Hydrogen Fuel Cell Development in Columbia (SC)

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University of South Carolina

May 2011

Project ID: FC073
Date: Tues., May 10, 2011
Time: 6:30-8:30 PM
Title/Topic: Hydrogen Fuel Cell Development in Columbia, SC (FY 2008)

OVERVIEW

Timeline:

- Start – July, 2008
- Finish – July, 2011
- 100% complete

Budget:

- Total DOE funding: $1,476,000
- Cost share: $369,000

Barriers:

- Cost – of catalysts, electrodes, & seals
- Durability of PEM & SOFC for transportation and portable power
- Performance under transient operation, and in the presence of hydrogen impurities

Partners:

- University of South Carolina

RELEVANCE

Objectives:

The **general objective** of this program is to contribute to the goals and objectives of the Fuel Cell Technologies Program of the Department of Energy by enhancing and supplementing the fuel cell research and development efforts at the University of South Carolina. The project **research activities** focus on the following **technical objectives**:

❑ The development of metal-free oxygen reduction catalysts to reduce cost, facilitate manufacturing, and enhance durability of fuel cells (Barriers A-C; Task 2 electrodes)

❑ The 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)

DOE Barriers: A-Cost, B-Durability, C-Performance, D-Transport, E,F-Thermal, air mgmt., G-Transient operation

RELEVANCE

Objectives (continued):

❑ The development of durable, low cost seals for PEM stacks, through the establishment of laboratory characterization methodologies and durability models that relate to cell/stack performance (Barriers A, C; Task 6 Seals)

❑ The 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)

❑ The 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)

- DOE Barriers: A-Cost, B-Durability, C-Performance, D-Transport, E,F-Thermal, air mgmt., G-Transient operation

Approach - Overview

Five sub-projects were selected by DOE to address technology challenges of cost, durability and reliability, system size, efficiency, and performance of PEM and SOFC fuel cells and systems. **Specific goals** addressed include specific power and energy density, cost, cycle capability, durability, transient response, and stack technologies.

1. Work on surface modification of carbon (previous DOE program DE-FC36-03GO13108) was leveraged to create new carbon-based, metal-free catalysts for oxygen reduction.

2. Work done under a partnership with NASA Glenn, Savannah River National Laboratory, and ENrG Inc. was leveraged to create a new symmetrical SOFC design with greatly increased durability, efficiency, and ease of manufacturing.

3. Recent advances at the University of South Carolina (USC) in controlled hydration and temperature characterization of polymer-based materials were used to establish a methodology for characterization of materials for seals in PEM stacks, leveraging work being done in the USC National Science Foundation Industry /University Cooperative Research Center for fuel cells at USC.

Approach – Overview (continued)

4. A partnership with NREL and investigators at other universities involved in the DOE Hydrogen Quality program at the national level formed the foundation of an effort to understand contaminant adsorption / performance relationships at high contaminant levels in PEM cells.

5. Conceptual foundations laid by previous and ongoing research supported by a variety of mission agencies and companies including DARPA, United Technologies Fuel Cells, ExxonMobil, and Henkel Loctite will be used to create a multiphysics engineering durability model based on multiphysics analysis and 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, to achieve attendant reductions in design, manufacturing, and maintenance costs and increases in reliability and durability.

PROJECT SUMMARY

The activities of the present program are contributing to the goals and objectives of the Fuel Cell Technologies Program of the Department of Energy through five sub-projects, which report significant progress since beginning in September, 2008, in the following areas:

- The development of **metal-free oxygen reduction catalysts** to reduce cost, facilitate manufacturing, and enhance durability of fuel cells
- The development of redox stable **mixed ionic and electronic conductors** (MIECs) for bi-electrode supported cell (BSC) symmetrical (and other) SOFC designs
- The development of durable, **low cost seals for PEM stacks**, through the establishment of laboratory characterization methodologies that relate to cell/stack performance
- The development of understandings and methodologies to establish **hydrogen quality** as it relates to PEM cell applications for transportation needs
- The development of first principles multiphysics durability models based on interpretations of Electrochemical Impedance Spectroscopy (EIS) data that form a foundation for **engineering durability during design and manufacture** of fuel cells

COLLABORATIONS

1. Member of the North American Fuel Quality Team organized by Dr. James Ohi (NREL) to addresses the impact of critical hydrogen fuel constituents as they affect the barriers of Durability, Cost, and Performance
2. SRNL: One invention disclosure on self-rising approach has been filed. Also collaborated with SRNL for nanostructured ceramic synthesis and AFRL for sulfur-tolerant ceramic anode work.
3. Air Force Research Laboratory (AFRL) - sulfur-tolerant anode development, with support for a summer faculty research fellowship for investigator on this program.
4. Dana and Dow-Corning – provided materials as well as their knowledge in seal materials to guide direction of our work
5. General Motors corporation – correlation with their stack testing results
6. Collaboration with ENrG Corporation on the modeling and design of the bi-electrode supported (BSC) SOFC electrode architecture.

Accomplishments

1. **Hydrogen quality -** 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.
2. **Carbon composite catalyst -** 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
3. **Hydrocarbon fuel SOFC -** 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
4. **Gaskets and Seals -** Developed life prediction methodologies using WLF concepts; initial model development and verification for predicting compressive stress retained in seals under realistic temperature cycles
5. **Durability modeling in SOFC -** A series of cathode and electrolyte materials have been successfully synthesized and characterized. CFD based multi-physics 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

Technical Accomplishments & Progress - Catalysts

DOE Hydrogen Program

Development of Carbon Composite Electro-Catalyst for the Oxygen Reduction Reaction (ORR)

Branko N. Popov

University of South Carolina

March 03, 2011

COLLEGE OF ENGINEERING AND COMPUTING
UNIVERSITY OF SOUTH CAROLINA

Technical Accomplishments & Progress – Catalysts

Objective:

OVERALL OBJECTIVE: To develop non-precious metal catalysts (NPMC):

- active reaction sites with strong Lewis basicity (π electron delocalization) to facilitate reductive O_2 adsorption in alkaline electrolyte
- nano-structured graphitic carbon with high stability in alkaline electrolyte

SPECIFIC FOCUS:

Metal-free NPMC

Surface modification of carbon black with:
(i) O-containing group
(ii) N-containing group
Pyrolysis

Metal-containing NPMC

"Nitrogen-containing carbon" prepared from carbon-supported metal-N chelate
Pyrolysis
Chemical treatment

Technical Accomplishments & Progress – Catalysts

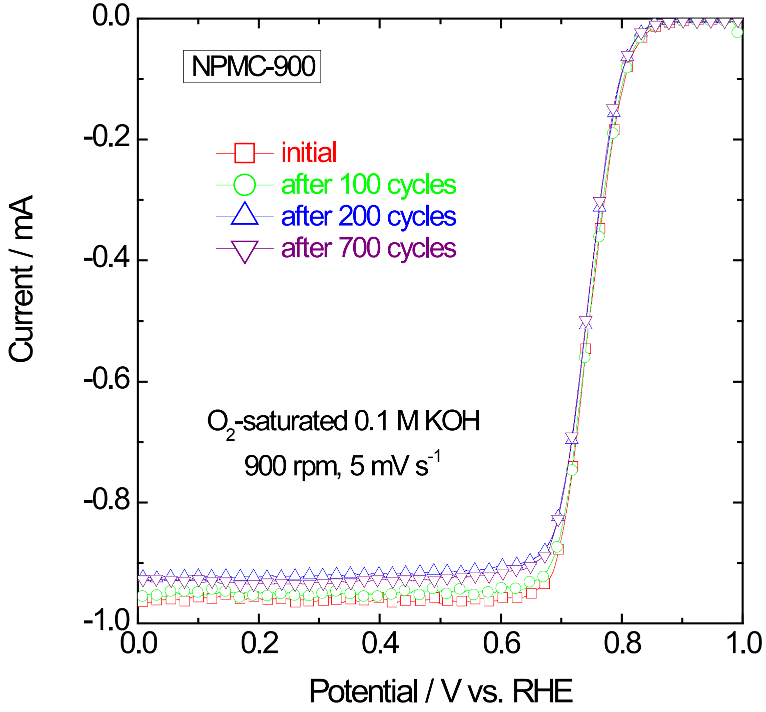
Technical accomplishments

- ☐ The non-precious metal catalysts (NPMCs) is developed with exceptional activity and stability for oxygen reduction in alkaline electrolyte by introducing N-based active sites on activated carbon.
- ☐ The pyridinic-N and graphitic-N are active sites in 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}.

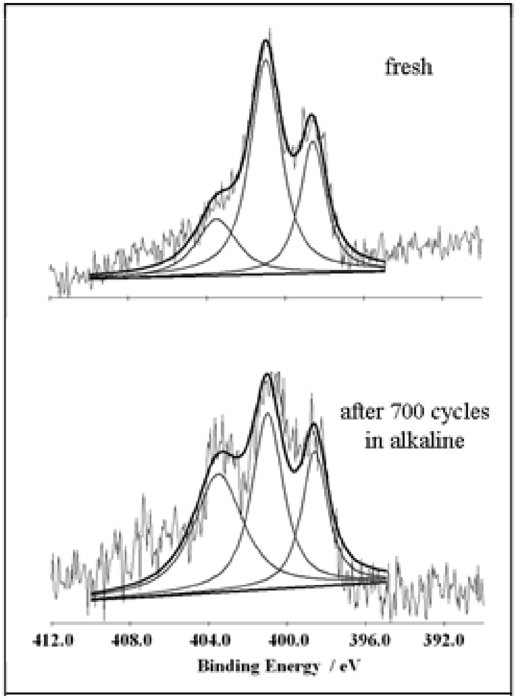
Technical Accomplishments & Progress – Catalysts

Stability in Alkaline Electrolyte and Nature of Active Sites

RDE



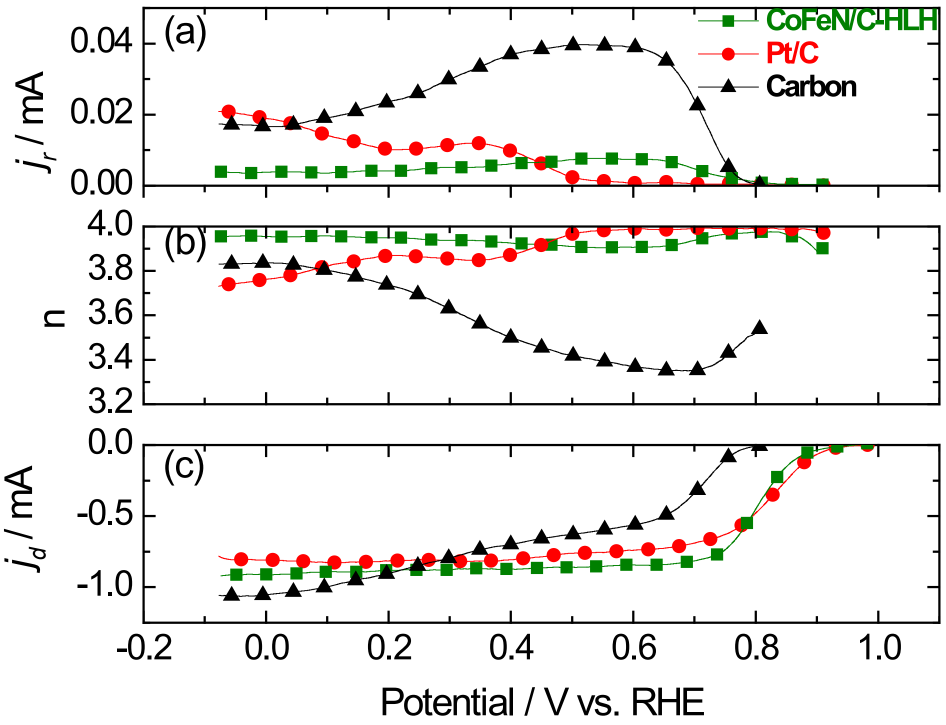
XPS



- The stability of NPMC in alkaline electrolyte is exceptionally high.
- The pyridinic-N and graphitic-N play important roles in the active sites of the NPMCs.

Technical Accomplishments & Progress – Catalysts

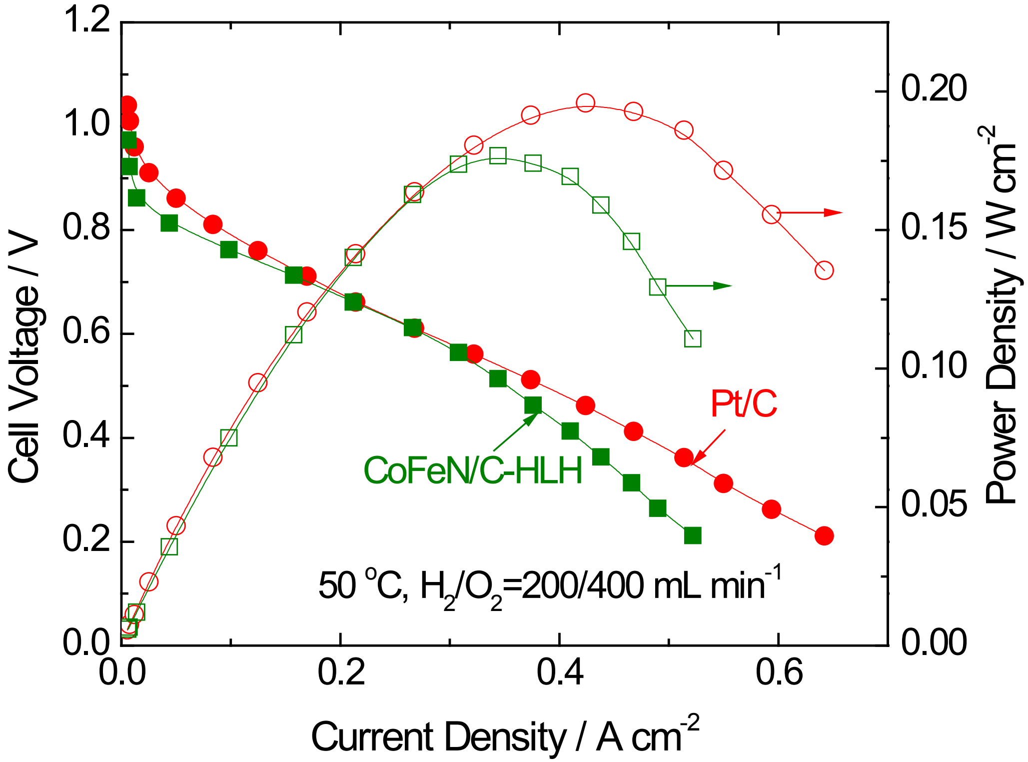
Activity and selectivity measured by RRDE



- Both CoFeN/C-HLH and Pt/C catalysts catalyze the ORR mainly via a four-electron pathway in alkaline electrolyte.
- The catalytic performance of CoFeN/C-HLH is very comparable with Pt/C for oxygen reduction in alkaline electrolyte.

Technical Accomplishments & Progress – Catalysts

Anion exchange membrane (AEM) fuel cell performance (in collaboration with Tokuyama Corp., Japan)



- The open circuit potentials are 0.97 and 1.04 V for CoFeN/C-HLH and Pt/C.
- The maximum power densities are 177 and 196 mW cm^{-2} for CoFeN/C-HLH and Pt/C, respectively.

SOFC - Technical Accomplishments & Progress

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

Frank Chen
Department of Mechanical Engineering
University of South Carolina

Technical Accomplishments & Progress – SOFC

Objectives / Relevance

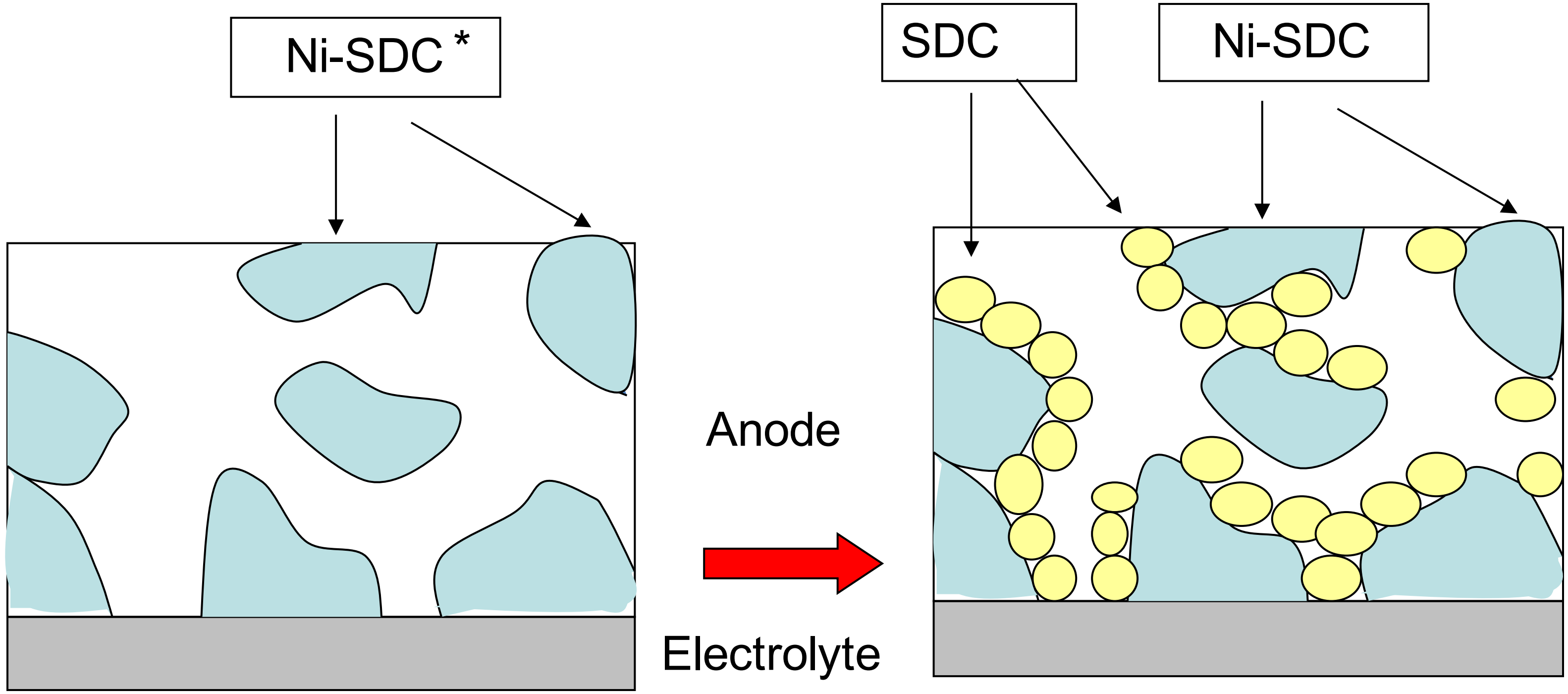
This main **focus** of this project is to develop a high performance solid oxide fuel cell (SOFC) which can directly operate on hydrocarbon fuels and achieve high power density.

In order to meet this goal, the experiments are designed with the following **tasks**:

- Develop Ni modified ceramic anodes for direct-methane SOFCs.
- 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.

Technical Accomplishments & Progress – SOFC

Approach - Ceria-infiltrated Ni-ceria Anode



Ni-SDC *

SDC

Ni-SDC

Anode

Electrolyte

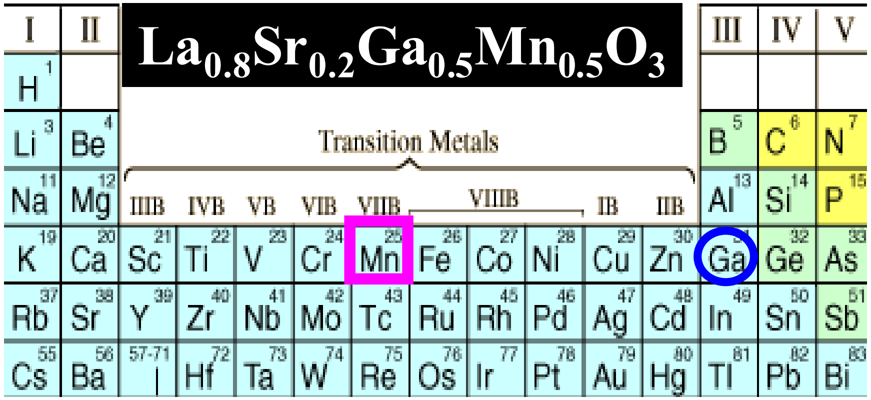
* SDC: Samaria Doped Ceria

1. **Ni particles covered by ceria, reduced activity for carbon formation**
2. **Ceria is a good catalyst to remove carbon.**

$$CeO_2 + C \leftrightarrow 1/2Ce_2O_3 + CO$$

Technical Accomplishments & Progress – SOFC

Approach - Mixed Conducting Anode



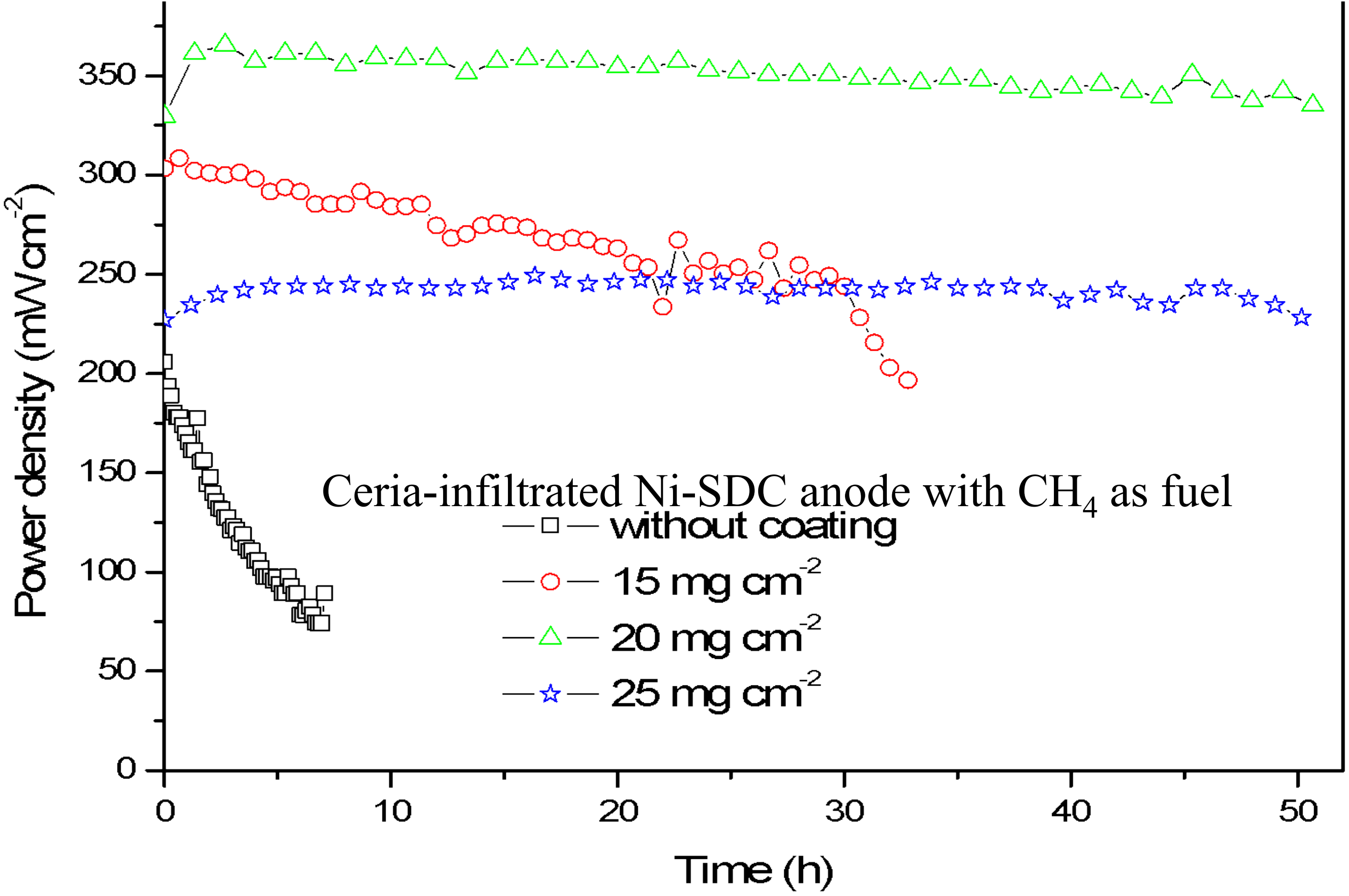
$La_{0.8}Sr_{0.2}Ga_{0.5}Mn_{0.5}O_3$

	Mn	**Ga**	**Mg**	**Sr**	**La**
Element radius (pm)	127	135	160	215	187
1+ ion radius (pm)		81			139
2+ ion radius (pm)	80		66	112	
3+ ion radius (pm)	66	62			102

- $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (LSGM) is an excellent ionic conductor
- $La_{0.8}Sr_{0.2}Ga_{0.5}Mn_{0.5}O_3$ (LSGMn) potential mixed conducting anode
- Introducing electronic conduction while maintaining ionic conduction

Technical Accomplishments & Progress – SOFC

Accomplishment / Milestone

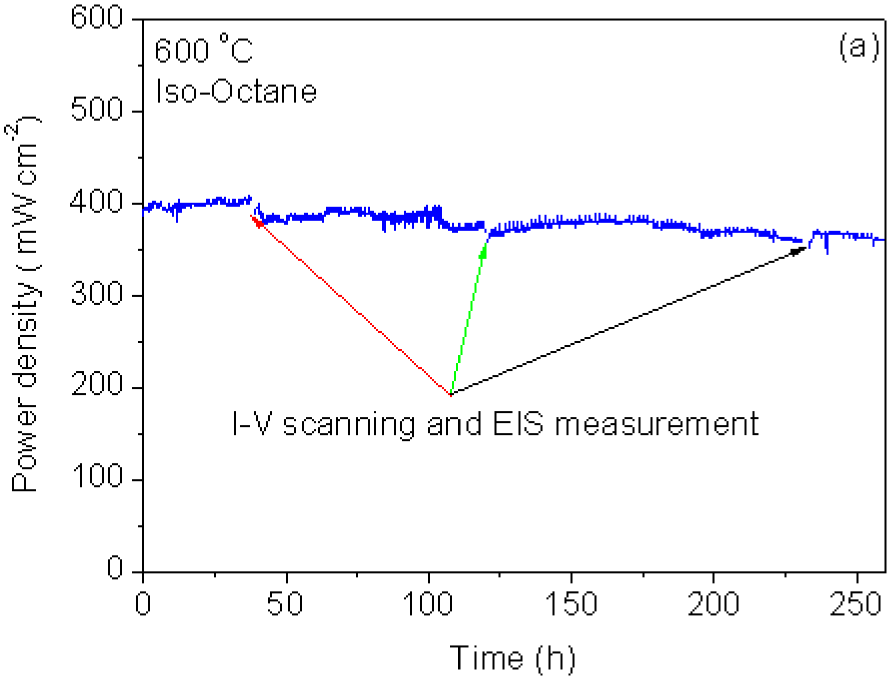


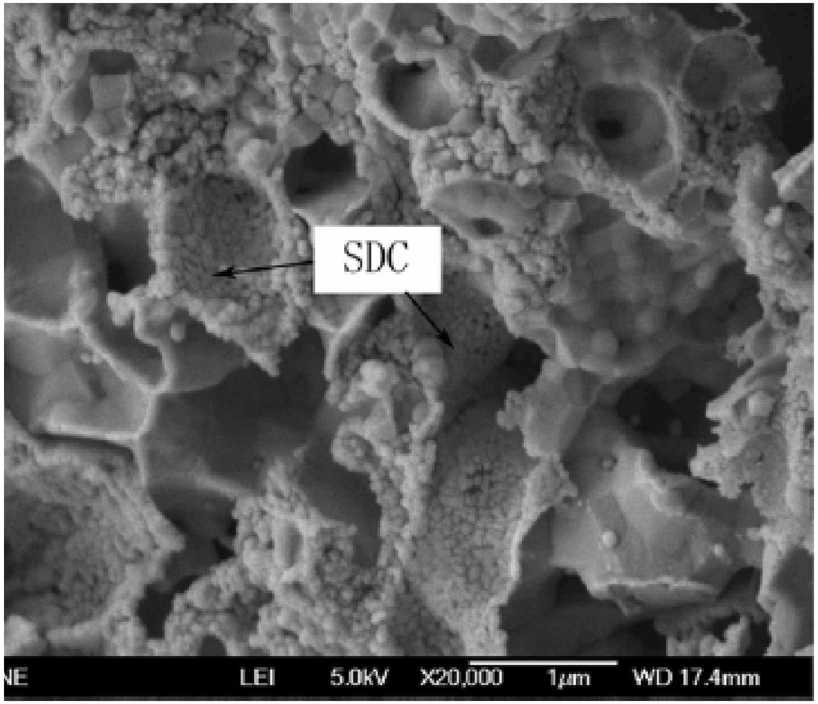
Ceria infiltrated anodes - Enhanced activity; Directly using hydrocarbons as fuel

Technical Accomplishments & Progress – SOFC

Accomplishment / Milestone

Ceria-infiltrated Ni-SDC anode with iso-octane as fuel

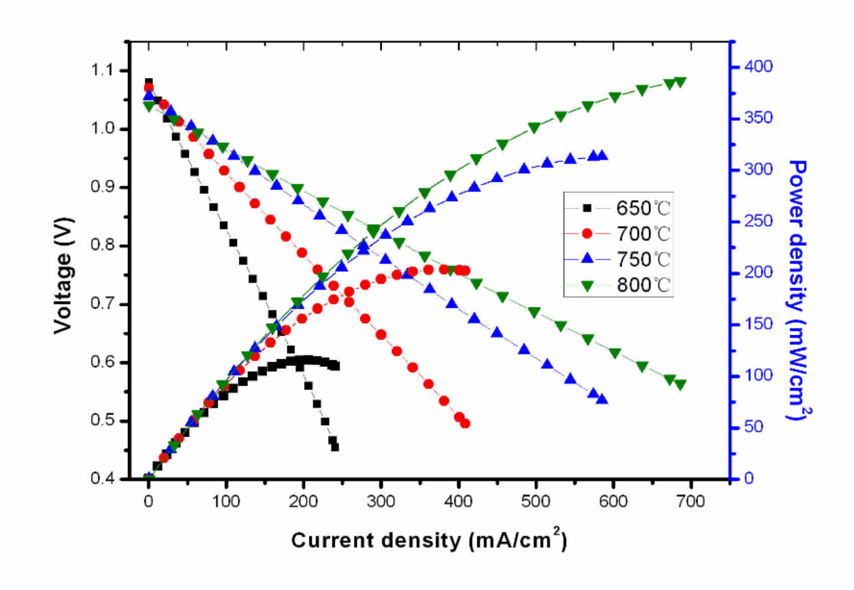


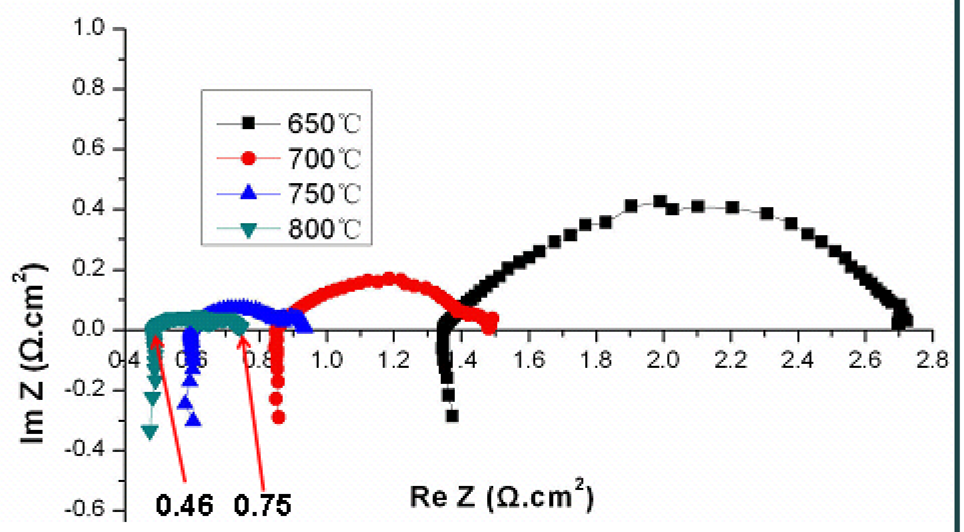


Ceria infiltrated anodes - Directly using iso-actane as fuel; Avoiding carbon formation

Technical Accomplishments & Progress – SOFC

Accomplishment / Milestone

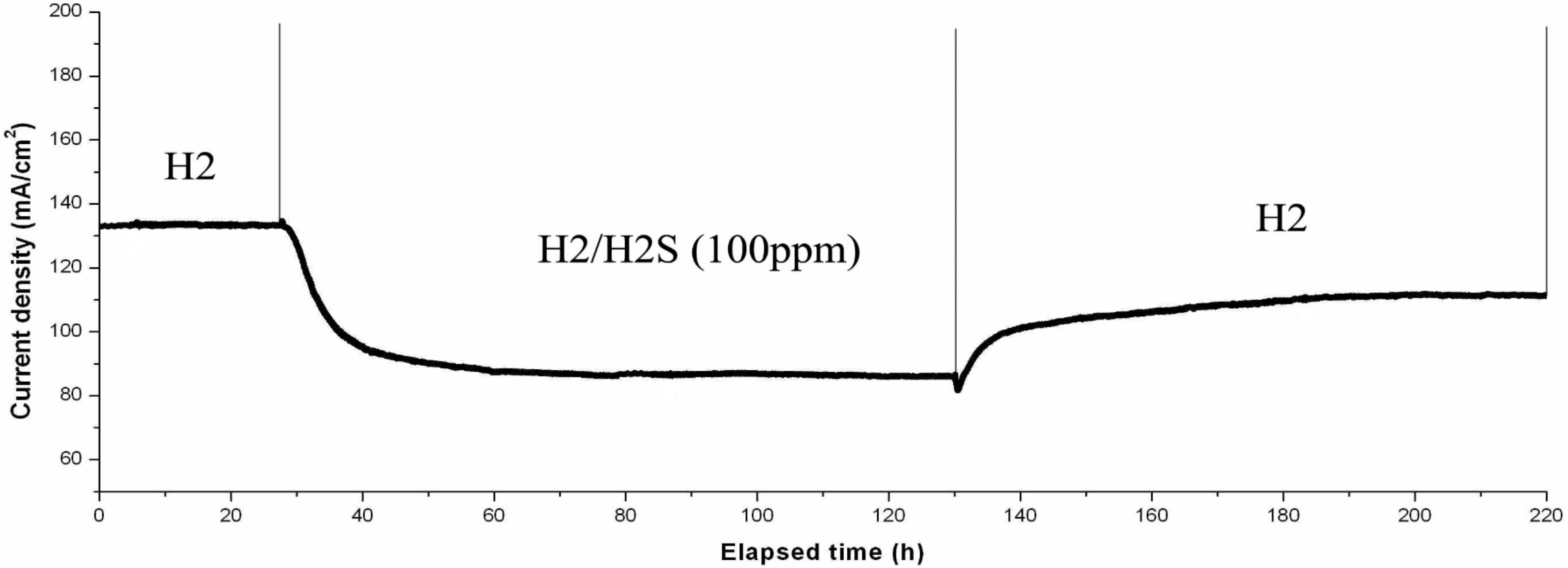




Electrolyte supported, LSGM electrolyte (~400mm)
LSGMn as anode and LSCF as cathode
LSGMn as anode materials has reasonable conductivity and cell performance

Technical Accomplishments & Progress – SOFC

Accomplishment / Milestone



Electrolyte supported, LSGM electrolyte (~400mm)

LSGMn as anode and LSCF as cathode

LSGMn as anode materials has reasonable sulfur tolerance

Technical Accomplishments & Progress – SOFC

Summary – Hydrocarbon Fuel SOFC

Relevance: Develop materials for a high performance solid oxide fuel cells which can directly operate on hydrocarbon fuels and achieve high power density.

Approach: Developing strategy to mitigate carbon deposition on the anode for direct utilization of methane-based hydrocarbon fuels; Demonstrating sulfur tolerance on the anode by utilizing advanced ceramic material.

Technical Accomplishment and Progress: Modified Ni-based anode and demonstrated excellent cell performance for direct oxidation of methane; Developed mixed conducting ceramic anode based on $LaGaO_3$ system and demonstrated excellent sulfur tolerance.

Technology Transfer / Collaborations: Two US patent applications on materials development for SOFCs have been filed. Collaborated with Air Force Research Laboratory and ENrG, Inc for SOFC developments.

Seals/PEM - Technical Accomplishments & Progress

Sub-Project 3: Durability of Gaskets and Seals in PEM Fuel Cells

Yuh J. Chao
Department of Mechanical Engineering
University of South Carolina

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

From Company 1

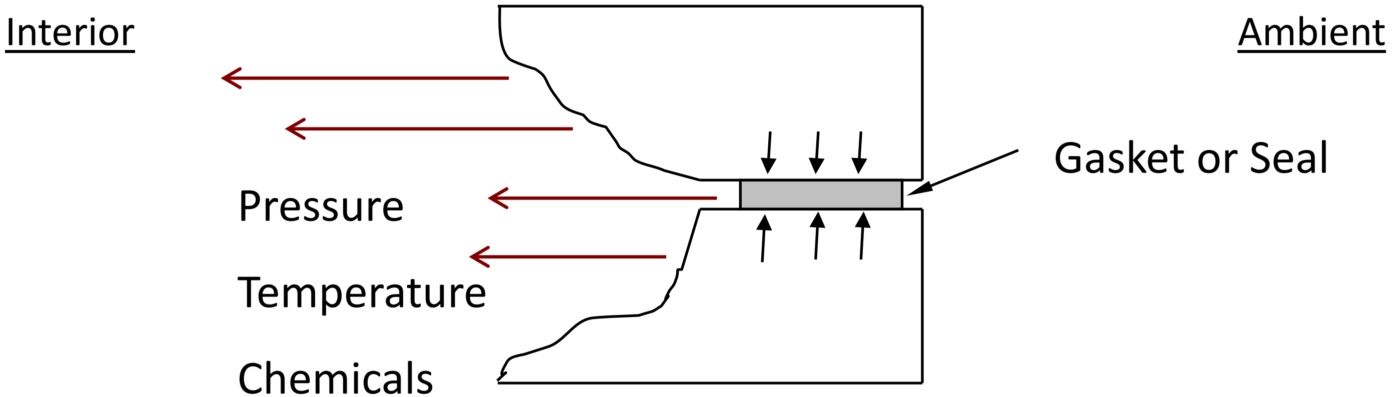
liquid silicone elastomer (**DLS**),
Fluorosilicone rubber(**DFS**),
copolymeric resin(**DC**)

From Company 2

EPDM,
Fluoroelastomer(**FKM**)

Technical Accomplishments & Progress – Seals/PEM

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



Interior

Ambient

Gasket or Seal

Pressure

Temperature

Chemicals

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)

Technical Accomplishments & Progress – Seals/PEM

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)*

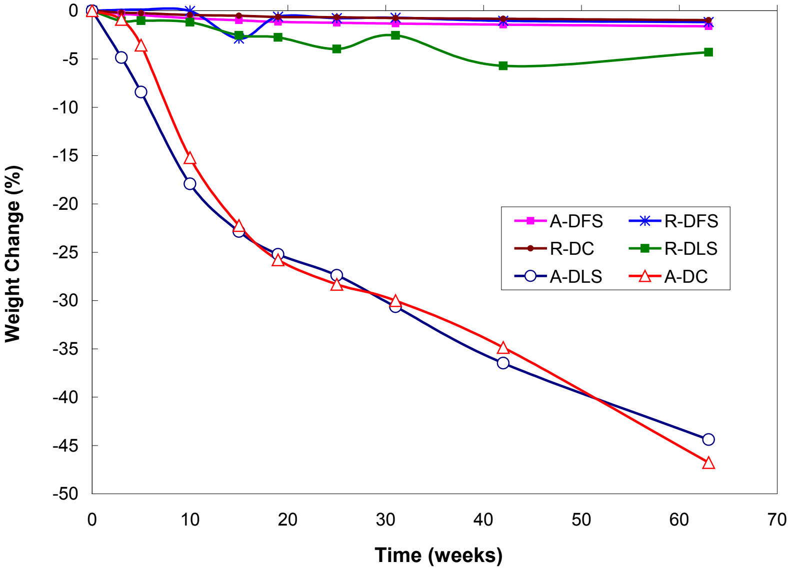
Tensile strength, ductility, DMA (Dynamic Mechanical Analyzer), micro-indentation, CSR (Compression Stress Relaxation)

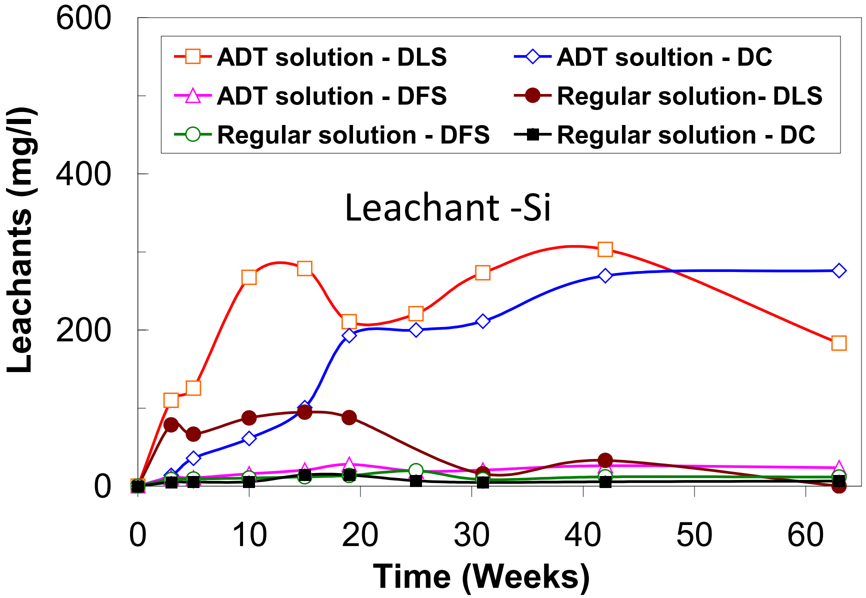
Task 5. Development of Accelerated Life Testing Procedures (on-going)

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

Technical Accomplishments & Progress – Seals/PEM

Weight loss and chemical leaching (63 wks in ADT or Reg. at 80 ^{0}C)

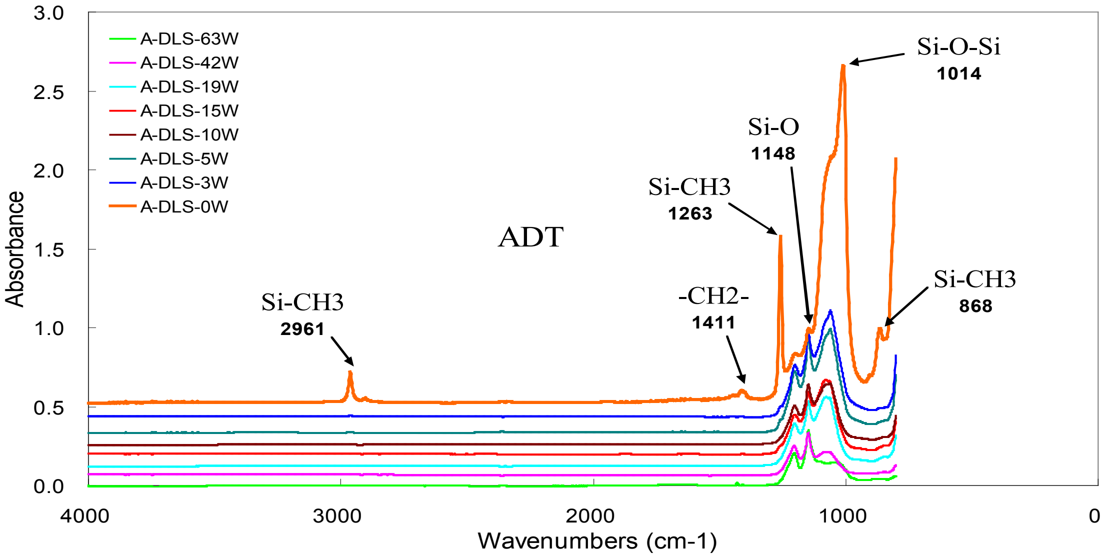




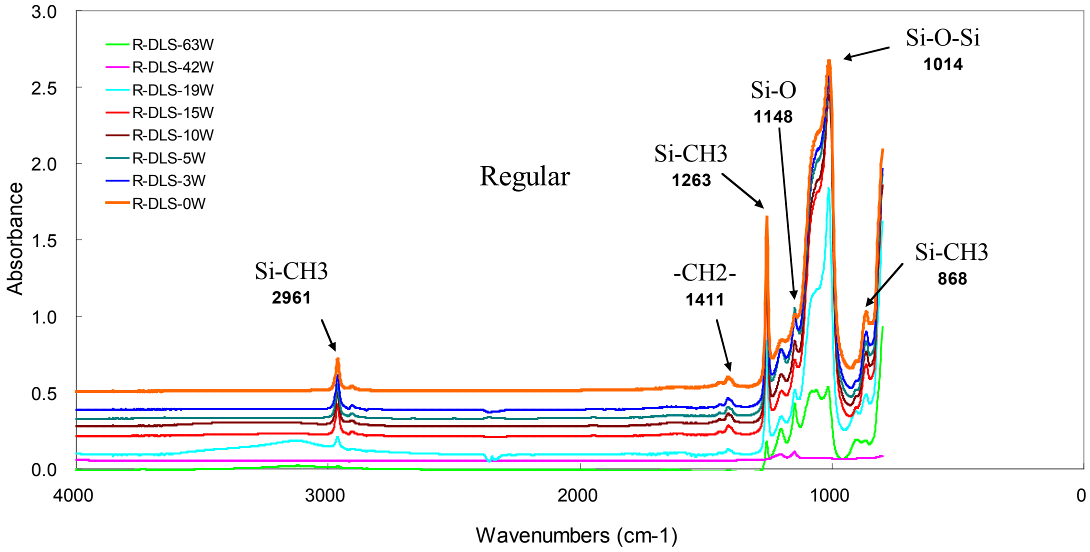
- A-DLS and A-DC → more weight loss and more Si leaching → **Lost Si is the cause of weight loss**
- Detectable Mg only in A-DLS
- The amount of Ca is negligible, except for R-DLS (0-3 mg/*l*) and A-DLS (0-12 mg/*l*)
- The amount of Si is in the range of 5-300 mg/l
- Note:
  - ADT (Accelerated Durability Test) solution - 1M H_2SO_4, 10ppm HF and reagent grade water
  - Regular solution (close to that in PEMFC)- 12ppm H_2SO_4 and 1.8ppm HF with reagent grade water

Technical Accomplishments & Progress – Seals/PEM

ATR-FTIR for DLS (ADT and Regular Solution)



Chemical changes in backbone and crosslinked domain after 3 week exposure



No significant Chemical Changes after 42 week exposure

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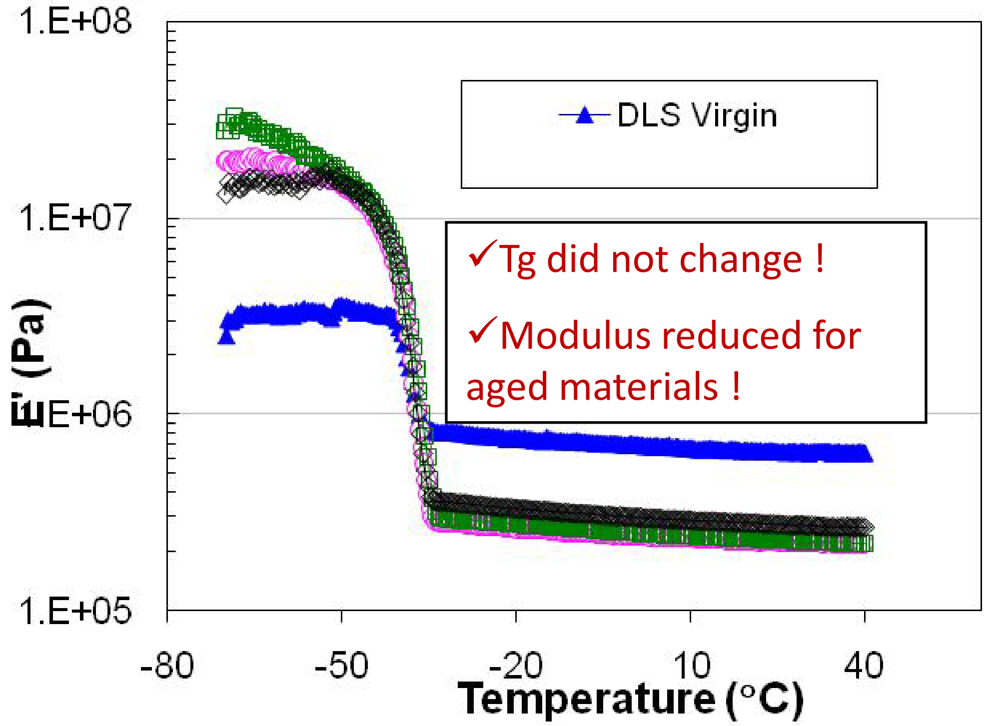
Technical Accomplishments & Progress – Seals/PEM

Dynamic Mechanical Analyzer (DMA) tests

- For polymers
- Temp scan from -70^{0}C to 200 ^{0}C
- Tensile, bending and compression
- Elastic modulus, loss modulus
- Tg: glass transition temp

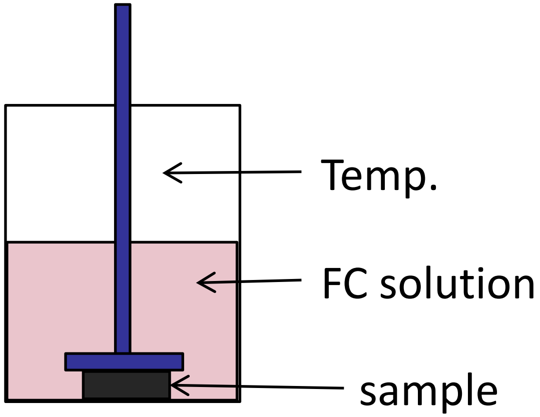


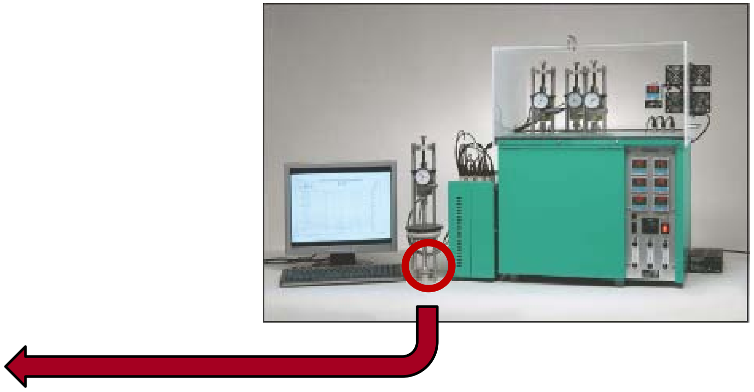
✓Tg did not change !

✓Modulus reduced for aged materials !

Technical Accomplishments & Progress – Seals/PEM

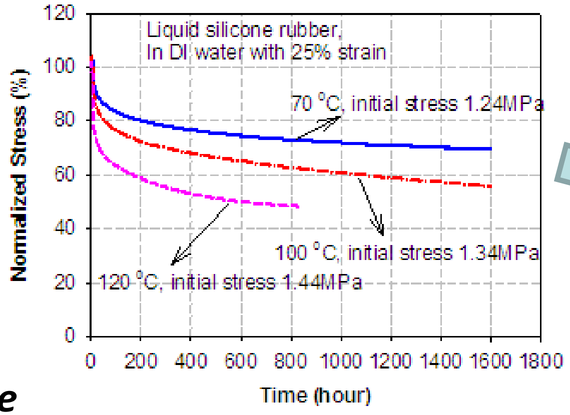
Stress relaxation and life prediction for polymeric gasket/seals in PEM fuel cell



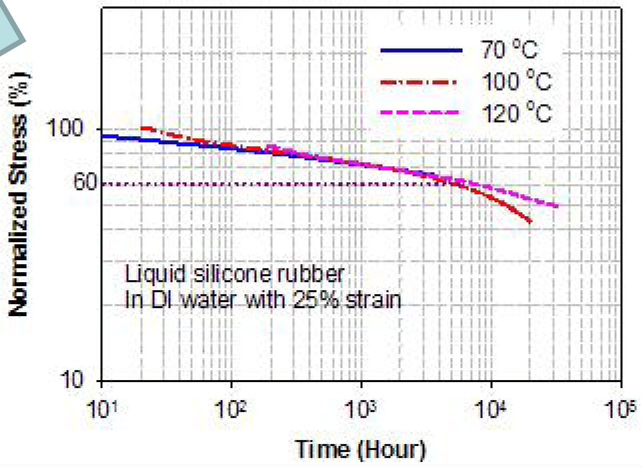


Life prediction using WLF time-temperature shift

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



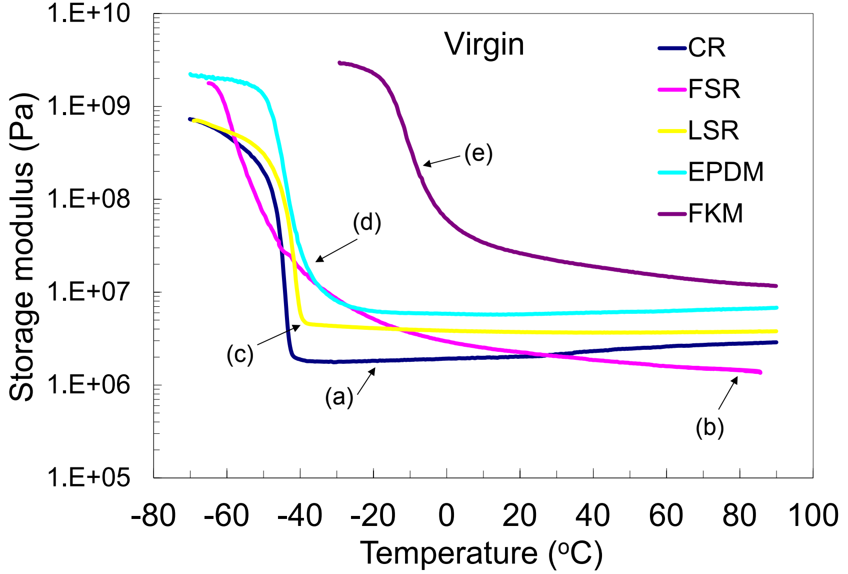
Master curve of stress relaxation of LSR in water at a reference temperature of 70°



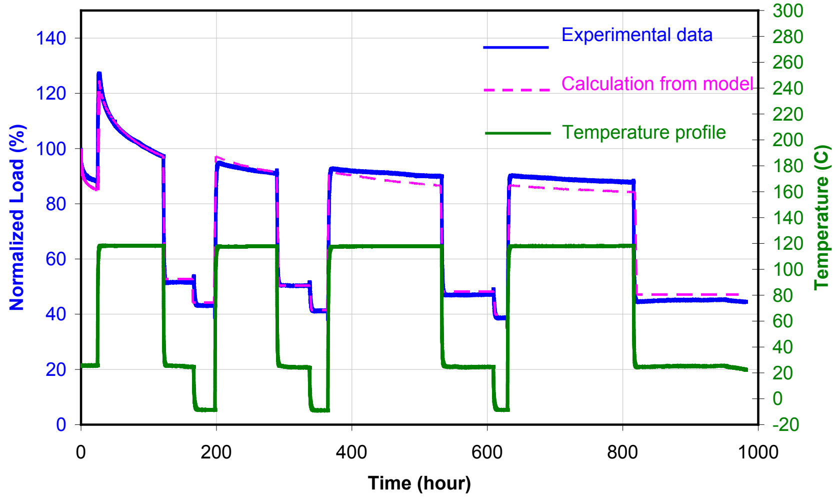
Technical Accomplishments & Progress – Seals/PEM

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)

Technical Accomplishments & Progress – Seals/PEM

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

H2 Quality - Technical Accomplishments & Progress

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.

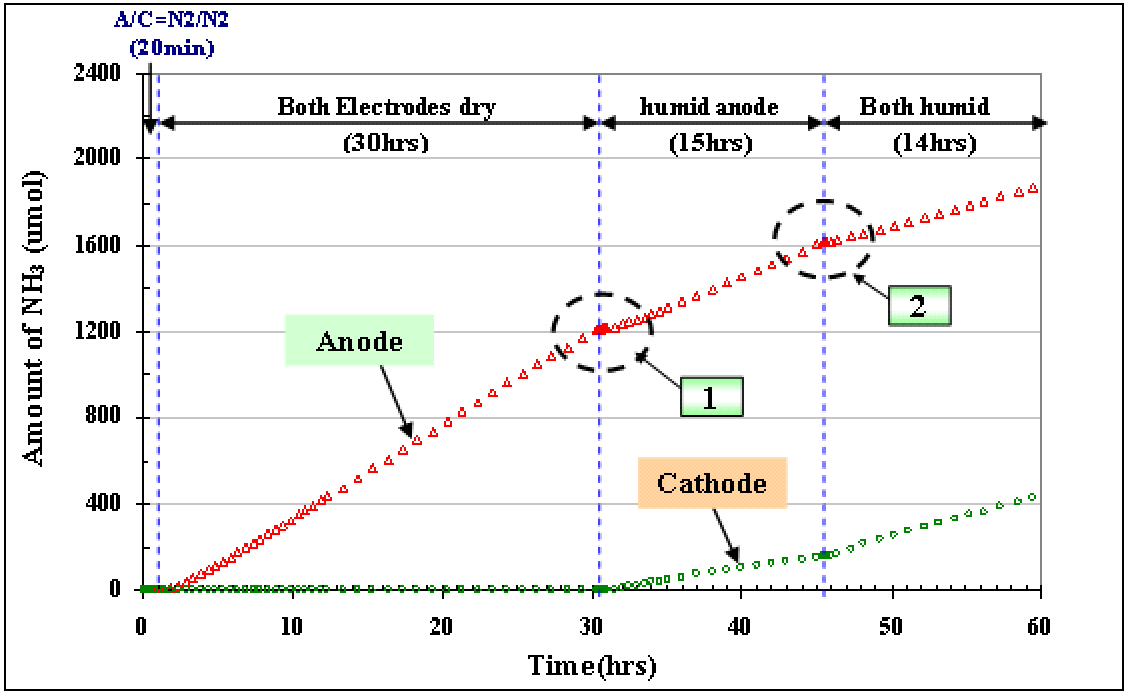
Technical Accomplishments & Progress – H Quality Approach

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
4.1	Develop techniques to assess transport of NH_3	09/30/09			100%	complete
4.1	Develop techniques to assess transport of Sulfur species;	09/30/09			100%	complete
4.1	Measure transport rates and assess effect on contamination	03/30/10			100%	complete
4.1	Develop improved activation-loss model	10/30/09			100%	On-Track
4.2	Develop techniques to measure the isotherms and rate constants of Sulfur species	06/30/10			100%	complete
4.2	Develop techniques to measure ion exchange and reaction rates of NH_3	08//30/10			100%	complete
4.3	Publish comparison of model with performance data	06/30/10			100%	On-Track.
4.3	Disseminate the data and findings	10/31/10			100%	Ongoing.

Technical Accomplishments & Progress – H_2 Quality

We have shown that the NH_3 fuel contamination mechanism is one of ion-exchange and that specification of the fuel quality concentration depends on dosage and capacity of the MEA.

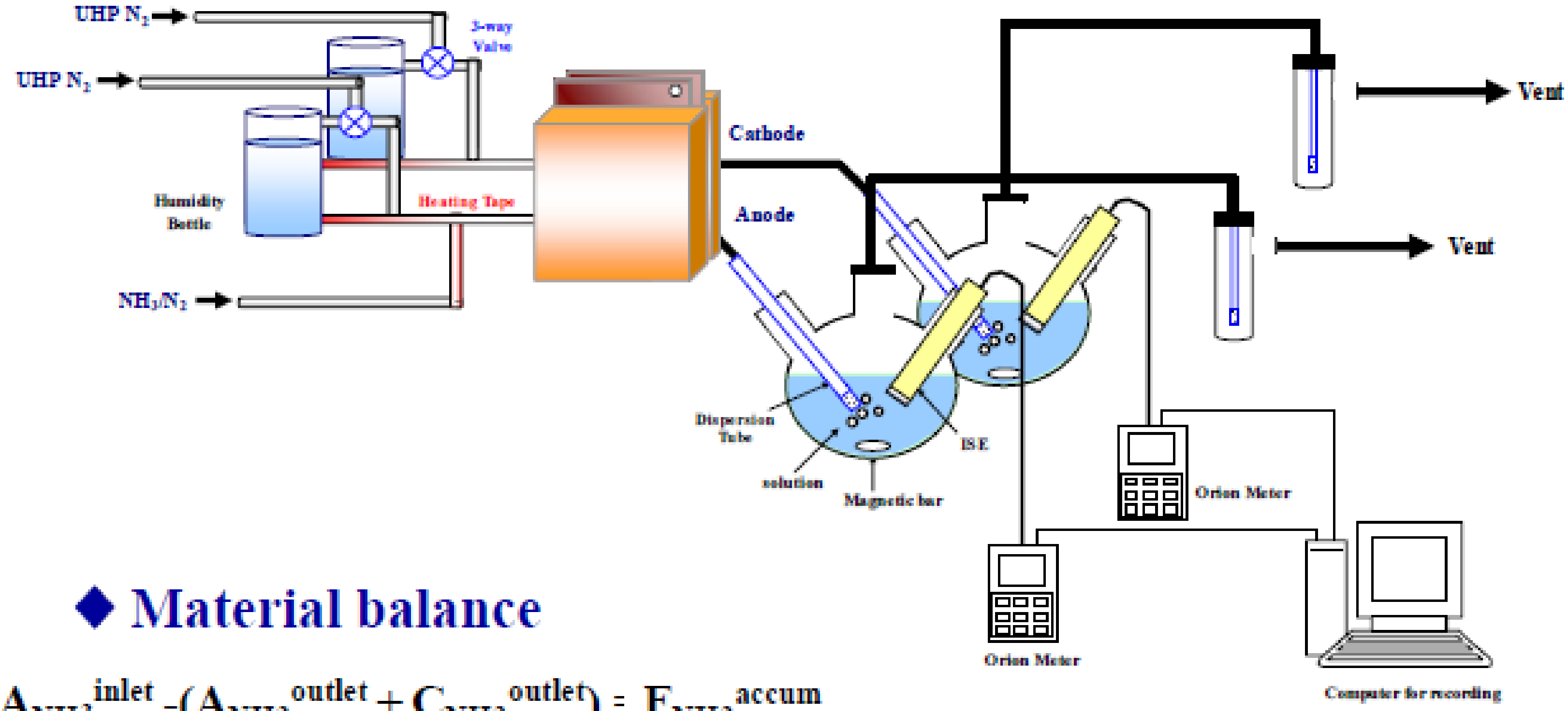
Amount of NH_3 detected from both electrodes by the effect of anode humidity with 100 ppm NH_3/N_2 (Flow rate A/C =150 sccm, Temp.: A/C/Cell =78/73/70°C)



We can explain these results by considering that under humid conditions NH_3 would be dissolved in water and converted to NH_4+ which could displace (by ion exchange?) an H+ in the ionomer of the electrode and/or the membrane.

Technical Accomplishments & Progress – H_2 Quality

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.



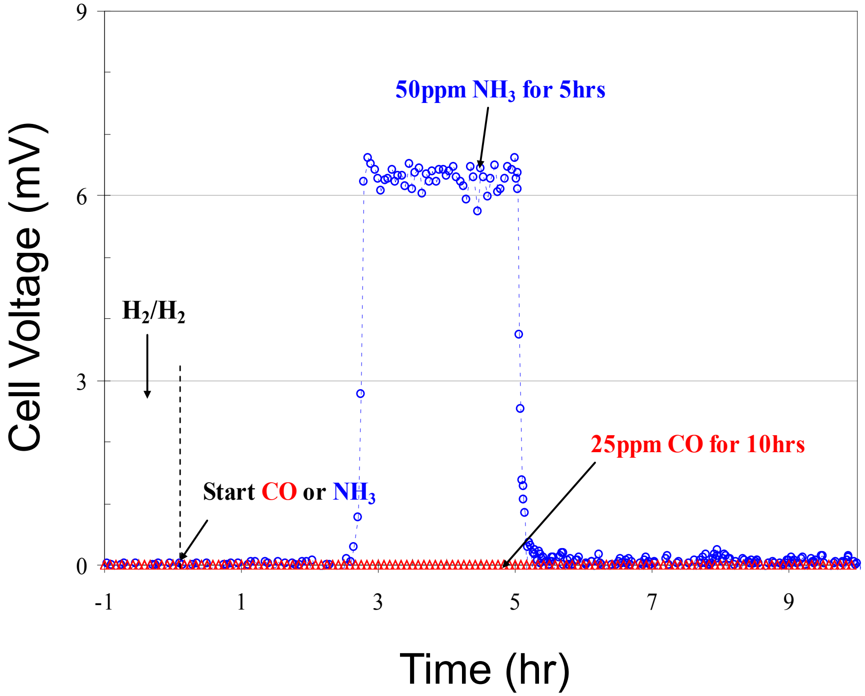
- Material balance

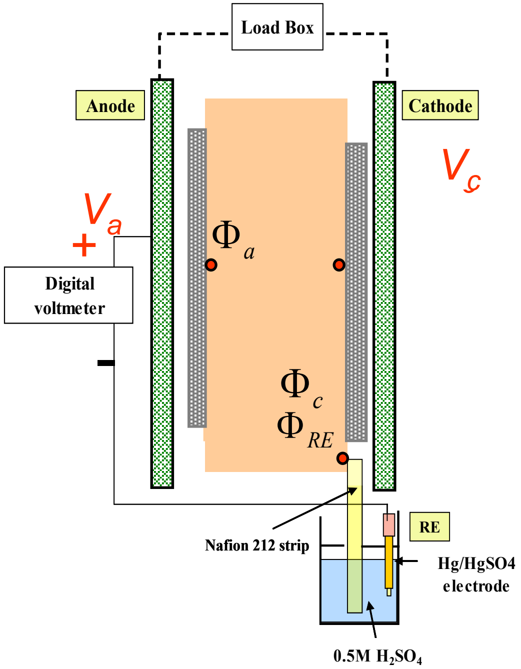
$$A_{NH3}^{inlet} - (A_{NH3}^{outlet} + C_{NH3}^{outlet}) = F_{NH3}^{accum}$$

A_{NH3}, C_{NH3}, F_{NH3} in moles

Technical Accomplishments & Progress – H_2 Quality

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





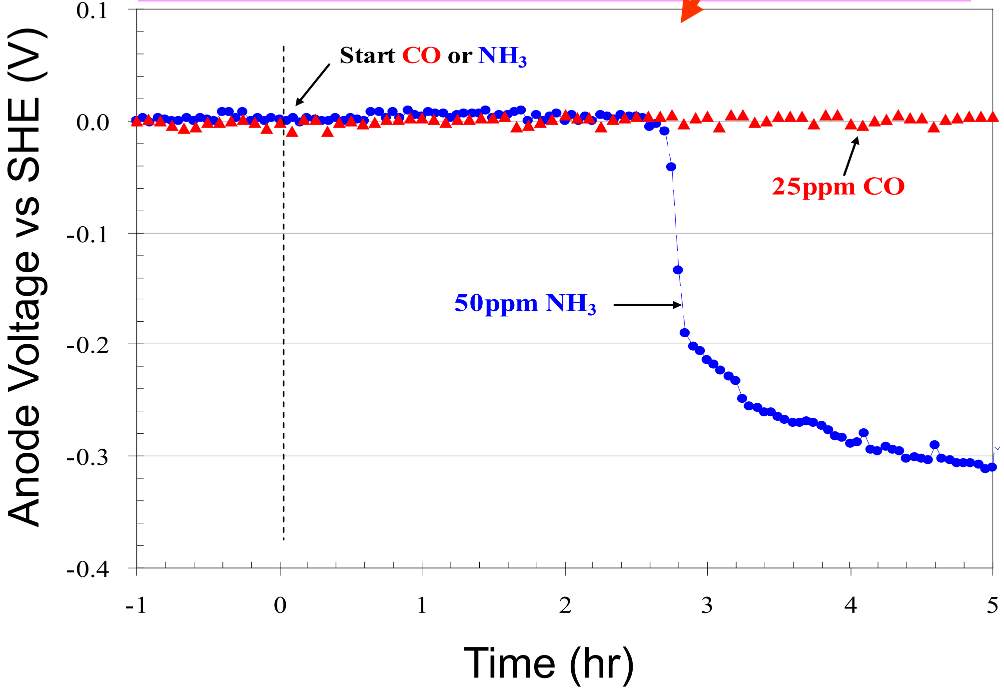
Here we show that 25 ppm CO does not affect the open circuit voltage but that 50 ppm NH_3 changes the cell voltage at open circuit after the MEA is fully exchanged. The 6 mV change corresponds to the NH_3 partial pressure s.

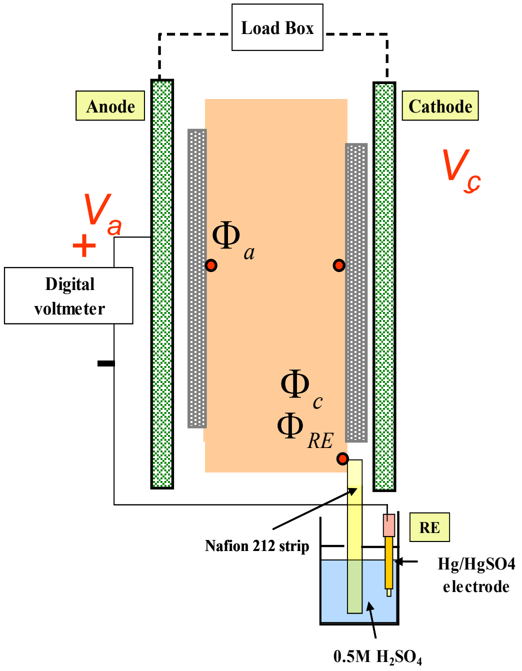
Technical Accomplishments & Progress – H_2 Quality

Here we show that 25 ppm CO does not affect the anode overpotential at open circuit voltage but that 50 ppm NH_3 changes the measured reference voltage at open circuit after the MEA is fully exchanged. The 310 mV change corresponds to the $2\,NH_3 + H_2 = 2\,NH_4^+ + 2\,e^-$ at these partial pressures.

at OCV

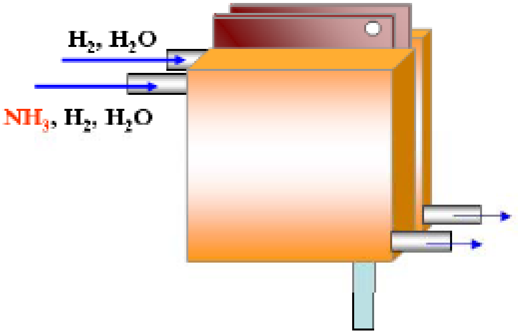
$$\text{Anode voltage} = V_a - \Phi_{RE} = \eta_a + \Phi_a - \Phi_{RE}$$



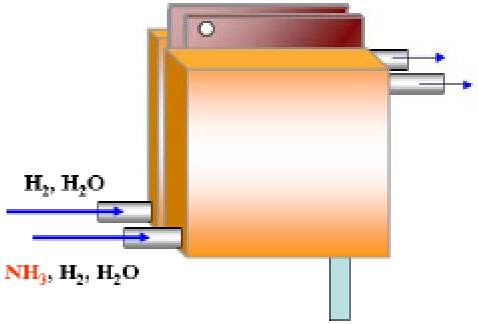


Technical Accomplishments & Progress – H_2 Quality

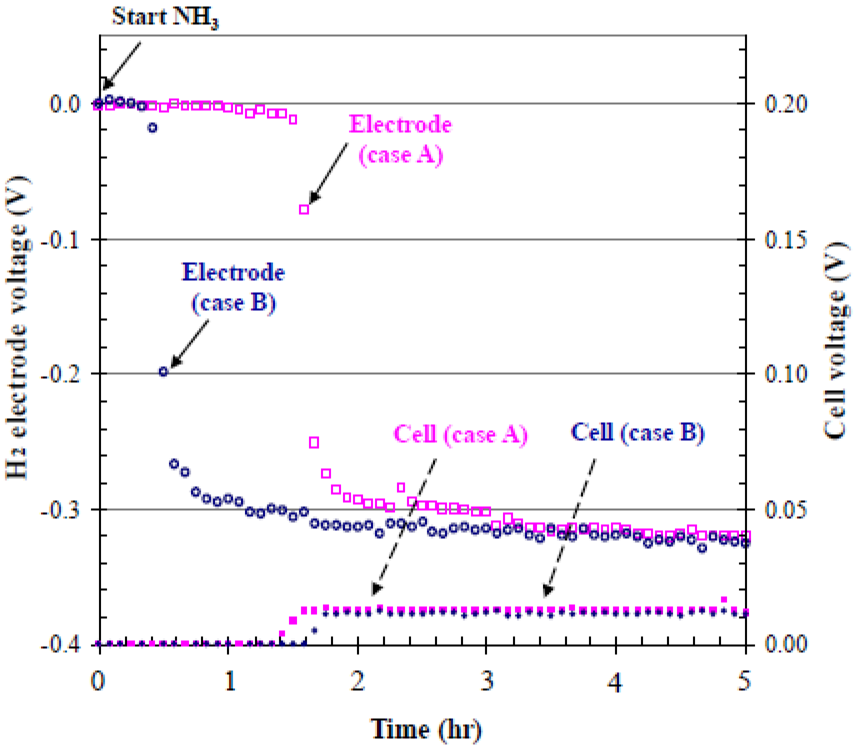
We have shown that the transport and breakthrough is a local process because the MEA is thin compared to the channel length. Here we positioned the reference electrode at two positions. Case A corresponds to the exit and Case B is close to the entrance. This indicates that transport occurrs after complete local exhange of the MEA.



<Case A>: NH_3 flow from top to bottom

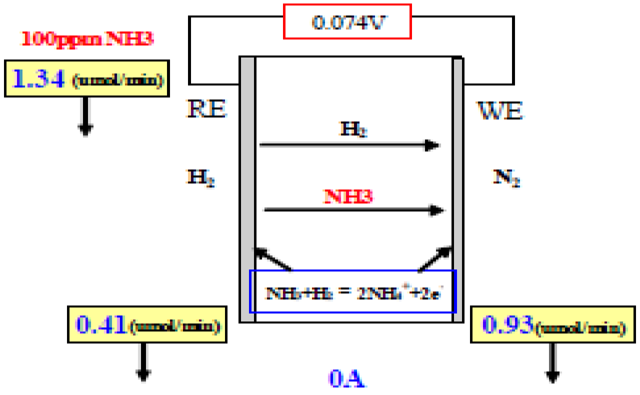


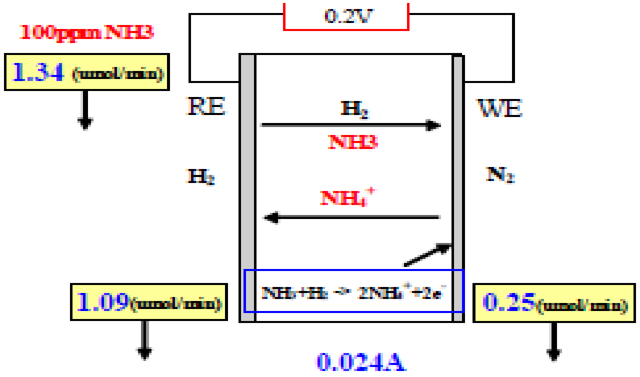
<Case B>: NH_3 flow from bottom to top

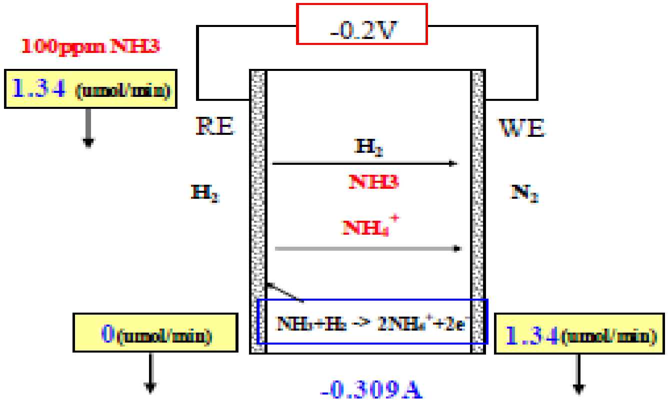


Technical Accomplishments & Progress – H_2 Quality

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 NH_3 exiting the cell which again corresponds to the partial pressure for the H_2 + NH_3 reaction. Reversal of the voltage changes the exit concentrations.







$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi$$

Diffusion **Migration**

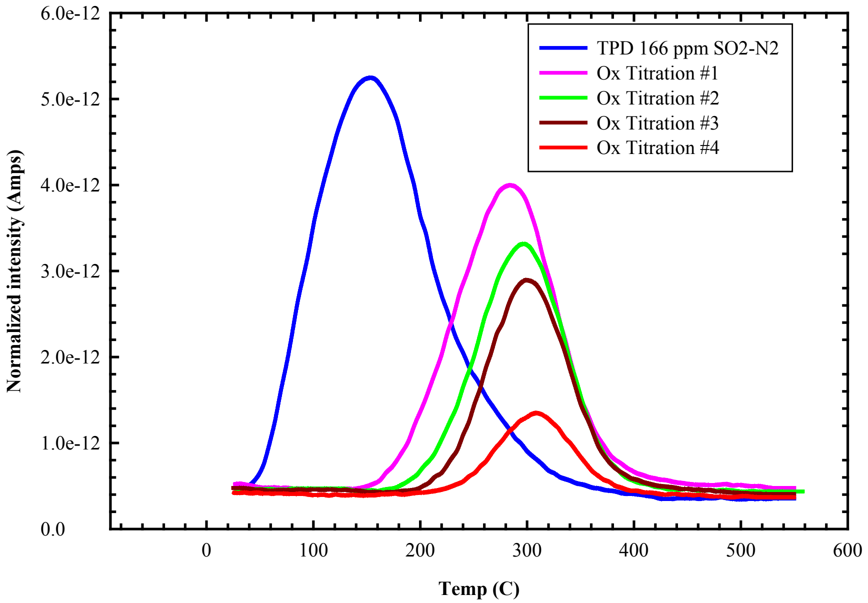
* NH_3 transport follows the charge transfer.

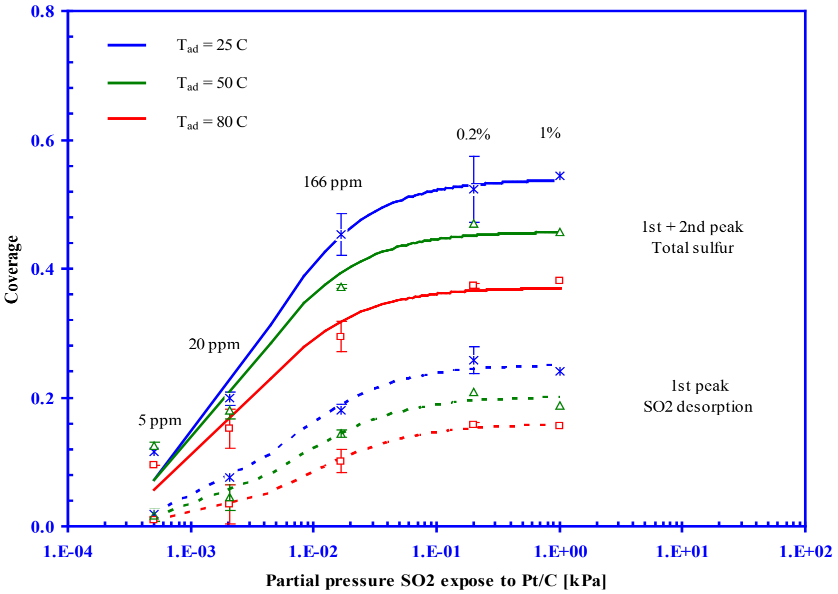
Thus, all NH_3 will be crossed over to the cathode in FC operation

Technical Accomplishments & Progress – H_2 Quality

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 SO_2 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 a important variable.





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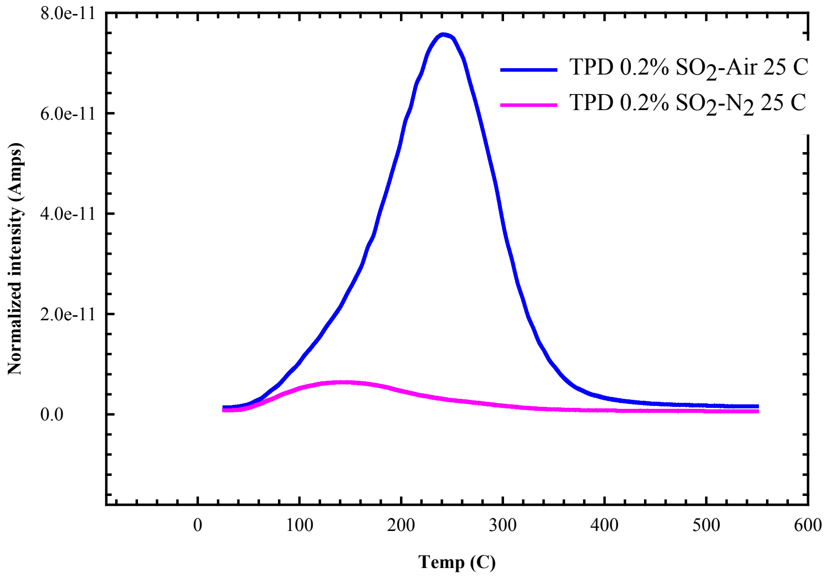
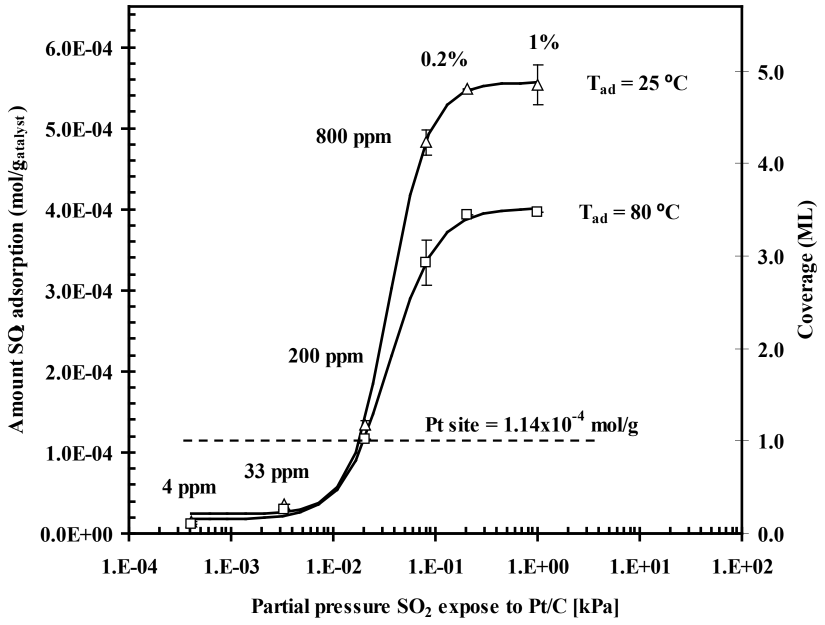
Technical Accomplishments & Progress – H_2 Quality

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.

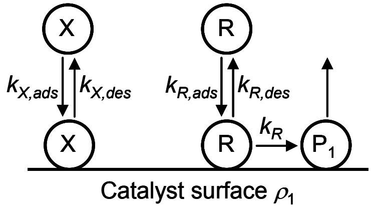


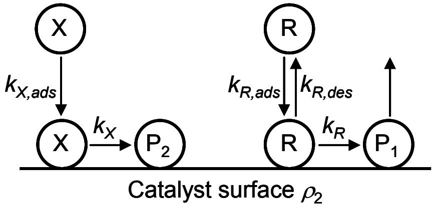


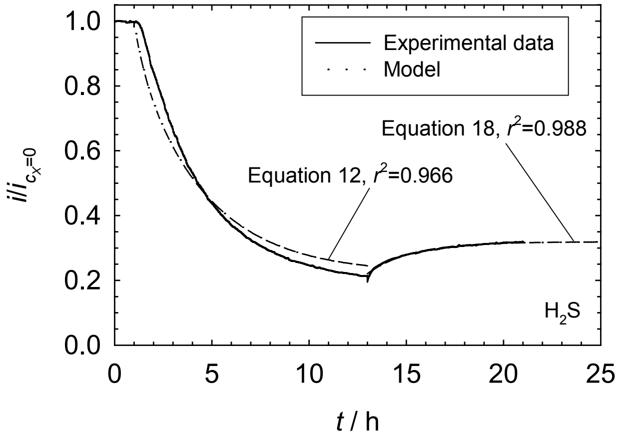
Technical Accomplishments & Progress – H_2 Quality

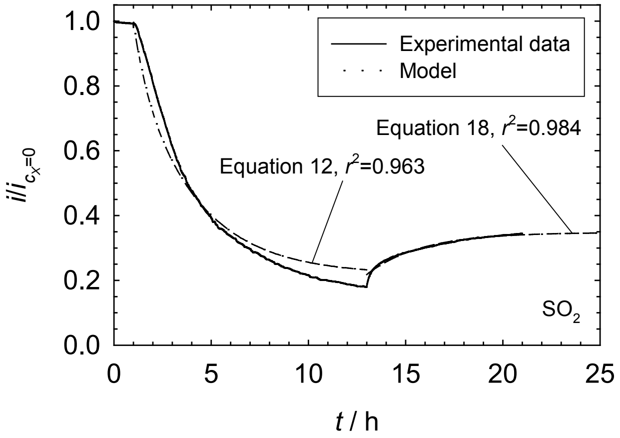
Accomplishments / milestones:

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_2S, SO_2, COS)





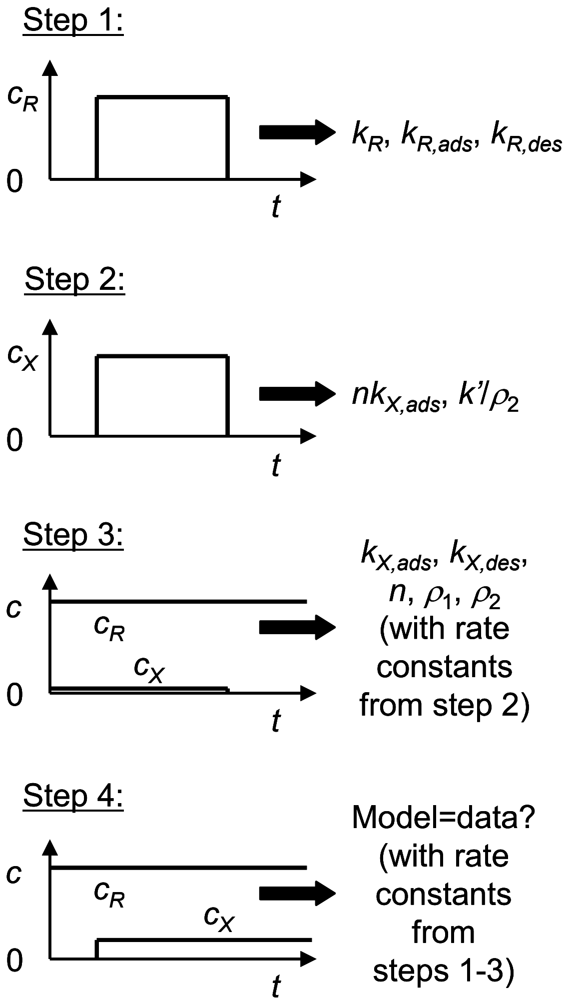




Technical Accomplishments & Progress – H_2 Quality

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.



Step 1: k_R, $k_{R,ads}$, $k_{R,des}$

Step 2: $nk_{X,ads}$, k'/ρ_2

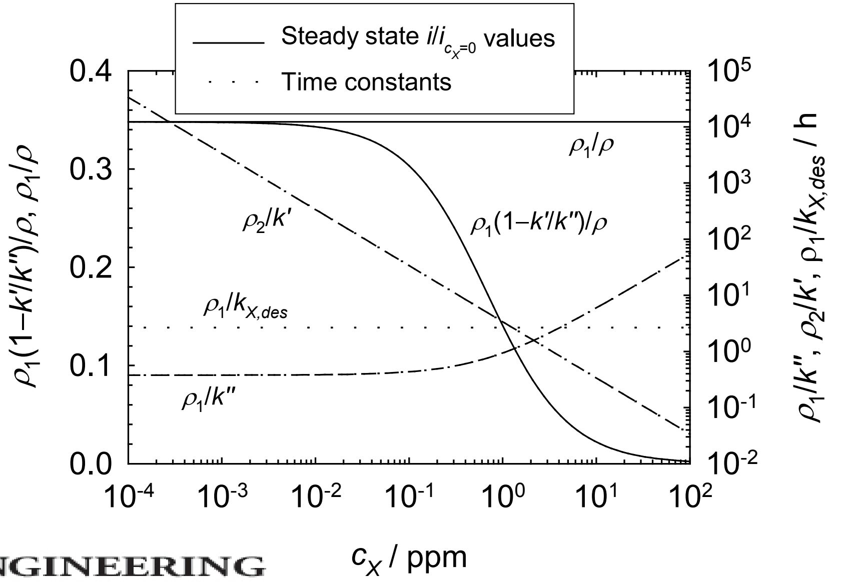
Step 3: $k_{X,ads}$, $k_{X,des}$, n, ρ_1, ρ_2 (with rate constants from step 2)

Step 4: Model=data? (with rate constants from steps 1-3)

Technical Accomplishments & Progress – H_2 Quality

Accomplishments / milestones:

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-ρ_1/ρ, 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.



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Technical Accomplishments & Progress – H_2 Quality

Accomplishments / milestones:

The model predicts a significant effect of catalyst loading. Performance loss due to contamination is dependent on total catalyst site density ρ and individual site densities ρ_1 and ρ_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.

Contamination

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

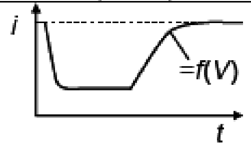
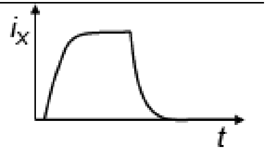
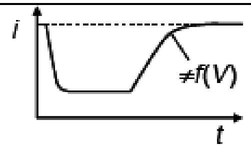
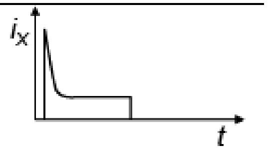
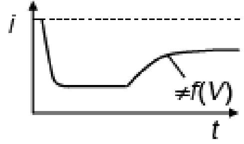
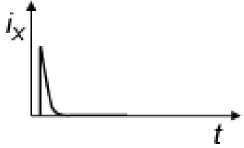
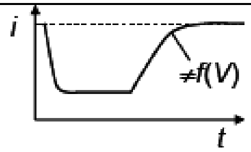
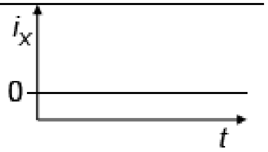
Recovery

$$\frac{i}{i_{c_X=0}} = \frac{\rho_1}{\rho}\left(1-\theta_{X,0}\, e^{\frac{-k_{X,des}t}{\rho_1}}\right)$$

Technical Accomplishments & Progress – H_2 Quality

Accomplishments / milestones:

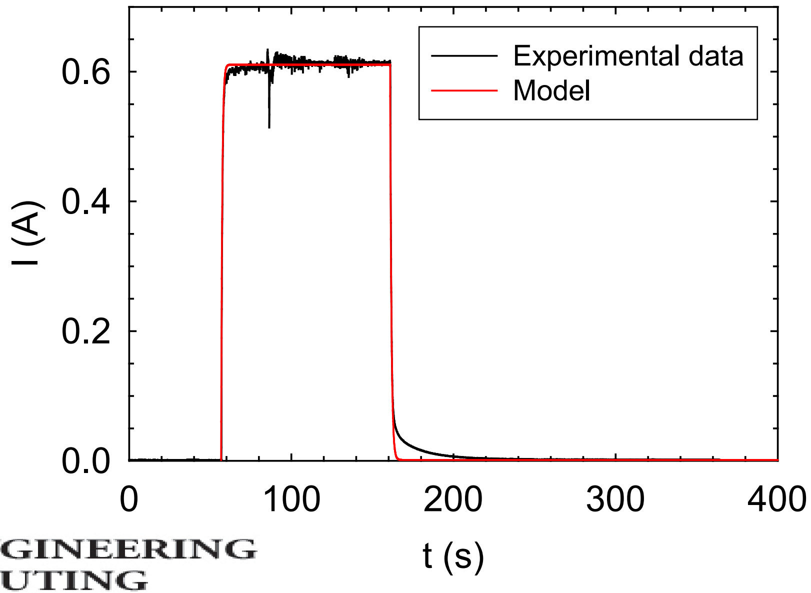
The present model increases the existing inventory of cases derived using similar assumptions. In presence of a reactant, models generally show a similar behavior. In absence of a reactant, reaction mechanism identification is facilitated because different current transients occur with only a contaminant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

Measured variable for step changes in c_X			i ($c_R\neq0$)	i_X ($c_R=0$)
Catalyst contamination kinetics	X electroactive ($k_X\neq0$)	X reaction rds		
		P_2 desorption rds		
		Irreversible P_2 adsorption		
	X electroinactive ($k_X=0$)			

Technical Accomplishments & Progress – H_2 Quality

Accomplishments / milestones:

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.



Technical Accomplishments & Progress – H_2 Quality

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_2O have been started. These studies have implications for sulfur species transport from fuel contaminants.

Technical Accomplishments & Progress – H_2 Quality

Sub-Project 4: Summary- Technical Accomplishments (continued)

- **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.**

Technical Accomplishments & Progress – Durability

Sub-Project 5: Multi-physics Materials System Foundations for Durability Modeling in Solid Oxide Fuel Cells and Electrolyzers

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.

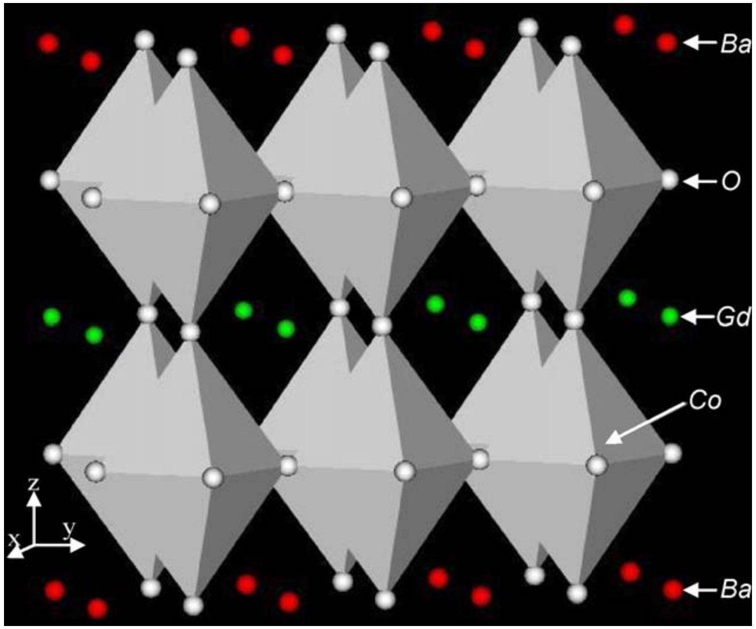
Technical Accomplishments & Progress – Durability

Specific focus

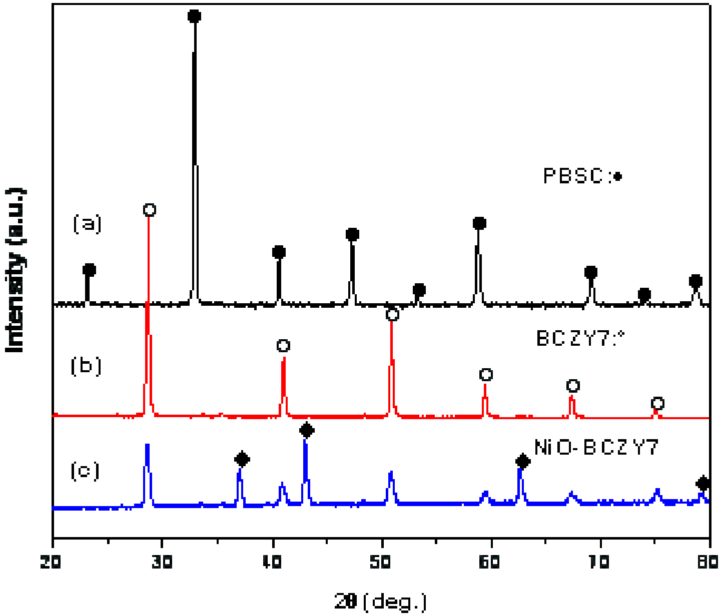
- Material synthesis for intermediate temperature(IT)-SOFC systems
  - Solid state and chemical methods for material synthesis
  - X-Ray diffraction to examine material phases
  - SEM to examine microstructure
- Electrochemical characterization
  - V-I curves
  - Electrochemical impedance spectroscopy
  - 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

Technical Accomplishments & Progress – Durability

Cathode and electrolyte material synthesis for IT-SOFC development



Crystal structure of layered perovskite

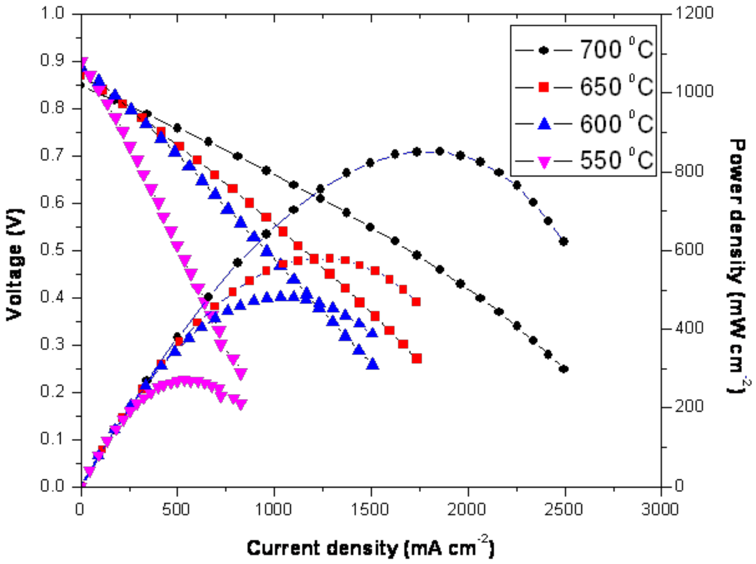


XRD of electrode and electrolyte

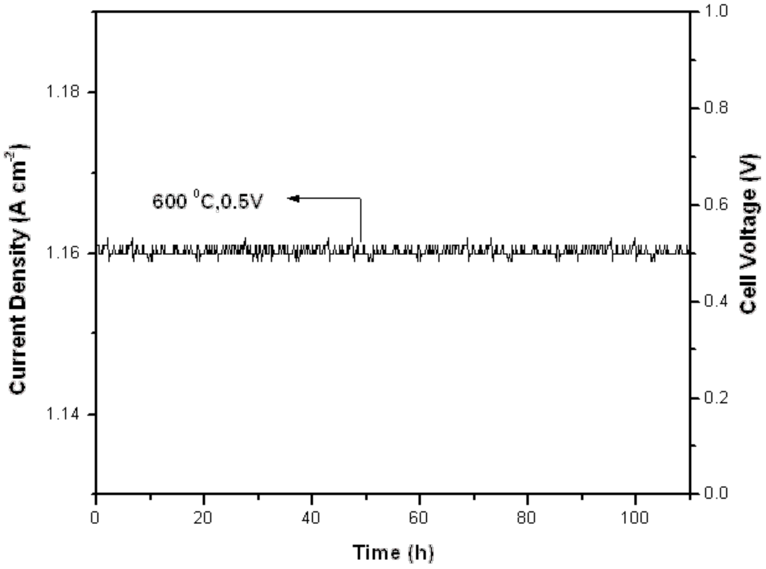
- A series of new layered perovskite cathode materials are synthesized for IT-SOFCs
- Both proton conducting and ion conducting electrolyte materials are synthesized
- H. Ding and X. Xue, "GdBa0.5Sr0.5Co2O5+*δ* layered perovskite as promising cathode for proton conducting solid oxide fuel cells," *Journal of Alloys and Compounds*, 2010, (in press)
- H. Ding and X. Xue, "A novel cobalt-free layered GdBaFe2O5+*δ* cathode for proton conducting solid oxide fuel cells," *Journal of Power Sources*, *Vol. 195, 2010*, *pp. 4139.*

Technical Accomplishments & Progress – Durability

Electrochemical characterization of IT-SOFC material systems



PrBaSrCo/SDC/SDC-NiO performance

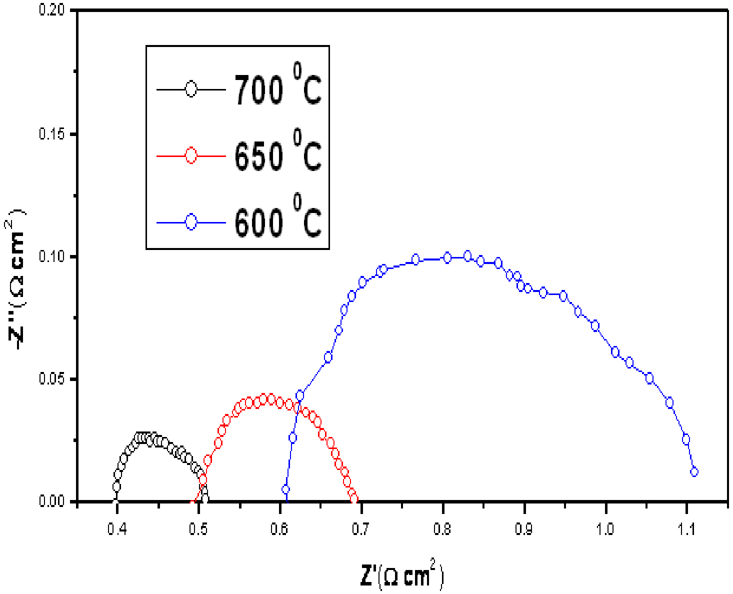


Durability test

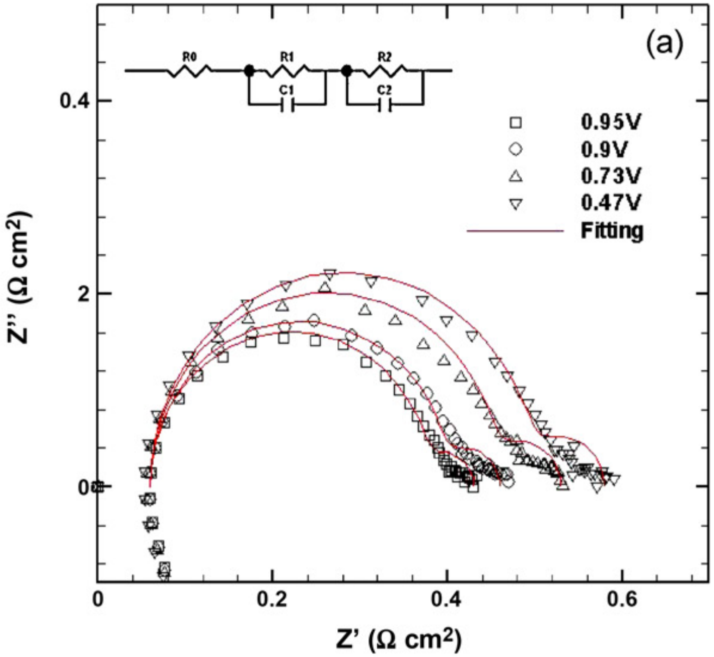
- Cell performance is very promising in intermediate temperature conditions
- Durability tests demonstrated that SOFC performance is quite stable
- H. Ding and X. Xue, “PrBa0.5Sr0.5Co2O5+δ layered perovskite cathode for intermediate temperature solid oxide fuel cells,” *Electrochimica Acta, Vol. 55,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

Technical Accomplishments & Progress – Durability

EIS characterization of IT-SOFC material systems



EIS of NiO–SDC/SDC/SBSC

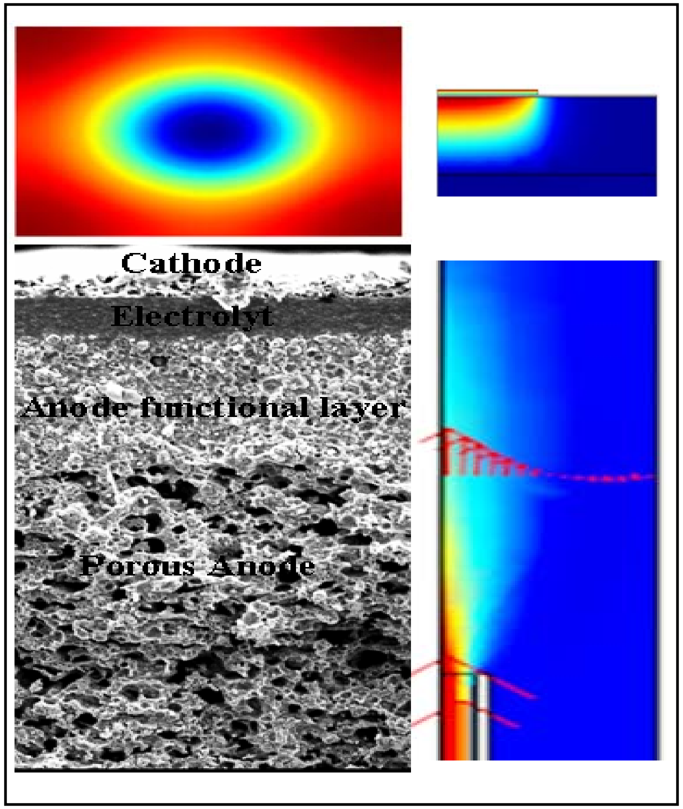


EIS evolution under different loadings

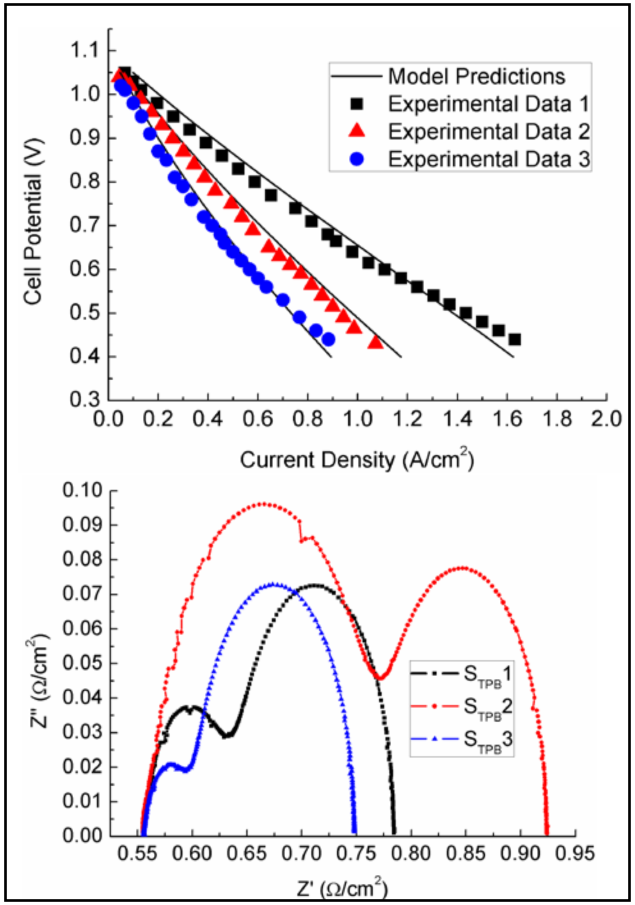
- Electrochemical impedance spectroscopy has been measured for SOFCs under different operating conditions;
- Fundamental mechanisms study using model based data interpretation

Technical Accomplishments & Progress – Durability

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.