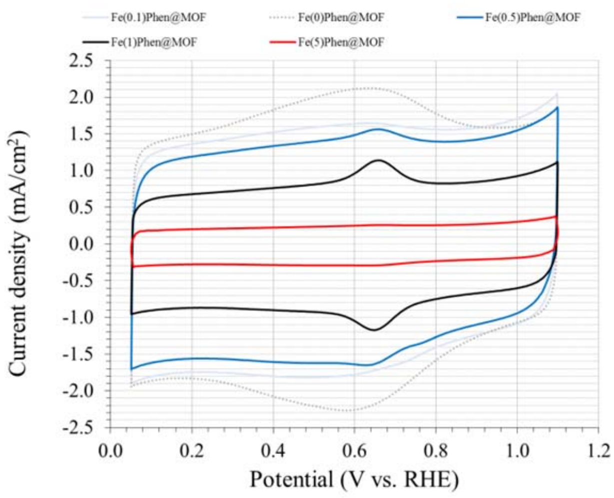
Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Develop high activity, low cost non-PGM fuel cell electrocatalyst and stable supports

A unique approach has been developed to probe the non-PGM catalyst active site for the Oxygen Reduction Reaction (ORR) for PEMFC. Iron based functionalities have been engineered into Metallic Organic Framework (MOF) catalysts to evaluate their impact on activity for the ORR. A series of FePhen@MOF catalysts have been synthesized with varying [Fe] to investigate the effect on electrochemical and electrocatalytic properties. The magnitude of the $Fe^{II/III}$ redox couple and the electrochemical surface area are analyzed to determine if there is a correlation between [Fe] and the ORR onset potential and/or the relative number of active sites.



Cyclic Voltammogram for FePhen@MOF catalysts showing the effect of varying Fe content

Awards and Recognition

Invention disclosure initiated.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature

Date

LDRD-2016-00025
LDRD Report

Develop high activity, low cost non-PGM fuel cell electrocatalyst and stable supports

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Subcontractor:
Savannah River Consulting, LLC

Project Type: Standard

Project Start Date: October 1, 2015
Project End Date: September 30, 2017

A unique approach has been developed to probe the non-PGM catalyst active site for the Oxygen Reduction Reaction (ORR) for PEMFC. Iron based functionalities have been engineered into Metallic Organic Framework (MOF) catalysts to evaluate their impact on activity for the ORR. A series of FePhen@MOF catalysts have been synthesized with varying [Fe] to investigate the effect on electrochemical and electrocatalytic properties. The magnitude of the $Fe^{II/III}$ *redox couple and the electrochemical surface area are analyzed to determine if there is a correlation between [Fe] and the ORR onset potential and/or the relative number of active sites.*

FY2016 Objectives

- Synthesize a series of FePhen@MOF catalysts
- Physical characterization (bulk composition, surface composition)
- Electrochemical characterization (CV, RRDE)

Introduction

Worldwide efforts to produce durable, highly active non-PGM electrocatalysts have resulted in slow, incremental improvements in activity as well as a partial understanding of the catalytically active site. To achieve a breakthrough in activity, a more complete understanding of the nature of the non-PGM ORR active site is needed. The composition of the active site is currently under debate, which has received heightened attention recently. In particular, the role of iron and/or Fe-N_4 complexes have in catalyzing the ORR is central to the debate. Most evidence suggests either iron has a direct role in the ORR catalysis or it influences the formation of the active site. This work focuses on developing a better understanding of the role iron has in the ORR.

A series of FePhen@MOF catalysts have been synthesized with varying [Fe] to investigate the impact, if any, on the electrochemical and electrocatalytic properties. The FePhen@MOF catalyst type was chosen for this work because it has excellent activity for the ORR and is easily synthesized with varying iron content. Elemental and surface analysis of the FePhen@MOF catalysts shows the incorporation of iron in a targeted and controlled manner. In conjunction with the electrochemical results, insight into the nature of the ORR active site and the role iron plays can be gained. This work has the potential to impact future catalyst development by improving the active site knowledge base.

Approach

FePhen@MOF catalysts consist of a MOF that is formed of the ZIF-8 type with Fe and phen (phen=1,10-phenanthroline) in situ, resulting in encapsulation of FePhen complexes. ZIF-8 is a zeolitic imidazole framework (ZIF) synthesized from 2-methylimidzaole and zinc(II) nitrate, has a cage structure with the SOD net with a cage diameter of 11.6 Å, which is of sufficient size to encapsulate Fe(phen)$_2$ complexes. The initial encapsulated FePhen@MOF is formed at room temperature followed by two high temperature heat treatments, first under argon for 1 hour at 1050 °C, and the second under ammonia for 30 min. at 900 °C, resulting in the catalytically active material.

Results/Discussion

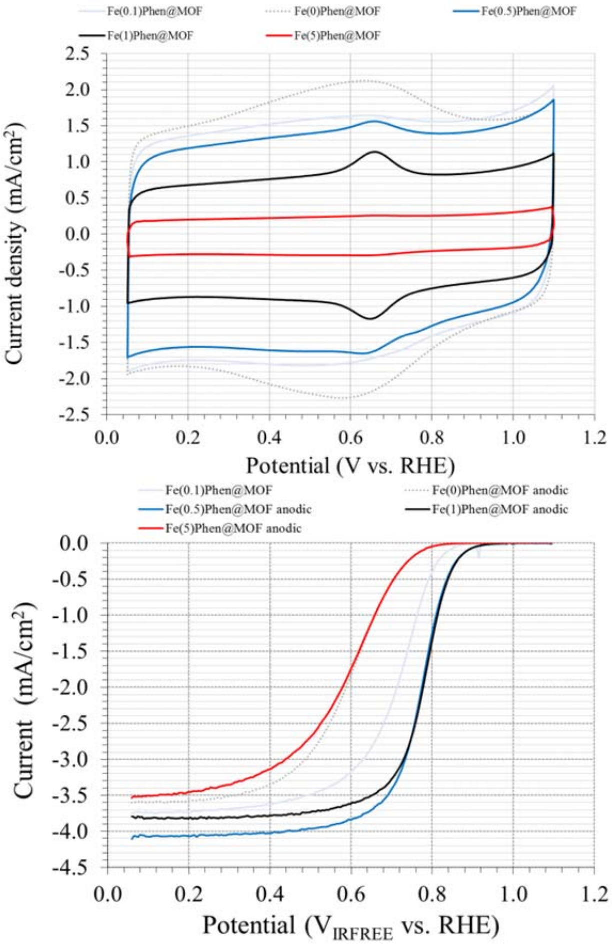

Figure 1. Cyclic Voltammetry (top) and RRDE (bottom) for a series of FePhen@MOF catalysts showing the effect of varying Fe content.

Elemental analysis, including inductively couple plasma atomic emission spectroscopy (ICP-AES) and CHN analysis, show iron incorporation in the FePhen@MOF catalysts in a predictable and controlled manner.

Electrochemical investigations, including cyclic voltammetry (CV) and rotating ring disk electrode (RRDE), show several trends relative to [Fe]. First, increasing iron content, resulted in decreasing electrochemical surface area, likely due to increased carbon degradation caused by the iron content during the heat treatments. Second, the redox couple at ~650 mV vs. RHE, suspected to be the Fe$^{II/III}$ couple, increases in magnitude with increasing iron content, with one exception. The Fe(5)Phen@MOF catalyst initially shows a significant redox couple at the same potential but rapidly degrades upon potential cycling. Most importantly are the findings relating iron content with the ORR data. As indicated by the Fe(0)Phen@MOF catalyst, no iron results in poor onset potential for the ORR, confirming the original hypothesis that either iron has a direct role in the ORR catalysis or it influences the formation of the active site. The series of catalysts that include Fe(0.1)Phen@MOF, Fe(0.5)Phen@MOF, and Fe(1)Phen@MOF, indicate that a certain amount or iron is needed to form the optimal catalyst material, but once this minimum amount is reached, additional iron does not further increase the onset potential or number of active sites. This is evident comparing the Fe(0.5)Phen@MOF and Fe(1)Phen@MOF catalysts which show approximately the same onset potential and number of active sites. This may indicate that iron does not have a direct role in catalyzing the ORR, that instead, it only influences the formation of the active site, and that only a minimum amount is needed for this purpose. Another possibility is that only some of the iron is incorporated into active sites that have a direct role in the ORR catalysis and that excess iron does not contribute to additional active site formation. The electrochemical results for the Fe(5)Phen@MOF material suggests that not only does excess iron not contribute to the formation of additional active sites, it has a detrimental effect, resulting in poor electrochemical surface area (ESA) and poor activity, due to the formation of unstable surface species that rapidly degrade upon potential cycling.

FY2016 Accomplishments

- Synthesized a series of FePhen@MOF catalysts with varying [Fe].
- Physical characterization (bulk composition, surface composition) of MOF catalysts consisting of ICP-AES and CHN analysis. Bulk compositions for iron content range from 0.03 % to 11.00 % while nitrogen content ranges from 6.92 % to 1.96 %
- Electrochemical characterization (CV, RRDE) of FePhen@MOF series of ORR electrocatalysts. Fe(0.5)Phen@MOF and Fe(1)Phen@MOF match-state-of-the-art activity performance.

Future Directions

- Continue the development of non-PGM catalysts, using SRNL's unique approach
- Finalize publication focusing on the iron effects on non-PGM ORR activity
- Apply for funding opportunity announcements from DOE-EERE

FY 2016 Publications/Presentations

1. M.C. Elvington, H.R. Colon-Mercado, "Fe redox couple in ZIF-8 based non-PGM electrocatalyst and its relation to ORR", article under preparation.
2. M.C. Elvington, H.R. Colon-Mercado, "Fuel Cell Catalyst Concepts", internal presentation to FCTO, DOE-EERE managers, July 2016.

Acronyms

CHN – carbon hydrogen nitrogen

CV – cyclic voltammetery

ESA- electrochemical surface area

ICP-AES – inductively couple plasma atomic emission spectroscopy

MOF – metallic organic framework

NET – three letter zeolite network code

non-PGM – non platinum group metal

ORR – oxygen reduction reaction

PEMFC – proton exchange membrane fuel cell

Phen – 1,10-phenanthroline

RHE – reversible hydrogen electrode

RRDE – rotating ring disc electrode

ZIF – zeolitic imidazole framework

Intellectual Property

Invention disclosure initiated

Total Number of Post-Doctoral Researchers

Dr. Mark C. Elvington, Savannah River Consulting, LLC