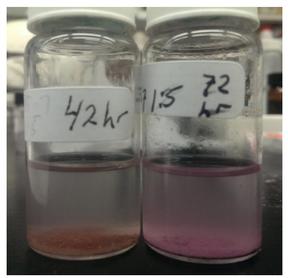

Figure 2. Approach 2 samples post metal and solvent exchange.

Figure 3. Approach 2 sample immediately following drying.

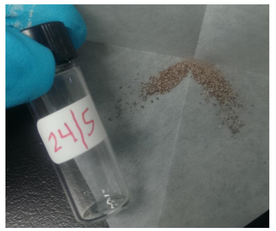

Figure 4. . Approach 2 sample 5 minutes after drying.

Figure 5. Approach 2 sample 10 minutes after drying.

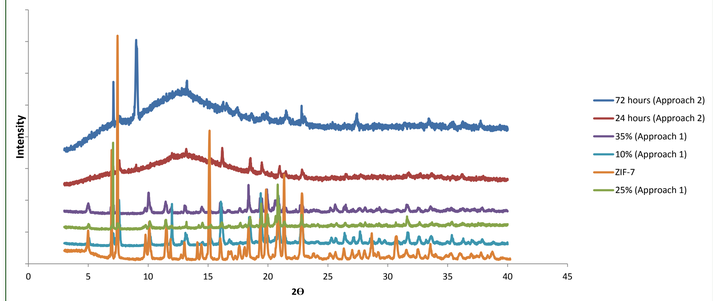

Figure 6. PXRD patterns for selected samples from Approaches 1 and 2.

Conclusions and Future Work

Although color change was evident in Approach 2, in comparison to Approach 1, the PXRD patterns showed more significant deviance from the parent ZIF-7. This can be attributed to either partial decomposition or a complete change in crystal structure. Further investigation in condition optimization for Approach 2 is needed. So far, Approach 1 is the most promising and least time consuming method for ME in this study.

References

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