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).

Non-PGM Fuel Cell Catalysts

A unique approach has been developed to probe the non-PGM catalyst active site for the Oxygen Reduction Reaction (ORR) for PEMFCs. Iron based functionalities have been engineered into a variety of catalysts to evaluate their impact on activity for the ORR. A series of high surface area catalysts were synthesized and the impact of the chemical structure on the electrochemical and electrocatalytic properties was investigated. Elemental and surface analyses of the prepared catalysts reveal the incorporation of iron in a targeted and controlled manner. A high surface area framework catalyst was prepared that shows exceptional activity, comparable to state-of-the-art materials. The results of this research project provided critical seed data for the newly awarded ElectroCat project, which focuses on rationally designed framework catalysts for the oxygen reduction reaction.

Awards and Recognition

Invention disclosure initiated.

SBIR phase 1 awarded

DOE-EERE Fuel Cell Technology Office ElectroCat project awarded

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**

Non-PGM Fuel Cell Catalysts

Project Team:
H. Colón-Mercado (Primary, SRNL),
M. Elvington (Primary, SRC)
P. Ganesan (SRC)

Subcontractor:
Savannah River Consulting, (SRC)

Thrust Area:
Clean Energy

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 PEMFCs. Iron based functionalities have been engineered into a variety of catalysts to evaluate their impact on activity for the ORR. A series of high surface area catalysts were synthesized and the impact of the chemical structure on the electrochemical and electrocatalytic properties was investigated. Elemental and surface analyses of the prepared catalysts reveal the incorporation of iron in a targeted and controlled manner. A high surface area framework catalyst was prepared that shows exceptional activity, comparable to state-of-the-art materials. The results of this research project provided critical seed data for the newly awarded ElectroCat project, which focuses on rationally designed framework catalysts for the oxygen reduction reaction.

FY2017 Objectives

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

Introduction

Worldwide efforts to produce durable, highly active non-PGM electrocatalysts have resulted in slow, incremental improvements in activity and an incomplete understanding of the catalytically active site. To achieve a breakthrough in activity, a greater 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 recently received heightened attention. In particular, the role of iron and/or Fe-N4 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 catalyst while increasing the understanding of the role iron has in the ORR.

A series of high surface area catalysts were synthesized and the impact of the chemical structure on the electrochemical and electrocatalytic properties was investigated. The materials prepared within this project can be categorized as 1.) high surface area N doped carbon; 2.) porphyrinic MOF; 3.) Fe-MOF; and 4.) triazine framework. Each material type was chosen for this work because of their high surface area, nitrogen content, and electrical conductivity. Elemental and surface analyses of the prepared catalysts show the incorporation of iron in a targeted and controlled manner. A high surface area framework catalyst was prepared that shows exceptional activity, comparable to state-of-the-art materials. The results of this research project provided critical seed data for the newly awarded ElectroCat project, which focuses on rationally designed framework catalysts for the oxygen reduction reaction.

Approach

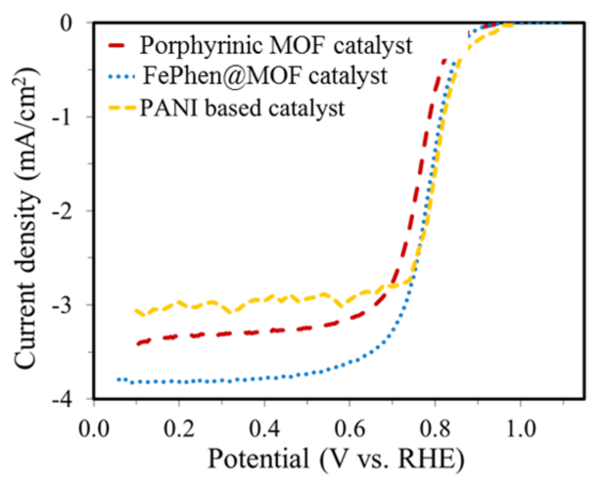
General catalyst preparation consisted of low temperature synthesis, metal incorporation and high temperature activation. Physical and elemental analysis were performed in-house and using an outside vendor. Materials were electrochemically characterized using rotating ring disc electrode in-house.

Results/Discussion

Elemental analysis, including inductively coupled plasma atomic emission spectroscopy (ICP-AES) and CHN analysis, shows iron incorporation in the FePhen@MOF catalysts in a predictable and controlled manner. The table below summarizes the surface properties of the prepared materials. The materials studied show surface areas between 339 m^2/g and 3033 m^2/g. The electrochemical capacitance measured by the integration of the cyclic voltammetry curves, mirrors the trend of BET surface areas. The only exception is the porphyrinic MOF which shows no measureable electrochemical capacitance despite showing high BET surface area. This result can be explained by the lack of electrical conductivity of the 'as prepared' material. After high temperature activation, the capacitance increases. The nitrogen content was measured for most samples using CHN analysis and XPS analysis. In general, most framework samples show nitrogen content of about 3-4 at% and more than 50 at% pyridinic content. Other materials, such as high surface area nitrogen doped carbon, show nitrogen content can vary between 1 and 10 at%, depending on the synthesis conditions. These carbon samples show less than 50 at% pyridinic content.

Material	Pore Volume (mL/g)	BET (m^2/g)	Capacitance (F/g)	N At.%	Pyrollic N At.%	Pyridinic N At.%
FePhen@MOF	0.32	339	52.9	4.3	31	59
CTF	1.32	1415	43.1	3.7	32	67
Porphyrinic MOF	--	2500	0.46	--	--	--
Carbon 3000	1.56	3033	233	1.0	97	--
Carbon 900	0.49	956	11.1	10	71	29

The figure (right) shows the electrochemical investigation by rotating ring disk electrode (RRDE) of the most successful catalysts. The preliminary data shows the unoptimized porphyrinic MOF catalyst and the FePhen@MOF catalyst have similar performance to the state-of-the-art catalyst prepared by LANL. It is expected that with further development, the catalyst's performance can meet or exceed the state-of-the-art.



LSV in 0.5 M sulfuric acid saturated with O_2 and collected at a scan rate of 5 mV/s and 900 rpm.

FY2017 Accomplishments

- Obtained external funding: ElectroCat project– $639k, SBIR – $40k
- Filled intellectual property: U.S. Patent Application
- Drafted peer Reviewed Paper: Joint Paper with LANL
- Synthesized a series of high surface area N doped carbon, porphyrinic MOF, Fe-MOF, and triazine framework with varying [Fe]
- Elemental analysis. Bulk compositions for nitrogen content range from 1 at% up to 10 at% with pyridinic N as high as 67at%
- FePhen@MOF and Porphyrinic MOF electrochemical activity for the ORR approaches state-of-the-art

Future Directions

- Explore additional organic frameworks in order to increase the number of active sites
- Utilize molecular modeling to explain experimental results
- Explore the use of various coordinated transition metal

FY 2017 Publications/Presentations

1. P. Ganesan, M.C. Elvington, H.R. Colon-Mercado, "PGM-free Engineered Framework Nano-Structure Catalysts", ElectroCat kickoff meeting, ElectroCat awardees and DOE-EERE managers, September 2017.

Acronyms

BET- Brunauer–Emmett–Teller
CHN – carbon hydrogen nitrogen
CTF – covalent triazine framework
CV – cyclic voltammetry
ICP-AES – inductively couple plasma atomic emission spectroscopy
MOF – metallic organic framework
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
SRC – Savannah River Consulting

Intellectual Property

Patent application submitted

Total Number of Post-Doctoral Researchers

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

Dr. Prabhu Ganesan, Savannah River Consulting, LLC