V.0.6 Hydrogen Fuel Cell Development in Columbia (SC)*

Ken Reifsnider (Primary Contact), F. Chen, B. Popov, J. Van Zee, W. Chao, C. Xue
University of South Carolina
300 Main Street
Columbia, SC 29208
Phone: (803) 777-0084
E-mail: Reifsnider@cec.sc.edu

DOE Technology Development Manager: Dimitrios Papageorgopoulos
Phone: (202) 586-5463
E-mail: Dimitrios.Papageorgopoulos@ee.doe.gov

DOE Project Officer: Reginald W. Tyler
Phone: (303) 275-4925
E-mail: Reginald.Tyler@go.doe.gov

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*Congressionally directed project

Objectives

- Development of metal-free oxygen reduction catalysts to reduce cost, facilitate manufacturing, and enhance durability of fuel cells.
- Development of redox stable mixed ionic and electronic conductors (MIECs) 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.
- Development of durable, low-cost seals for proton exchange membrane (PEM) stacks, through the establishment of laboratory characterization methodologies that relate to cell/stack performance.
- Development of understandings and methodologies to establish hydrogen quality as it relates to PEM cell applications for transportation needs.
- 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.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance
(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.

Carbon-Based Catalysts: 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.

Accomplishments

- Metal-free oxygen reduction catalysts have been developed to reduce cost, facilitate manufacturing, and enhance durability of PEM fuel cells.
- Redox stable MIECs for BSC symmetrical (and other) SOFC designs have been developed.
- 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

quality as it relates to PEM cell applications for transportation needs
- 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.

Introduction

The activities of the present project are contributing to the goals and objectives of the Fuel Cell element of the Fuel Cell Technologies Program of the Department of Energy through five sub-projects. Three of these sub-projects focus 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 address 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 electrochemical impedance spectroscopy 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 materials 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 will be 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 (ANL), Savannah River National Laboratory, and Los Alamos National Laboratory forms 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 will provide equilibrium and rate constants suitable for use in new and existing models, and in computer codes at ANL.
- Conceptual foundations laid by research supported by the National Science Foundation, Air Force Office of Scientific Research and several industries including United Technologies Fuel Cells are being expanded to create a multiphysics engineering durability model based on EIS 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.

Sr- and Mn-doped $LaGaO_3$ ($La_{0.8}Sr_{0.2}Ga_{0.5}Mn_{0.5}O_{3-\delta}$, LSGMn) have recently been synthesized in Dr. Chen's group and applied as sulfur tolerant anode materials for SOFCs [1]. LSGMn has demonstrated very promising catalytic activity for hydrogen oxidation. In an all perovskite-type fuel cell consisting of a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) pellet with a thickness of 400 μm as the electrolyte, LSGMn as the anode, and LSCF as the cathode, an impressive power density of 400 mW/cm^2 has been achieved at 800°C, as shown in Figure 1, using H_2 as fuel and ambient air as oxidant. Furthermore, LSGMn exhibits a mixed ionic and electronic conductivity of 10 S/cm at 800°C in air and can be potentially used as an oxygen electrode. Figure 2 shows the performance of a fuel cell pellet constructed with this combination of materials subjected to a sulfur containing fuel for a period of about 100 hours. The drop in performance quickly stabilizes and when hydrogen is re-introduced as the fuel about 80% of the original performance is recovered.

Dr. Chen's group has also recently discovered a perovskite material with a composition of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) [2], showing remarkable redox stability and high conductivity (>100 S/cm at 750°C) in either a reducing or an oxidizing environment. This new perovskite material has been applied as both hydrogen and oxygen electrode materials in a symmetrical SOFC, demonstrating very promising cell performance as shown in Figure 3 [3]. In addition, such redox stable mixed ionic and electronic conducting material will potentially simplify the electrode infiltration process since both the electrodes can be infiltrated in the same step.

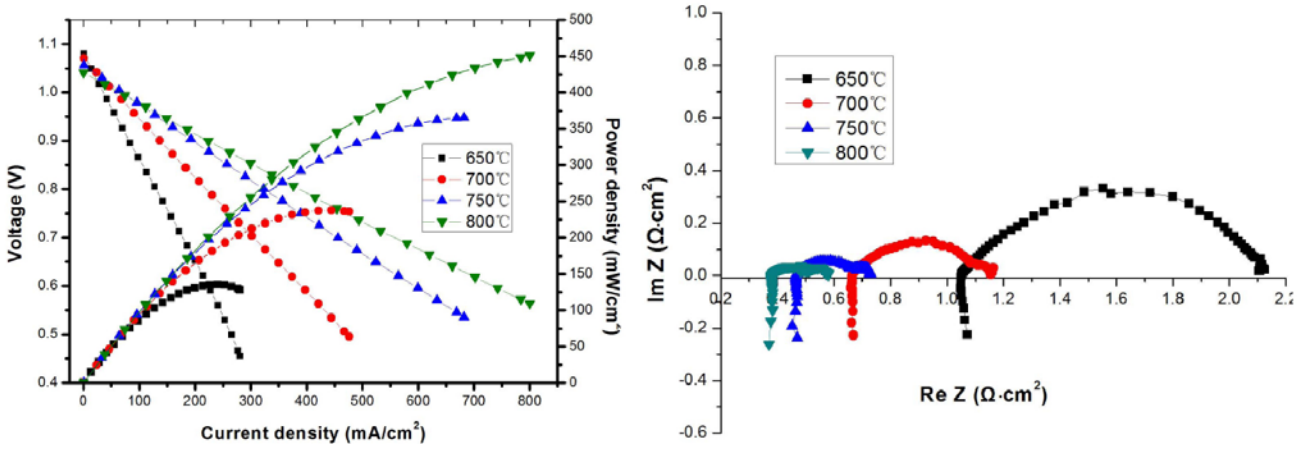

FIGURE 1. Measured performance of LSGM electrolyte supported (~400 μm) SOFC with LSGMn as an anode and lanthanum strontium cobalt iron oxide as the cathode (left) and the cell impedance (right) for materials developed under this program.

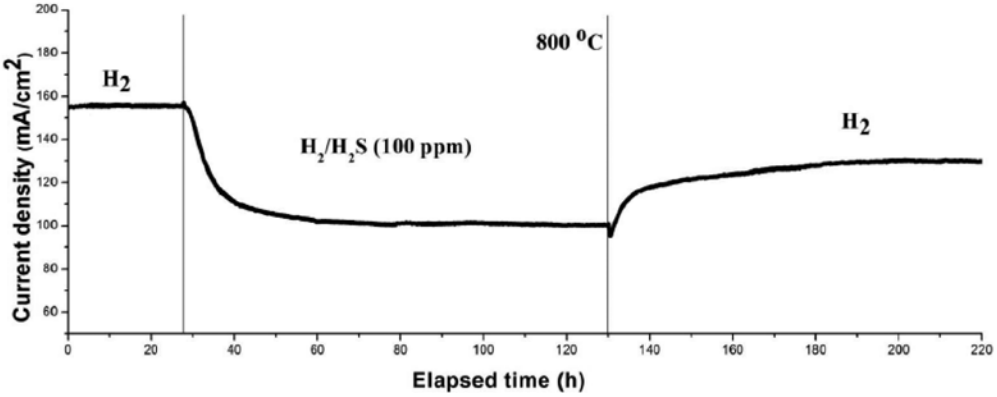

FIGURE 2. Measured performance of LSGM-electrolyte supported (~400μm) SOFC with LSGMn as an anode and LSCF as the cathode when subjected to a sulfur containing fuel.

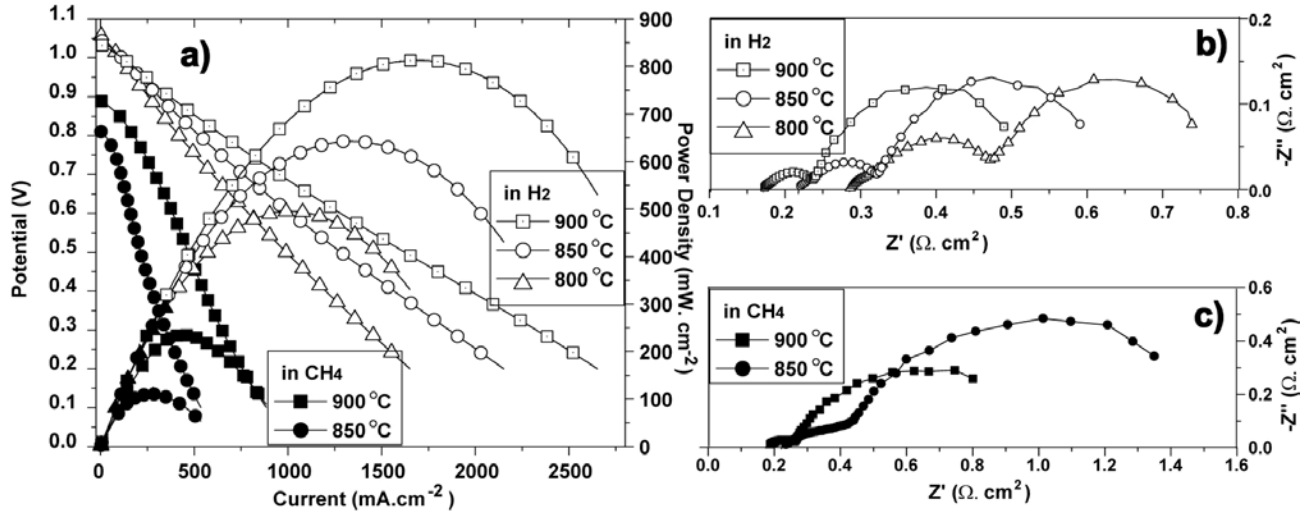

FIGURE 3. Symmetrical fuel cell SFM|LSGM|SFM performance with wet (3 vol% H_2O) H_2 or CH_4 as fuel. a) current/potential and current/power density curves; impedance spectra of single cells in b) wet H_2 and c) wet CH_4.

Conclusions and Future Directions

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 SOFC performance using hierarchically porous electrode and $LaGaO_3$- 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.
- Durability SOFC Modeling - complete button cell test system and EIS test protocols; complete conductivity model of BSC electrode configuration.

Special Recognitions & Awards/Patents Issued

1. Prof. Ken Reifsnider, PI of this effort gave an invited keynote lecture at the ACS meeting in San Francisco in May, 2010.

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.

3. Q. Liu and F. Chen, "Porous Metal Oxide Particles and Their Methods of Synthesis", US Patent Application, 12/634,092, 12/09/2009.

FY 2010 Publications/Presentations

1. G. Liu, X. Li, B.N. Popov, "Stability Study of Carbon-Based Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells", *216th Meeting of the Electrochem. Soc*., Vienna, Austria, October, 2009.

2. Q. Liu and F. Chen "Self-Rising Approach to Synthesize Hierarchically Porous Metal Oxides", Materials Research Bulletin, 44 (2009) 2056-2061.

3. F. Zhao, L. Zhang, Z. Jiang, C. Xia and F. Chen, "A High Performance Intermediate Temperature Solid Oxide Fuel Cell using Impregnated $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ Cathode", Journal of Alloys and Compounds, 487 (2009) 781-785.

4. F. Zhao, F. Chen and C. Xia "Infiltrated Electrodes for Intermediate-Temperature Solid Oxide Fuel Cells", ECS Transactions, 19 (18) 43-50 (2009).

5. Q. Liu, F. Chen and W. Song "Synthesis, Characterization and Application of Nanostructured Porous Metal Oxides", ECS Transaction, 19 (15) 1-8 (2009).

6. Q. Liu, F. Zhao, X. Dong, C. Yang, F. Chen, "Synthesis and Application of Porous $Sm_{0.2}Ce_{0.8}O_{1.9}$ Nano-crystal Aggregates", Journal of Physical Chemistry, 113 (2009) 17262-17267.

7. Q. Liu, X. Dong, C. Yang, S. Ma and F. Chen, "Self-Rising Synthesis of Ni-SDC Cermets as Anodes for SOFCs", Journal of Power Sources, 195 (2010) 1543-1550.

8. *Yang, C.; Jin, C.; and* ***Chen, F.****, "Chara*cterization of infiltrated (La0.75Sr0.25)0.95MnO3 as oxygen electrode for solid oxide electrolysis cells," *International Journal of Hydrogen Energy,* 35 (2010): 5187–5193.

9. Yang, C.; Jin, C.; and **Chen, F.**, "Characterization of novel micro-tubular solid oxide fuel cells fabricated by phase-inversion method," *Electrochemistry Communications,* 12 (2010) 657–660.

10. Liu, Q., and **Chen, F.**, "Self-rising approach to synthesize porous hollow metal oxides," *Journal of Nanoscience and Nanotechnology,* 10 (2010) 4317–4321.

11. Yang, C.; Coffin, A.; and **Chen, F.**, "High temperature solid oxide electrolysis cell employing porous structured (La0.75Sr0.25)0.95MnO3 with enhanced oxygen electrode performance," *International Journal of Hydrogen Energy,* 35 (2010) 3221–3226.