Hydrogen Fuel Cell Development in Columbia (SC)

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Final Report

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Executive Summary

This is an update to the final report filed after the extension of this program to May of 2011. The activities of the present program contributed 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 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 programs 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 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.

The principal accomplishments of the effort are listed below:

1. **Metal-free oxygen reduction catalysts** have been developed to reduce cost, facilitate manufacturing, and significantly enhance the durability of PEM fuel cells. Non-precious metal catalysts (NPMCs) were developed with exceptional activity and stability for oxygen reduction in alkaline electrolytes by introducing N-based active sites on activated carbon.

2. **Redox stable mixed ionic and electronic conductors** (MIECs) for bi-electrode supported cell (BSC) symmetrical (and other) SOFC designs have been developed. Hierarchically porous LSCF has been successfully prepared using a newly patented “self-rising” technique; LSGM samples were prepared and have shown promising conductivity in air; patent filed on the synthesis method developed during this program activity.

3. The development of durable, **low cost seals for PEM stacks** through the establishment of laboratory characterization methodologies that relate to cell/stack performance has been achieved. Developed life prediction methodologies using WLF concepts; initial model development and verification for predicting compressive stress retained in seals under realistic temperature cycles.

4. Understandings and methodologies have been developed to enable the **establishment of hydrogen quality** as it relates to PEM cell applications for transportation needs. A new model that describes partial recovery of performance indicative of simple sulfur based inorganic contaminants was completed. A procedure was proposed to determine all model rate constants. The model was used to predict a tolerance limit (worse case scenario) and the effect of a catalyst loading reduction.

5. First principles multiphysics durability models based on interpretations of Electrochemical Impedance Spectroscopy (EIS) data have been developed that form a foundation for **engineering durability during design and manufacture** of BSC SOFC fuel cell designs. A series of cathode and electrolyte materials have been successfully synthesized and characterized. CFD based multiphysics SOFC/SOEC models have been developed; A multi-physics model based mechanistic EIS simulation approach has been established for experimental data interpretation of degradation and prognosis of performance.
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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 (MIECs) for bi-electrode supported cell (BSC) symmetrical 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 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)

Technical Barriers

This project addressed the following technical barriers from section 3.4 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:
(A) Cost of PEM and SOFC fuel cells
(B) Durability of PEM and SOFC fuel cells
(C) Performance of PEM and SOFC fuel cells
(D) Transport in PEM cells
(E,F) Thermal and air management in SOFC fuel cells
(G) Transient operation
Technical Targets

*Carbon-based catalysts:* To develop non-precious-metal catalysts for PEMFC 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 0.2g (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\textsubscript{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\textsubscript{2}O and O\textsubscript{2}.

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

Background for Approach

1. Work on a previous DOE program, DE-FC36-03GO13108, was leveraged to create new carbon-based, metal-free catalysts for oxygen reduction.
2. Leveraged previous work in the SOFC SmartState Center at the University of South Carolina to develop new materials and materials designs to create a high performance SOFC that can directly operate on hydrocarbon fuels with high power density.
3. 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 PEMFC
4. On-going work with NREL, ANL, SRNL, and LANL 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.
5. Conceptual foundations laid by research supported by NSF, AFOSR 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.
SubProject 1:
Development of Carbon Composite Electro-Catalyst for the Oxygen Reduction Reaction (ORR)

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”
- Durability
- Cost
- Performance

Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst > 130 A cm\(^{-3}\) (stack) at 0.8 \(iR\)\(_{\text{free}}\)
- 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 PEMFCs 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, chevrel 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 PEMFC 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 non-precious metal catalysts (NPMCs) for the oxygen reduction reaction (ORR) [1-10]. 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 anion exchange membrane (AEM) 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. RHE. The polarization curves 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 XPS spectra of N1s for the NPMC-900 before and after the potential cycling stability test in 0.1 M KOH. The peaks of N1s 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 N1s 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 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 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.

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 H2-O2 anion exchange membrane (AEM) fuel cell. The operation temperature is 50°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 mg Pt cm−2 for Pt/C. Anode and cathode gases are humidified at 50 °C. The flow rates of H2 and O2 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 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

- Non-precious metal catalysts (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$^{-2}$.

Figure Captions

Figure 1a. Polarization curves for the oxygen reduction reaction in O$_2$-saturated 0.1 M KOH of non-precious metal catalysts heat-treated at 900 °C before and after the potential cycling stability test; scan rate: 5 mV s$^{-1}$; rotation rate: 900 rpm.

Figure 1b. XPS spectra of N1s obtained for: (a) fresh non-precious metal catalyst and for catalyst cycled 700 cycles in 0.1 M KOH.

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°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 mg Pt cm$^{-2}$ for Pt/C. Anode and cathode gases are humidified at 50°C. The flow rates of H$_2$ and O$_2$ are 200 and 400 mL min$^{-1}$.

Example Publications:

Conference Proceedings


Fig. 1.a

Fig. 1.b

Fig. 2

Fig. 3
Sub-Project 2: Hydrocarbon Fuel Powered High Power Density SOFC

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This main focus of this project was to develop a high performance solid oxide fuel cell (SOFC) which can directly operate on hydrocarbon fuels and achieve high power density. In order to meet this goal, the experiments are designed with the following tasks:

• Infiltrate ceria to conventional Ni-based anode to mitigate coking.
• Develop mixed ionic and electronic conducting electrode materials.
• Develop anode materials which are capable of direct utilization of hydrocarbon fuels with tolerance to carbon formation and sulfur poisoning.
• Demonstrate high power density SOFCs using hydrocarbon fuels

A schematic of a Ni based anode-supported cell with Sm doped ceria (SDC, Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$) electrolyte and infiltrated nanoparticles within the co-sintered electrodes is shown in Figure 1. For the Ni-SDC anode, the infiltrated particles could be ionic conductive materials. While at the cathode side, SDC could be the cathode skeleton material since it had no reaction with the electrolyte in the co-sintering process. Since SDC has high ionic conductivity, the electronic conductive materials or mixed ionic and electronic conductors were suitable for the infiltrated particles to increase the electronic conductivity of the cathode.

Figure 1. Schematic diagram of an anode-supported cell with infiltrated electrodes

The anode is based on the traditional Ni as an electronic conducting backbone covered with doped ceria. Ni particles can be covered with doped ceria using infiltration method to reduce their activities for carbon formation. And nickel is used as the backbones to ensure electronic conduction and to make the co-firing technique applicable to SOFC fabrication. At the same time, doped ceria, which is also a good anode material for direct electrochemical oxidation of methane and a good catalyst to remove carbon, is used to coat nickel to block hydrocarbon from accessing to Ni surface (5). The infiltrated anode is shown in Figure 2.
The optimized single cells with SDC infiltrated anodes were investigated when hydrocarbons were used as the fuels. The stability of the cells with different SDC infiltrated loadings were investigated with humidified methane as fuel (shown in Figure 3). No significant degradation was observed for anode infiltrated by 20 and 25 mg cm\(^{-2}\) SDC. This verified that the SDC infiltrated anodes were very effective in suppressing catalytic carbon formation by blocking methane from approaching the Ni, which is catalytically active towards methane pyrolysis. The high performance of infiltrated anode showed high promise in the developing field of direct hydrocarbon SOFCs.

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Figure 3. Time dependence of power densities for cells with different SDC loaded anodes operated at 600°C with a constant output voltage of 0.5V.

Mixed ionic and electronic conductors (MIECs) have recently been explored as anode materials for direct-hydrocarbon SOFCs. However, the electrical conductivity and the catalytic activity of the most reported MIEC ceramics are still not satisfactory. Without precious metal catalysts, the cell performances are limited, especially when directly operated with hydrocarbon fuels. Recently, a novel perovskite Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$ (SFMO) has been reported to show high electrochemical performance as anode material in SOFCs operating with hydrogen as fuel and the relatively high electrical conductivity may potentially promote the catalytic activity of other metallic catalysts. Accordingly, dispersing a small amount of Ni on the SFMO anode as catalyst may be expected to improve the anode performance while avoiding carbon deposition from the conventional Ni-cermet anode for direct methane SOFCs.

In this study, La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_3$ (LSGM) electrolyte supported single cells with La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSFC) as the cathode and Ni-modified SFMO as the anode were fabricated and tested for direct utilization of methane fuel. The reason for using SFMO as anode material is its high electrical conductivity and redox stability. A small amount of NiO (~2wt%) was applied to modify the performance of the ceramic anode by infiltrating the SFMO anode with nickel nitrate solution followed by heat-treatment. The chemical stability between NiO and SFMO, the single cell performance as well as the cell performance stability of the Ni-modified SFMO anode using wet CH$_4$ (3%H$_2$O) as fuel were evaluated.

The chemical stability between SFMO and NiO was investigated by firing the mixed powders of SFMO and NiO (50: 50 wt %) at 1000°C for 10h in air. The XRD pattern of the mixed powder is shown in Figure 4. Only XRD peaks corresponding to those of NiO and SFMO are present, indicating that there is no chemical compatibility issue for Ni modified SFMO anode under the cell operating conditions.
Figure 4. XRD patterns of (a) the mixed powders of SFMO and NiO (50: 50 wt %) fired at 1000°C for 10h in air, (b) NiO and (c) SFMO

The performance of the fuel cells with either Ni-SFMO anode or SFMO anode at 800°C is shown in Figure 5. It can be seen that introduction of small amount of Ni phase in the SFMO anode has significantly enhanced the cell performance in both H₂ and CH₄. With the ambient air as the oxidant, the peak power density of the fuel cells with t SFMO as anode is 0.291 W cm⁻² in wet H₂ (3vol%H₂O) and only 0.033 W cm⁻² in wet CH₄ (3vol%H₂O) at 800°C. It is noticed that the OCV of the cell drops to 0.68V with wet CH₄ (3vol%H₂O) as the fuel, indicating the low catalytic activity of the SFMO material to CH₄. With the same testing conditions, the peak power density of fuel cells with Ni-SFMO as anode reaches 1.134 W cm⁻² in wet H₂ (3vol%H₂O) and 0.669 W cm⁻² in wet CH₄ (3vol%H₂O). The OCV of the cells with the Ni-SFMO anode in wet CH₄ is 1.08 V, suggesting that the catalytic activity of the SFMO anode is greatly improved by loading a small amount of Ni catalyst in the SFMO phase. The performance of cells with the Ni-SFMO anode in H₂ and CH₄ is much higher than those of fuel cells with the ceramic anodes ever reported (e.g. the highest reported peak power density of cells is 0.735 W cm⁻² in H₂ with the Sr₂CoMoO₆ anode and 0.55 W cm⁻² in wet CH₄ (3vol%H₂O) with the Sr₁.2La₀.8MgMoO₆ anode at 800°C). High performance of the Ni-SFMO anode is probably due to not only the catalytic activity of the highly dispersed Ni particles, but also the high electrical conductivity and good electrochemical activity of the SFMO ceramics.
The performance stability of cells with the Ni-SFMO anode in CH$_4$ was investigated by recording the current density of the cell operating at 0.7V at 800°C. As shown in Figure 6a, the cell performance is very stable in the tested period, indicating that Ni-SFMO anode has excellent catalytic activity and stability when directly operating on CH$_4$ fuel. The stability of the cell is further confirmed by the impedance spectra of the cells measured under open circuit conditions in CH$_4$ before and after the performance stability test. Very similar impedance spectra are obtained, indicating that Ni modified SFMO anode has good stability and no significant carbon deposition occurred upon operating the cell directly with CH$_4$ fuel. This result would be attributed to the enlarged reaction sites on the SFMO oxide and the high dispersion of fine Ni particles which may accelerate the anode electrochemical reactions and suppress carbon formation on the confined Ni surfaces.
Figure 6. (a) Dependence of the current density as a function of the operating time of the cells with Ni-SFMO anode operated in CH₄ (3vol% H₂O) at cell voltage of 0.7 V at 800°C and (b) the impedance spectra of the cell before and after operating in CH₄ (3vol% H₂O) at cell voltage of 0.7 V at 800°C for 18h.

- La₀.₈Sr₀.₂Ga₀.₅Mn₀.₅O₃ (LSGM) is an excellent ionic conductor
- La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂O₃ (LSGM) potential mixed conducting anode
- Introducing electronic conduction while maintaining ionic conduction
Figure 7 shows the fuel cell performance of the electrolyte-support single fuel cell at different operating temperatures. The maximum open cell potential is about 1.08 V at 650°C in humidified H₂, and this value decreases with the increase in the cell testing temperature. The higher conductivity will result in lower resistance polarization and hence higher performance. The peak power density reached 400mW cm⁻² at 800°C, despite the relative thick electrolyte (400 μm). It is expected that further performance improvement can be obtained by decreasing the electrolyte thickness or optimizing the microstructure of the LSGMn anodes.

![Figure 7](image1)

Figure 7. Fuel cell performance for cell with LSGMn as anode

Shown in Figure 8 are the impedance spectra for the cell operated at different temperatures, indicating that the total impedance decreases with the increase of the cell operating temperature from 650°C to 800°C. The intercept of high-frequency arc with the real axis is related to the ohmic resistance of the cell, mainly the resistance of the electrolyte, while the difference between the real axis intercepts of the impedance is due to the interfacial polarization resistance. With the increase of the operating temperature, both the ohmic and interfacial polarization resistances decrease, resulting in improvement of cell performance, as shown in Figure 8.

![Figure 8](image2)

Figure 8. Impedance spectra of cells at different temperatures
Figure 9 shows a typical current change as a function of time when the cell was operated at a constant voltage of 0.7V with either H$_2$ or H$_2$ with 100ppm H$_2$S as fuel gas in the anode while air as the oxidant in the cathode. Cell current decreased rapidly when 100ppm H$_2$S was introduced in the fuel gas stream, and the degradation rate slowed down with time and the cell performance was eventually stabilized. Upon removing H$_2$S from the fuel gas stream, the current started to improve rapidly with time, with cell performance partially recovered.

![Figure 9. Long-term test of the cell with LSGMn anode in H$_2$ and H$_2$ with 100ppm H$_2$S](image)

**Concluding remarks:**

The objective of this project is to develop a high performance solid oxide fuel cell (SOFC) which can directly operate on hydrocarbon fuels and achieve high power density. Over the course of the two-year project, this project goal has been achieved and the project accomplishments can be briefly highlighted below:

- Infiltration of Ni into ceria backbone has been shown to achieve cell performance stability with hydrocarbon fuels;
- Mixed ionic and electronic conducting electrode materials based on Sr- and Mn-doped LaGaO$_3$ has been developed;
- Anode materials based on double provskite Sr$_2$Fe$_{1+x}$Mo$_{1-x}$O$_6$ which are capable of direct utilization of hydrocarbon fuels with tolerance to carbon formation and sulfur poisoning have been discovered;
- High power density SOFCs using hydrocarbon fuels (methane) have been demonstrated.
**Relevance:** Develop materials for a high performance solid oxide fuel cells which can directly operate on hydrocarbon fuels and achieve high power density.

**Approach:** Prepared hierarchically porous electrode using self-rising technique and develop mixed conducting ceramic anode based on LaGaO$_3$ system.

**Technical Accomplishment and Progress:** Hierarchically porous LSCF has been successfully prepared using self-rising technique; LSGM samples are prepared and shown promising conductivity in air.

**Technology Transfer / Collaborations:** One invention disclosure on self-rising approach has been filed. Collaborated with SRNL for nanostructured ceramic synthesis and AFRL for sulfur-tolerant ceramic anode work.

**Proposed Future Research:** Evaluated solid oxide fuel cell performance using hierarchically porous electrode and LaGaO$_3$-based ceramic anode.

**Example Technical Publications**


4. Q. Liu, F. Zhao, X. Dong, C. Yang, and F. Chen, "Synthesis and application of porous Sm$_{0.2}$Ce$_{0.8}$O$_{1.9}$ nanocrystal aggregates", *Journal of Physical Chemistry C*, 113 (2009) 17262-17267.


6. Z. Jiang, C. Xia, F. Zhao and F. Chen, "La$_{0.85}$Sr$_{0.15}$MnO$_{3-δ}$ infiltrated Y$_{0.5}$Bi$_{1.5}$O$_3$ cathodes for intermediate-temperature solid oxide fuel cells", *Electrochemical and Solid-State Letters*, 12 (2009) B91-B93.
**Sub-Project 3: Durability of Gaskets and Seals in PEM Fuel Cells**

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**Objective:** Develop a fundamental understanding how the degradation mechanisms of polymeric materials affects the performance and life of gasket/seals in PEMFC.

**Relevance:** Gasket/Seal as a structural member in Fuel Cells

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**Characteristics of gasket/seal:**

Under compression, exposed to chemicals, high temperature, pressure, cyclic conditions, etc.

**Loss of functionality:** by cracking and/or stress relaxation

- **Cracking:** due to corrosion under compression (Chemical stability)
- **Stress Relaxation:** material degradation... loss its sealing ability (mechanical stability)

**Leachants:** detrimental sometimes (chemical stability)
Approach

Task 1. Selection of Commercially Available Seal Materials (complete)

Task 2. Aging of Seal Materials (completed)
   In simulated regular and accelerated FC environment (ADT)
   With and without stress/deformation

Task 3. Characterization of Chemical Stability (completed)
   FTIR, XPS, Weight loss, Atomic Absorption for leachants detection

Task 4. Characterization of Mechanical Stability (completed)
   Tensile strength, ductility, DMA (Dynamic Mechanical Analyzer), micro-indentation, CSR (Compression Stress Relaxation)

Task 5. Development of Accelerated Life Testing Procedures (on-going)

Task 6. Industrial Interaction and Presentations (on-going)

Weight loss and chemical leaching (63 wks in ADT or Reg. at 80 °C)
Dynamic Mechanical Analyzer (DMA) tests

- For polymers
- Temp scan from -70°C to 200°C
- Tensile, bending and compression
- Elastic modulus, loss modulus
- Tg: glass transition temp

- ✓ Tg did not change!
- ✓ Modulus reduced for aged materials!

Chemical changes in backbone and crosslinked domain after 3 week exposure

No significant Chemical Changes after 42 week exposure
Stress relaxation and life prediction for polymeric gasket/seals in PEM fuel cell

Life prediction using 
WLF  time-temperature 
shift

Life prediction under 
actual PEMFC temp cycle 
and humidity – on-going

A comparison 
of storage modulus E' of five 
seal materials (a)CR, (b)FSR, 
(c)LSR, (d)EPDM, and (e)FKM

Data reflect the glass transition 
temp. (i.e. temp at the sharpest 
drop) and stiffness of the 
materials at different 
temperatures

Seal pressure prediction – 
predictive model 
development and 
verification

Comparison between experiment and prediction (LSR)
**Sub-Project 3: Summary- Technical Accomplishment**

1. **Optical microscope** and SEM analysis to examine the degradation of surface.
2. ATR-FTIR test to elucidate the material surface chemical degradation.
3. **Atomic adsorption spectrometry** analysis to identify leachants from seals into the soaking solutions.
4. **Microindentation** test for assessing the mechanical properties of the gasket materials.
5. DMA for assessing the dynamical mechanical properties of the gasket materials.
6. **Compression Stress relaxation** test system to monitor the retained seal force under fuel cell condition
7. **Developed** life prediction methodologies using WLF concepts
8. **On-going** - model development and verification for predicting compressive stress retained in seals under realistic temperature cycles
9. **Publications** in Journal and Conferences and discussions with members in the USC NSF IUCRC Center for Fuel Cells

**Example Technical Publications – Seals/PEM**

*Publications from Sub-project #3 – seal/gasket durability in PEM fuel cells*

Sub-Project 4: Hydrogen Quality

John Van Zee & Jean St. Pierre, Department of Chemical Engineering

Objective: To quantify the mechanisms of performance and durability loss resulting from contaminants in the fuel for PEMFCs by performing experiments, analyzing data, and developing models. The study will provide equilibrium and rate constants suitable for use in new and existing models, and in computer code at Argonne National Laboratory.

Objectives / Relevance

- Critical constituents for H2 quality are listed in Appendix C of the 2007 Technical Plan-Fuel Cells section of the Multi-Year Research, Development and Demonstration Plan. A North American Fuel Quality Team has been organized by Dr. James Ohi (NREL) to addresses the impact of these critical constituents as they affect the barriers of Durability, Cost, and Performance that are labeled A-C on page 3.4-25 of the Technical Plan. This project supports that team by obtaining experimental data, and is part of the cross-program effort on H2 quality that addresses parts of Tasks 1-3 and 8-10 of Table 3.4.15 entitled “Technical Task Descriptions” of the 2007 Technical Plan-Fuel Cells section of the Multi-Year Research, Development and Demonstration Plan.
### Approach

<table>
<thead>
<tr>
<th>Task Number</th>
<th>Project Milestones</th>
<th>Task Completion Date</th>
<th>Percent Complete</th>
<th>Progress Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>Develop techniques to assess transport of NH₃</td>
<td>09/30/09</td>
<td>100%</td>
<td>complete</td>
</tr>
<tr>
<td>4.1</td>
<td>Develop techniques to assess transport of Sulfur species</td>
<td>09/30/09</td>
<td>100%</td>
<td>complete</td>
</tr>
<tr>
<td>4.1</td>
<td>Measure transport rates and assess effect on contamination</td>
<td>03/30/10</td>
<td>100%</td>
<td>complete</td>
</tr>
<tr>
<td>4.1</td>
<td>Develop improved activation-loss model</td>
<td>10/30/09</td>
<td>100%</td>
<td>On-Track</td>
</tr>
<tr>
<td>4.2</td>
<td>Develop techniques to measure the isotherms and rate constants of Sulfur species</td>
<td>06/30/10</td>
<td>100%</td>
<td>complete</td>
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<tr>
<td>4.2</td>
<td>Develop techniques to measure ion exchange and reaction rates of NH₃</td>
<td>08/30/10</td>
<td>100%</td>
<td>complete</td>
</tr>
<tr>
<td>4.3</td>
<td>Publish comparison of model with performance data</td>
<td>06/30/10</td>
<td>100%</td>
<td>On-Track</td>
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<tr>
<td>4.3</td>
<td>Disseminate the data and findings</td>
<td>10/31/10</td>
<td>100%</td>
<td>Ongoing</td>
</tr>
</tbody>
</table>

We have shown that the NH₃ fuel contamination mechanism is one of ion-exchange and that specification of the fuel quality concentration depends on dosage and capacity of the MEA.

Amount of NH₃ detected from both electrodes by the effect of anode humidity with 100 ppm NH₃/N₂ (Flow rate A/C =150 sccm, Temp.: A/C/Cell =78/73/70°C)

![Graph with data points and trend lines showing the effect of humidity on NH₃ detection](image)

We can explain these results by considering that under humid conditions NH₃ would be dissolved in water and converted to NH₄⁺ which could displace (by ion exchange?) an H⁺ in the ionomer of the electrode and/or the membrane.
We have developed material balance techniques which allow for measurement of the flux and concentration during operation. We couple this material balance technique with reference electrode techniques.

We have developed reference electrode techniques to measure the change in electrode reactions during the transport of NH$_3$ from the anode to the cathode during open circuit conditions.

Here we show that 25 ppm CO does not affect the open circuit voltage but that 50 ppm NH$_3$ changes the cell voltage at open circuit after the MEA is fully exchanged. The 6 mV change corresponds to the NH$_3$ partial pressure s.
Here we show that 25 ppm CO does not affect the anode overpotential at open circuit voltage but that 50 ppm NH₃ changes the measured reference voltage at open circuit after the MEA is fully exchanged. The 310 mV change corresponds to the reaction:

\[ 2 \text{NH}_3 + H_2 = 2 \text{NH}_4^+ + 2 e^- \]

at these partial pressures.

We have shown that the transport and breakthrough is a local process because the MEA is thin compared to the channel length. Here we positioned the reference electrode at two positions. Case A corresponds to the exit and Case B is close to the entrance. This indicates that transport occurs after complete local exchange of the MEA.
We have shown that the transport is enhanced by migration in our hydrogen pump experiments. Below, with no current, there is a partition of the NH₃ exiting the cell which again corresponds to the partial pressure for the H₂ + NH₃ reaction. Reversal of the voltage changes the exit concentrations.

Accomplishments / milestones:

We have developed temperature programmed desorption techniques to identify the sulfur species that adsorb on the cathode through temperature programmed desorption and reaction. We chose SO₂ as a preliminary model compound for sulfur species in the fuel that may be transported to the cathode. It also serves the purpose as an air contaminant. The strongly adsorbed species may accumulate so that dosage is an important variable.
When we separate the effect of O$_2$ from N$_2$ we observe a “spillover” effect that is facilitated by Pt. This spillover gives an apparent isotherm which exceeds the Pt sites. We found that this effect is not reversible because the C-SO$_2$ is strong enough that once the SO$_2$ is removed from the Pt, the Pt sites are not re-contaminated.

Accomplishments / milestones:

A model was developed for the case of a contaminant that leads to a catalyst surface adsorbate that does not desorb. Two catalyst sites are required to reproduce the main experimental observation (partial performance recovery). The model appears valid with simple inorganic sulfur based contaminants (H$_2$S, SO$_2$, COS)
Technical Accomplishments & Progress – H₂ Quality
Accomplishments / milestones:

A method to extract kinetic rate constants is proposed and consists in the sequential measurement of current changes in the presence of a reactant, a contaminant and their combination. Use of model current change expressions (initial and steady state values, linear regime slopes) with corresponding experimental data is sufficient to determine all rate constants required for predictions. Comparison between model predictions and experimental data with both reactant and contaminant provides a steric effect diagnosis.

In the absence of recovery (liquid water, potential changes, etc), the model is able to predict a sulfur contaminant tolerance limit (worse case scenario) because rate constants and steady state current values are either independent or directly proportional to contaminant concentration. Because the steady state current loss is always at least equal to \(1 - \frac{k_1}{k''}\), the contaminant concentration is set to less than 0.7 ppb ensuring the dominant rate constant is larger than the application life of 5000 h.
The model predicts a significant effect of catalyst loading. Performance loss due to contamination is dependent on total catalyst site density $\rho$ and individual site densities $\rho_1$ and $\rho_2$. A catalyst loading reduction significantly impacts the steady state current loss $1 - \rho_1/\rho$. Validation data obtained with a 0.4 mg Pt/cm$^2$ leads to a 0.65 loss whereas a catalyst loading decrease to 0.1 mg Pt/cm$^2$ leads to a 0.91 loss corresponding to a 40% increase.

$$\frac{i}{i_{c_x=0}} = \frac{1}{\rho} \left[ \rho_1 \left( 1 - \frac{k'}{k''} \left( 1 - e^{-\frac{k't}{\rho_1}} \right) \right) + \rho_2 e^{-\frac{k't}{\rho_2}} \right].$$

The present model increases the existing inventory of cases derived using similar assumptions. In presence of a reactant, models generally show a similar behavior. In absence of a reactant, reaction mechanism identification is facilitated because different current transients occur with only a contaminant in the reactant stream.

<table>
<thead>
<tr>
<th>Measured variable for step changes in $c_Y$</th>
<th>$t$ ($c_x=0$)</th>
<th>$i_I$ ($c_x=0$)</th>
<th>$i_2$ ($c_y=0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst contamination kinetics</td>
<td>$i$</td>
<td>$i_1$</td>
<td>$i_2$</td>
</tr>
<tr>
<td>X electroactive ($k_\alpha=0$)</td>
<td>$i$</td>
<td>$i_1$</td>
<td>$i_2$</td>
</tr>
<tr>
<td>X reaction rds</td>
<td>$i$</td>
<td>$i_1$</td>
<td>$i_2$</td>
</tr>
<tr>
<td>$P_2$ desorption rds</td>
<td>$i$</td>
<td>$i_1$</td>
<td>$i_2$</td>
</tr>
<tr>
<td>Irreversible $P_2$ adsorption</td>
<td>$i$</td>
<td>$i_1$</td>
<td>$i_2$</td>
</tr>
<tr>
<td>X electroinactive ($k_\alpha=0$)</td>
<td>$i$</td>
<td>$i_1$</td>
<td>$i_2$</td>
</tr>
</tbody>
</table>
A method to extract rates constants for the case of a contaminant that desorbs from the catalyst surface was proved and the limitations were illustrated. For instance, the figure shows the current resulting from a pulse of hydrogen. Different electrode potentials and hydrogen concentrations were investigated. Subsequently, mixtures of hydrogen and carbon monoxide were investigated.

Example Publications:

Sub-Project 4: Summary - Technical Accomplishments

- The extent of transport of NH$_3$ has been quantified as a function of humidity in the anode and cathode streams; a mechanism for the transport and contamination has been verified at open circuit conditions to serve as a baseline for studying transport and reaction under load.

- Ex-situ methods have been developed to measure and identify sulfur species that remain on the catalysts and to measure isotherms for SO$_2$ adsorption on Pt/C catalysts using temperature programmed desorption/reaction techniques. At least two sulfur species on the surface of Pt catalysts in the presence of N$_2$ are indicated. Studies in the presence of O$_2$ and H$_2$O have been started. These studies have implications for sulfur species transport from fuel contaminants.

- A new model that describe partial recovery of performance indicative of simple sulfur based inorganic contaminants was completed. A procedure was proposed to determine all model rate constants. The model was used to predict a tolerance limit (worse case scenario) and the effect of a catalyst loading reduction.

- Rate constants were extracted from experimental data for the case of a contaminant that desorbs from the catalyst surface. More specifically, establishing correlations between experimental data and model allowed predictions of the effect of contaminant concentration and electrode potential.

Chris Xue and Ken Reifsnider, Department of Mechanical Engineering

Objective: To build a first principles multiphysics durability model based on interpretations of Electrochemical Impedance Spectroscopy (EIS) data that link the multiphysics processes, the microstructure, and the material states (and their changes), with cell impedance responses and global performance mechanistically.

Specific focus

• Material synthesis for intermediate temperature (IT)-SOFC systems
  – Solid state and chemical methods for material synthesis
  – X-Ray diffraction to examine material phases
  – SEM to examine microstructure

• Electrochemical characterization
  – V-I curves
  – Electrochemical impedance spectroscopy
  – Durability

• Mechanistic EIS model and mechanism study
  – CFD based multi-physics model for SOFCs and electrolyzers
  – Mechanistic EIS simulation
  – Mechanistic EIS model based experimental data interpretation
Cathode and electrolyte material synthesis for IT-SOFC development

- A series of new layered perovskite cathode materials are synthesized for IT-SOFCs
- Both proton conducting and ion conducting electrolyte materials are synthesized
- H. Ding and X. Xue, “GdBa0.5Sr0.5Co2O5+δ layered perovskite as promising cathode for proton conducting solid oxide fuel cells,” *Journal of Alloys and Compounds*, 2010, (in press)
Electrochemical characterization of IT-SOFC material systems

PrBaSrCo/SDC/SDC-NiO performance

- Cell performance is very promising in intermediate temperature conditions
- Durability tests demonstrated that SOFC performance is quite stable
- H. Ding and X. Xue, “PrBa0.5Sr0.5Co2O5+δ layered perovskite cathode for intermediate temperature solid oxide fuel cells,” *Electrochimica Acta, Vol. 55, 2010, pp. 3812.*

Durability test

EIS characterization of IT-SOFC material systems

- Electrochemical impedance spectroscopy has been measured for SOFCs under different operating conditions;
- Fundamental mechanisms study using model based data interpretation
SOFC model and EIS simulation

CFD based multi-physics model

Simulations of polarization performance and EIS

- Linked the distributed transport and electrochemical reaction processes, material state and microstructure to SOFC polarization performance
- Successfully built mechanistic EIS simulation approach
- A few journal papers are under review
Technical accomplishments — milestones

1. A series of cathode and electrolyte materials have been successfully synthesized and characterized;
2. A series of SOFCs have been fabricated and tested;
3. Extensive electrochemical characterizations have been performed, including V-I curves, impedance spectroscopy, durability test;
4. CFD based multi-physics SOFC/SOEC models have been developed;
5. Multi-physics model based mechanistic EIS simulation approach has been established for experimental data interpretation;
6. **Publications**: so far 18 journal papers, one book chapter, and 4 conference papers have been published from this funding support;
7. **Presentation and poster**: research results have been presented in various conferences, such as fuel cell seminar and exposition, American ceramic society, ASME fuel cell science and technology, etc.;
8. Instrument purchased: Solartron 1260 frequency response analyzer, Solartron 1287 potentiostat for EIS measurement.
Technical accomplishments — Example Publications

**Book Chapter**

**Journal papers**
1. Ding, H.; Xie, Y.; Xue, X., “Electrochemical performance of BaZr0.1Ce0.97Y0.1Yb0.135-δ electrolyte based proton-conducting SOFC with layered perovskite PrBaCo2O5+δ cathode,” Journal of Power Sources, Volume 196, Issue 5, pp. 2692-2697, (2011).
6. Ding, H.; Xue, X., “BaZr0.1Ce0.97Y0.1Yb0.135-δ electrolyte-based solid oxide fuel cells with cobalt-free PrBaFe2O5+δ layered perovskite cathode,” Journal of Power Sources, Vol. 195, 2010, pp 7038-7041.

**Conference Papers**
2. Shi, J. and Xue, X., “CFD analysis of anode-supported solid oxide fuel cells with heterogeneous electrode properties,” 34th International Conference and Exposition on Advanced Ceramics and Composites, Jan 24-29, 2010, Daytona Beach, FL.