

V.L.4 Hydrogen Fuel Cell Development in Columbia (SC)*

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*Congressionally directed project

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Cost
- (B) Durability
- (C) Performance
- (D) Water Transport within the Stack
- (E) System Thermal and Water Management
- (F) Air Management
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

Carbon-based catalysts: To develop non-precious-metal catalysts for PEM fuel cells with high selectivity and durability which perform as well as conventional Pt catalysts with a cost of at least 50% less than the target of 0.2 g (Pt loading)/peak kW.

SOFC materials: Develop SOFC electrode materials that enable direct operation on hydrocarbon fuels.

Low-cost seals: Determine PEM seals materials that have no appreciable weight loss or leachants over a 60-week test period.

Hydrogen contamination: Establish the rate and mechanism of NH_3 transport in PEM cells over a 60-week period; identify the species of sulfur contamination on Pt catalysts in the presence of various gas species, e.g., H_2O and O_2 .

Multiphysics-based durability modeling: Use impedance spectroscopy to identify specific material state change driven degradation mechanisms during SOFC operation.

FY 2011 Accomplishments

- Metal-free oxygen reduction catalysts have been developed to reduce cost, facilitate manufacturing, and enhance durability of PEM fuel cells.
- Redox stable mixed ionic and electronic conductors for BSC symmetrical (and other) SOFC designs have been developed (completed 2010).
- The development of durable, low cost seals for PEM stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance.
- Understandings and methodologies have been developed to enable the establishment of hydrogen

Fiscal Year (FY) 2011 Objectives

- Development of metal-free oxygen reduction catalysts to reduce cost, facilitate manufacturing, and enhance durability of fuel cells (Barriers A-C; Task 2-electrodes)
- Development of redox stable mixed ionic and electronic conductors for bi-electrode supported cell (BSC) symmetrical solid oxide fuel cell (SOFC) designs, to reduce cost by simplifying manufacturing, enhance durability, and greatly reduce sensitivity to thermal cycling (Barriers A-C,G; Tasks 8-portable power, 11-innovative fuel cells, 10-long term failure mechanisms)
- Development of durable, low cost seals for polymer electrolyte membrane (PEM) stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance (Barriers A, C; Task 6-seals)
- Development of understandings and methodologies to establish hydrogen quality as it relates to PEM cell applications for transportation needs (Barriers B,C,G; Tasks 9-models for impurities, 8-portable operation)
- Development of a first principles multiphysics durability models based on interpretations of electrochemical impedance spectroscopy (EIS) data that link the multiphysics processes, the microstructure, and the material states, with cell impedance responses and global performance, mechanistically, as a foundation for engineering durability during design and manufacture of fuel cells (Barriers A-G; Tasks 9-models, 10-long term failure mechanisms, 11-innovative fuel cell design and manufacture)

quality as it relates to PEM cell applications for transportation needs (completed 2010).

- First principles multiphysics durability models based on interpretations of EIS data have been developed that form a foundation for engineering durability during design and manufacture of BSC SOFC fuel cell designs (completed 2010).



Introduction

The activities of the present project are contributing to the goals and objectives of the Fuel Cell element of the Hydrogen, Fuel Cells and Infrastructure Technologies Program of the Department of Energy through five sub-projects. Three of these sub-projects have focused on PEM cells, addressing the creation of carbon-based metal-free catalysts, the development of durable seals, and an effort to understand contaminant adsorption/reaction/transport/performance relationships at low contaminant levels in PEM cells. Two sub-projects addressed barriers in SOFCs: an effort to create a new symmetrical and direct hydrocarbon fuel SOFC designs with greatly increased durability, efficiency, and ease of manufacturing; and an effort to create a multiphysics engineering durability model based on EIS interpretations that associate the micro-details of how a fuel cell is made and their history of (individual) use with specific prognosis for long term performance, resulting in attendant reductions in design, manufacturing, and maintenance costs and increases in reliability and durability.

Approach

- Work on a previous DOE project, DE-FC36-03GO13108, was leveraged to create new carbon-based, metal-free catalysts for oxygen reduction.
- Develop new materials and material designs to create a high performance SOFC that can directly operate on hydrocarbon fuels with high power density.
- Recent advances at the University of South Carolina in controlled hydration and temperature characterization of polymer-based materials were used to establish a methodology for characterization of materials in seals in PEM stacks, and to develop a fundamental understanding how the degradation mechanisms of polymeric materials affects the performance and life of gasket/seals in PEM fuel cells.
- On-going work with the National Renewable Energy Laboratory, Argonne National Laboratory, Savannah River National Laboratory, and Los Alamos National Laboratory formed a foundation for the work on developing an understanding of the contaminant adsorption/reaction/transport/performance relationships at low contaminant levels in PEM cells. The study provided equilibrium and rate constants

suitable for use in new and existing models, and in computer codes at Argonne National Laboratory.

- Conceptual foundations laid by research supported by the National Science Foundation, the Air Force Office of Scientific Research and several industries including United Technologies Fuel Cells were expanded to create a multiphysics engineering durability model based on electrochemical impedance spectroscopy interpretations that associate the micro-details of how SOFC fuel cells are made and their history of individual use with long term performance, to achieve reductions in design, manufacturing and operating costs.

Results

Only one example of salient results is presented in the limited space available here. Other results appear in the quarterly reports.

Project 1. Development of Carbon Composite Electro Catalyst for the Oxygen Reduction Reaction (ORR) – Dr. Branko Popov

Objectives

- Synthesize carbon-based metal-free catalysts and carbon composite catalysts for ORR.
- Optimize catalytic active reaction sites as a function of carbon support, surface oxygen groups, nitrogen content, surface modifiers, pyrolysis temperature and porosity.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- Cost
- Durability
- Performance

Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst $>130 \text{ A cm}^{-3}$ (stack) at 0.8 internal resistance (iR_{free}).
- Cost: at least 50% less than a target of 0.2 g (Pt loading)/peak kW.

- Durability: >2,000 h operation with less than 10% power degradation.

Accomplishments

- The non-precious metal catalysts (NPMCs) with the exceptional activity and stability for oxygen reduction in alkaline electrolyte are developed by introducing N-based active sites.
- The pyridinic-N and graphitic-N are believed to play important roles in the active sites of NPMCs.
- The NPMCs shows comparable performance with Pt/C in alkaline fuel cells with the open circuit potential of 0.97 V and maximum power density of 177 mW cm⁻².



Introduction

Pt and Pt-based alloy catalysts are widely used in PEM fuel cells because of their high catalytic activity and selectivity as well as high corrosion resistance. In the last few years, several transition metal compounds such as macrocycle-based metal porphyrin system, chevre phase-type compounds and other transition metal chalcogenides have been proposed as selective catalysts for ORR. However, significant increase in activity and stability of the catalyst is still essential for PEM fuel cell applications. The goal of this project is to develop highly active and stable carbon-based metal-free catalysts and carbon composite catalysts with strong Lewis basicity (π electron delocalization) to facilitate ORR.

We have systematically studied the activity and stability, as well as the nature of active sites of NPMCs for the ORR. In this work, the NPMC with high activity and stability in alkaline electrolyte was developed. The fuel cell performance of the catalyst was studied using an anion exchange membrane fuel cell.

Approach

The approach used to synthesize the catalyst includes the following steps: (i) the modification of a porous carbon black support; (ii) the deposition of Co-N or Co-Fe-N chelate complex on the support; (iii) the first high-temperature pyrolysis; (iv) the chemical post-treatment (acid leaching); and (v) the second high-temperature pyrolysis.

Results

Figure 1a shows polarization curves for oxygen reduction of NPMC heat-treated at 900°C (NPMC-900 or CoFeN/C-HLH) before and after potential cycling in 0.1 M KOH. The cycling was performed in N₂-saturated 0.1 M KOH with a scan rate of 10 mV s⁻¹ between 0.8-1.2 V vs. the reference hydrogen electrode. The polarization curves

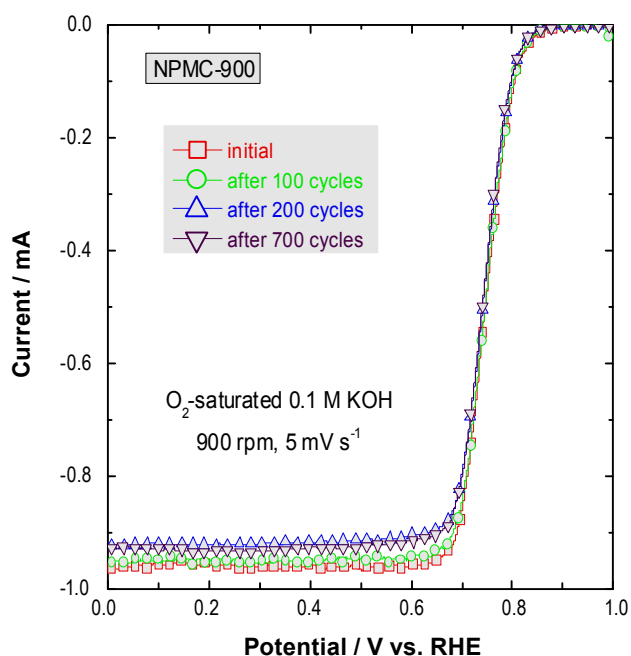


FIGURE 1A. Polarization curves for the oxygen reduction reaction in O₂-saturated 0.1 M KOH of NPMC heat-treated at 900°C before and after the potential cycling stability test; scan rate: 5 mV s⁻¹; rotation rate: 900 rpm.

were measured before and after 100, 200, and 700 cycles, respectively. It is evident that the NPMC-900 catalyst does not show any performance degradation during 700 cycles indicating that the catalyst is very stable in alkaline solution.

Figure 1b shows the X-ray photoelectron spectroscopy (XPS) spectra of N_{1s} for the NPMC-900 before and after the potential cycling stability test in 0.1 M KOH. The peaks of N_{1s} at 398.6 ± 0.3 eV, 401.3 ± 0.3 eV, and 403.3 ± 0.3 eV can be attributed to the pyridinic-N, graphitic-N, and pyridine-N-oxide, respectively. The pyridinic-N and graphitic-N are believed to be active catalytic sites for oxygen reduction. As shown in Figure 1b, the profile of the N_{1s} spectra of NPMC-900 is still similar to that of fresh catalyst indicating high stability of NPMC for oxygen reduction in alkaline electrolytes.

The kinetic parameters for oxygen reduction reaction on CoFeN/C subject to heat-treatment, leaching, and re-heat-treatment (CoFeN/C-HLH) and Pt/C catalysts including the ring currents, the numbers of electron exchanged and polarization curves were obtained using a rotating ring disc electrode (RRDE) system in O₂-saturated 0.1 M KOH. Figure 2 summarizes the RRDE results. The data of carbon black are also presented for comparison. The ring currents were measured on a Pt ring electrode held at 1.2 V for CoFeN/C-HLH and Pt/C catalysts. It is evident that the ring currents for CoFeN/C-HLH and Pt/C are comparable. In contrast, the ring current for carbon is much higher. The number of electrons exchanged in the redox reaction for CoFeN/C-HLH and Pt/C is 3.9-4.0 at high potentials.

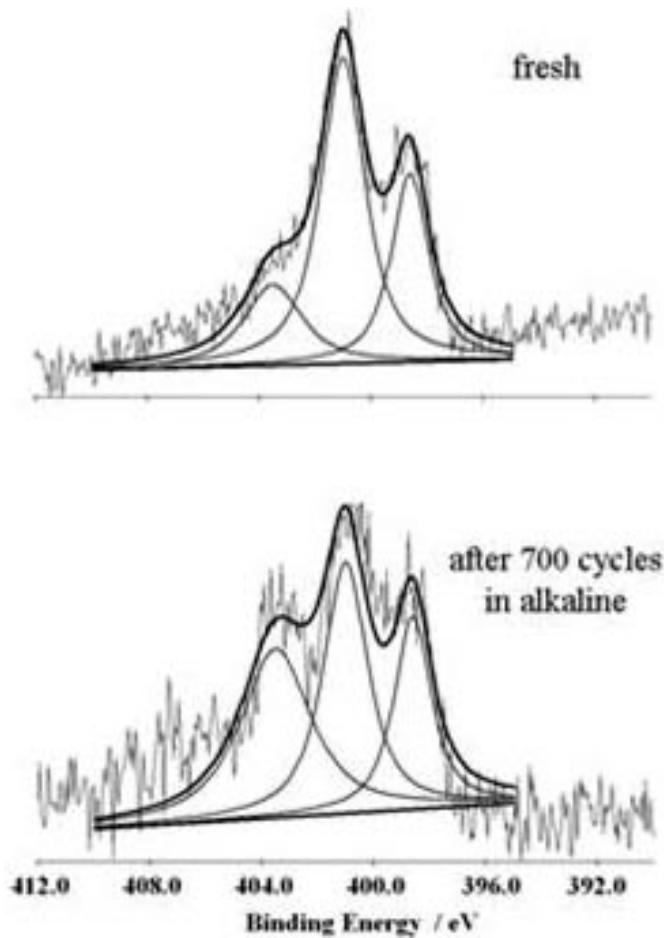


FIGURE 1B. XPS spectra of N1s obtained for: (a) fresh NPMC and for catalyst cycled 700 cycles in 0.1 M KOH.

The results indicate that both CoFeN/C-HLH and Pt/C catalysts catalyze the ORR mainly via a four-electron pathway in alkaline electrolyte. For carbon black alone, a lower selectivity with number of electrons exchanged in the range of 3.3-3.6 was observed at high potentials. The catalytic performance of CoFeN/C-HLH is comparable with Pt/C for oxygen reduction in alkaline electrolytes.

Figure 3 shows the preliminary performance of a H_2 - O_2 anion exchange membrane fuel cell. The operation temperature is $50^\circ C$. The Pt loading at anode is 0.4 mg cm^{-2} , whereas the catalyst loadings at cathode are 4 mg cm^{-2} for CoFeN/C-HLH and $0.4 \text{ mg}_{Pt} \text{ cm}^{-2}$ for Pt/C. Anode and cathode gases are humidified at $50^\circ C$. The flow rates of H_2 and O_2 are 200 and 400 mL min^{-1} . The open circuit potentials are 0.97 and 1.04 V for CoFeN/C-HLH and Pt/C, respectively. The maximum power densities are 177 and 196 mW cm^{-2} for CoFeN/C-HLH and Pt/C, respectively. At high potential, the performance of CoFeN/C-HLH is slightly lower than Pt/C. At intermediate potential, they show very similar performance. The lower performance of

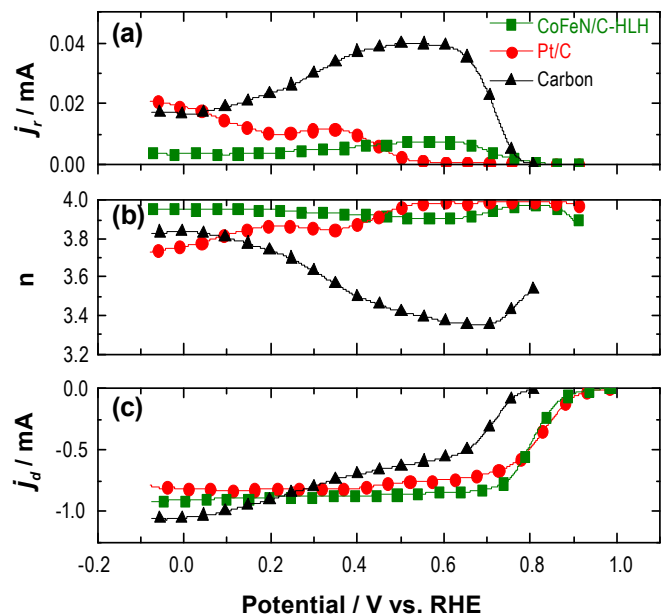


FIGURE 2. Comparison of CoFeN/C-HLH and Pt/C catalysts for the oxygen reduction reaction in O_2 -saturated 0.1 M KOH. Scan rate: 5 mV s^{-1} ; rotation rate: 900 rpm. (a) ring currents; (b) the number of electron exchanged during oxygen reduction; (c) polarization curves.

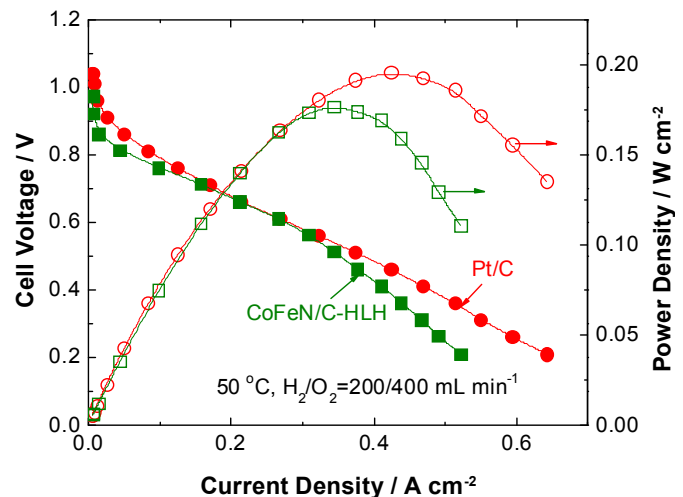


FIGURE 3. Preliminary performance of a H_2 - O_2 anion exchange membrane fuel cell. The operation temperature is $50^\circ C$. The Pt loading at anode is 0.4 mg cm^{-2} , whereas the catalyst loadings at cathode are 4 mg cm^{-2} for CoFeN/C-HLH and $0.4 \text{ mg}_{Pt} \text{ cm}^{-2}$ for Pt/C. Anode and cathode gases are humidified at $50^\circ C$. The flow rates of H_2 and O_2 are 200 and 400 mL min^{-1} .

CoFeN/C-HLH over Pt/C at low potential may be attributed to higher mass-transfer resistance of the former resulting from higher catalyst loading and thus higher thickness of catalyst layer.

Conclusions and Future Directions

- NPMCs for oxygen reduction in alkaline electrolyte are developed by heating metal-nitrogen containing chelates followed by chemical post-treatment.
- The pyridinic-N and graphitic-N supported on graphitized carbon are active sites for oxygen reduction with high stability in alkaline electrolytes.
- The NPMCs exhibits comparable performance with Pt/C in anion exchange membrane fuel cells with the open circuit potential of 0.97 V and maximum power density of 177 mW cm⁻².

Future work includes the following tasks:

- Hydrogen Quality - Extract rate constants from experimental data for the case of a contaminant that desorbs from the catalyst surface; establish correlations between experimental data and model that will allow predictions of the effect of contaminant concentration and electrode potential.
- Carbon Composite Catalyst – Confirm protocol for preparation of mesoporous carbon support; improve integrity of the carbon composite catalyst layer in the membrane electrode assembly (MEA); reduce MEA resistance by decreasing the catalyst layer thickness and by increasing the specific gravity and activity of the catalyst.
- Hydrocarbon-Fueled SOFC - Evaluate solid oxide fuel cell performance using hierarchically porous electrode and LaGaO₃- as well as SFM-based ceramic anode.
- Gaskets and Seals - Design new compression set tests to include various compression strains and more realistic heating/cooling cycles to fuel cell operation; develop a life prediction model; and compare the performance of several off-the-shelf seal materials in the fuel cell environment.
- Durability Modeling in SOFC - Complete button cell test system and EIS test protocols; complete conductivity model of bi-supported cell electrode configuration.

Special Recognitions & Awards/Patents Issued

1. Prof. Ken Reifsnider, PI of this effort, is Director of the DoE Energy Frontiers Research Center on Heterogeneous Functional Materials, the “HeteroFoaM Center.”
2. The Crystal Flame Innovation Award in Research from FuelCell South was presented to Dr. Popov’s research group for research work in the field of non-precious catalyst development and preparation thin film assemblies with nano-structured catalysts and the development of the pulse deposition technique for preparation of membrane electrode assemblies.

FY 2011 Publications/Presentations

1. Chih-Wei Lin, Chi-Hui Chien, Jinzhu Tan, Yuh J. Chao, and J.W. Van Zee, “Chemical Degradation of Five Elastomeric Seal Materials in a Simulated and an Accelerated PEM Fuel Cell Environment,” *Journal of Power Source*, 196(4), 2011, 1955-1966.
2. Cui,Tong, Lin, C-W., Chien,C.H., Chao, Y.J., Van Zee, J.W., “ Service Life Estimation of Liquid Silicone Rubber Seals in Polymer Electrolyte Membrane Fuel Cell Environment,” *Journal of Power Source*, 196 (2011) 1216-1221.
3. B.N. Popov, X. Li, G. Liu, *Int. J. Hydrogen Energy* 36 (2011) 1794-1802.