Project Manager: Dr. Lane Wilson
DOE National Energy Technology Laboratory

Meilin Liu
Center for Innovative Fuel Cell and Battery Technologies
School of Materials Science and Engineering
Georgia Institute of Technology

September 30 - October 1, 2003
The Research Team

- **Rupak Das and Robert Williams** (NSF Fellow)
  - Modeling/simulation of FGE
- **Erik Koep and Chuck Compson** (NASA Fellow)
  - Patterned Electrodes
- **Qihui Wu and Harry Abernathy** (NSF Fellow)
  - In-situ Characterization: FTIR/Raman, IS, GC/MS
- **Ying Liu and Yuelan Zhang**
  - Fabrication of FGE and performance testing
• Technical Issues Addressed
• R&D Objectives & Approach
• Results to Date
  – Modeling of Functionally Graded Electrodes
  – Patterned Electrodes
  – In-situ Characterization Techniques
  – Fabrication of Graded Electrodes
• Applicability to SOFC Commercialization
• Activities for the next 6-12 Months
Critical Factor: Interfacial Resistance

Performance is determined by $R_p$ at low temperatures

Functionally Graded Electrodes
Origin of $R_p$ for a Porous MIEC Electrode

**The Concept of FGE**

- **Macro-porous structure**
  - Large pores for fast Transport
  - High Electronic Conductivity
  - Compatible with Interconnect

- **Inter-Mixed Layer**
  - Produce Turbulence Flow

- **Nano-porous structure**
  - Highly Catalytic Active
  - Compatible with electrolyte

**Ions & e’**
(current flow path)

**Mass Transport**
- gas through pores

**Reaction Zones:**
- TPBs & MIEC Surfaces

**O$_2$**

**Electrolyte**

**Functionally Graded Electrodes**
A probable model of O₂ reduction on MO
Critical Issues

- **Intrinsic Properties of MIEC Cathodes**
  - Fundamental processes at the surfaces?
  - Effect of surface defects/Nano-structure?
  - Effect of ionic and electronic transport?
  - In-situ characterization tools and predictive models?

- **Effect of Microstructure/Architecture**
  - Surface area/reaction sites
  - Rapid gas transport through pores
  - Predictive models for design of better electrodes

- **Fabrication of FGE with desired microstructure and composition**
Objectives

• To develop novel tools for *in-situ* characterization of surface reactions;

• To gain a profound understanding of the processes occurring at cathode-electrolyte interfaces; and

• To rationally design and fabricate efficient cathodes for low temperature operation to make SOFC technology economically competitive.
Technical Approach

Patterned Electrodes
- Reaction Pathway
- Active sites

Modeling
- Transport in Porous Media
- Active Reaction Sites
- Reaction Pathways
- Mechanism

In-situ Characterization
- FTIR, Raman, IS, GC/MS
- Reaction Mechanism
- Catalytic Properties

Fabrication of FGE
- Optimal Microstructure
- Graded in Composition
- Cost-effective/Reproducible

SOFC Performance
- High Performance
- Long-Term Stability
Modeling of Functionally Graded Electrode

Key Input Parameters:

- Porosity
- Pore Size and Size Distribution
- Grain Size and Size Distribution
- Diffusivity/Tortuosity
- Knudsen Diffusion
- Effective Ionic Conductivity
- Effective Electronic Conductivity
- Ambipolar Conductivity
- Exchange Current Density
- Cathodic Transference Numbers

1st Order Approximation
Ionic Transport Limited

Key Input Parameters:

- Porosity
- Pore Size and Size Distribution
- Grain Size and Size Distribution
- Diffusivity/Tortuosity
- Knudsen Diffusion
- Effective Ionic Conductivity
- Effective Electronic Conductivity
- Ambipolar Conductivity
- Exchange Current Density
- Cathodic Transference Numbers

1.0 µm

200 nm

Functionally Graded Electrodes

Dense Electrolyte
Tape Cast Substrates for Patterned Electrodes

Low cost, reproducible, and easy scale-up

Great Flexibility: Co-casting of multi-layers of different materials

Functionally Graded Electrodes
Microstructures of Patterned Electrodes

2 μm Pt Lines

10 μm SSC Lines
50 μm Pt Current Collector
While initial thin film resembles SSC standard, the surface structure changes upon heating.
O₂ Reduction On a Metal Oxide

Probable surface reaction models

\[
\begin{align*}
\text{Sr (Sm)} - & \text{O} - M^{n+1} \text{ V.} \\
\text{Sr (Sm)} - & \text{O} - M^{n+2} \text{ V.} \\
\end{align*}
\]
Possible Surface Reaction Processes

For (101) phase

Oxygen vacancy

Adsorbed Oxygen

Diffusion
In-Situ Characterization Techniques

- Process Control System
- Mass Flow Controllers
- Air/O₂
- Fuel Gas
- FTIR
- Raman
- Impedance Spectroscopy (IS)
- Electroanalytical measurements
- Mass Spectrometer
- Gas Chromatograph
- Drier
- To Vent

• pd-FTIR ES
• Raman Spectroscopy
• Impedance Spectroscopy
• Mass Spectrometry/GC
Gas Switching Effect

SSC/SDC/SSC, at 550°C

From 1% O₂ to N₂, take background in 1% O₂
40 spectra (4s/spectrum)

From N₂ to 1% O₂, take background in N₂
40 spectra (4s/spectrum)

Functionally Graded Electrodes
Catalytic Properties of Cathode Materials

O$_2^-$ species
Different catalytic properties

PEAK Height:
Fast Screening Tool for Materials Development

Maximum O$_2^-$ signals for cathode materials at 600°C in 1% O$_2$ atmosphere
Functionally Graded Electrodes

Height of 1124 cm⁻¹ peak during gas switching experiment for different materials at 600°C.

First derivative of 1124 cm⁻¹ peak height vs. time curve

Reactivity for oxygen adsorption and desorption: SSC ≥ LSF > LSC
Gas Switching Effect

Height of 1124 cm\(^{-1}\) peak during gas switching experiment for SSC at different temperatures.

First derivative of 1124 cm\(^{-1}\) peak height vs. time curve for SSC at different temperatures

Reaction rate: 700 ≥ 650 ≥ 600

Temperature is not a significant parameter for oxygen adsorption but is for oxygen desorption
1% Oxygen

Height of 1124 cm\(^{-1}\) peak during gas witching experiment for LSF and LSC at different temperatures.

**LSF and LSC show different temperature dependence for oxygen adsorption and desorption**
Effect of Oxygen Partial Pressure

The intensity of 1124 cm\(^{-1}\) peak at different temperatures and in different atmospheres for LSF electrode

The saturated CO\(_2\): 20% (Air)
The FTIR spectra of an SSC pellet at different temperatures in oxygen

High O₂ concentration $\rightarrow$ O$_2^{2-}$: 873 cm$^{-1}$
Normalized height of 1124 cm\(^{-1}\) and 875 cm\(^{-1}\) peaks during gas switching experiment from Ar to O\(_2\) and back to Ar.

- O\(_2^-\) and O\(_2^{2-}\): fast adsorption
- O\(_2^{2-}\): slowly reach the max
  Faster desorption
The active sites for the oxygen reduction (oxygen adsorption) is not limited to the triple boundaries, but extended to surfaces of the MIEC electrodes.

As expected, different cathode materials have different catalytic activity for the oxygen adsorption and desorption. In particular, SSC appears to have the highest activity for oxygen adsorption while LSF has the fastest kinetics for the oxygen desorption.

The saturation partial pressure of oxygen is about 20% for the FTIR measurements.

The intensity of the peroxide peaks are much weaker than those of the superoxide peak. The formation rate of peroxide species appears to be as fast as that of superoxide; however, there is some delay for peroxide to reach the maximum point. The desorption of peroxide is much faster than that of superoxide.
Fabrication of Functionally Graded Electrodes

- Templated Synthesis
- Combustion CVD
Schematics – Templated Synthesis

PMMA spheres
Assembly with binder
PMMA aggregate by the attraction of the binder
After impregnate with slurry and template removal
Wall is composed of smaller pores
Periodic interconnected porous structure
Preliminary Results

- SEM pictures

PMMA template

Porous GDC-SSC MIEC
Walls consist of particles of about 100 nm in diameter.

Porous GDC-NiO MIEC
Combustion CVD

**High fuel-to-gas ratio**
→ Reducing atmosphere

- Ni
- GDC

**Moderate fuel-to-gas ratio**
→ Oxidizing atmosphere

- Flow Controller
- Fuel and Oxidant Gases
- Filter
- Solutions Pump
- Control & Data Acquisition
- CCVD
- Nozzles
- Support
- Fuel and Oxidant Gases
- Solutions Pump
- Filter

**Low cost**
- Open-air, flame-assisted deposition process
- No furnace or reaction chamber required
- Inexpensive precursors (e.g., metal nitrates)

**Great Flexibility**
- Multi-element and/or multi-layer coating capability
- Capable of producing vastly different microstructure and morphologies;

**Functionally Graded Electrodes**
Nano Box-Beams of Semiconductor SnO$_2$

**A**

**B**

**C**

**D**

**E**

**F**

Functionally Graded Electrodes
Effect of Deposition Temperature

Functionally Graded Electrodes

(a) 800°C

(b) 1000°C

(c) 1200°C

(d) 1400°C

Intensity

2 θ°

Temperature (°C)

Interfacial resistance (Ω cm²)

1000/T (K⁻¹)

800°C

1000°C

1200°C

1400°C
Deposition Time: Microstructures

Functionally Graded Electrodes
Deposition Time: Thickness and $R_P$

![Graphs showing interfacial resistance vs. 1000/T and film thickness vs. deposition time.]

- Interfacial resistance ($\Omega \cdot \text{cm}^2$) vs. $1000/T$ (K$^{-1}$)
- Film thickness (µm) vs. deposition time (min)

Functionally Graded Electrodes
Effect of Concentration

Functionally Graded Electrodes

Effect of Concentration

Interfacial resistance ($\Omega \text{ cm}^2$)

$1000/T$ (K$^{-1}$)

Temperature ($^\circ$C)

Interfacial resistance ($\Omega \text{ cm}^2$)

$1000/T$ (K$^{-1}$)

Temperature ($^\circ$C)
Effect of Substrate (Electrolyte)

Functionally Graded Electrodes

- GDC
- YSZ

Graph showing interfacial resistance vs. temperature for GDC and YSZ substrates.

Temperature (°C)

Interfacial resistance (Ω cm²)

1000/T (K⁻¹)
An SOFC Fabricated by CCVD

Functionally Graded Electrodes

Anode
Ni + SDC

Cathode
SSC + SDC

250 µm GDC

200nm

100.0 um

200nm

5.0 um

Cathode
SSC + SDC
Functionally Graded Electrodes

Interfacial Resistances and Performance of an SOFC supported by 250 \( \mu \text{m} \) GDC
Performance of an Anode-Supported Cell with Cathode by CCVD

30 µm Electrolyte

[Graph showing the relationship between voltage, current density, and power density at different temperatures (650°C, 600°C, 550°C, 500°C).]
Functionally Graded Cathode (fabricated on 250µm YSZ) by CCVD, along with the EDS dot mapping of Mn and Co element distributions.
Impedance Spectra/Resistance – Combustion CVD

![Graph showing impedance spectra and resistance as functions of temperature.](image)

- Functionally Graded Electrodes

- GDC-impregnated LSM, Jiang [10]

- Graded LSM-LSC-GDC, CCVD

- Interfacial resistance, $\Omega \text{ cm}^2$

- $1000/T$, K$^{-1}$

- $\triangle$ LSM, Murray [9]

- $\diamond$ Graded LSM-LSC-GDC, Hart [17]

- $\square$ LSM-GDC50, Murray [9]

- $\blacktriangledown$ GDC-impregnated LSM, Jiang [10]

- O Graded LSM-LSC-GDC, CCVD
Summary of Accomplishments

- Started 3-D Modeling of graded multi-layer cathodes
- Started Microscopic modeling of surface reaction processes
- Developed micro-fabrication techniques capable of producing MIEC electrodes (SSC and LSM) with well-defined geometries
- Understanding of reduction mechanisms on different cathode materials using in-situ characterization techniques
- Used Raman spectroscopy to better characterize surface structures of electrodes under practical operating conditions
- Used combustion CVD and templated synthesis to produce vastly different microstructure and morphologies of porous mixed-conducting electrodes
- Demonstrated cathodes of lowest polarization resistances for low temperature SOFCs
• Generated some basic understanding of electrode reaction mechanisms in an effort to better design of efficient electrodes

• Developed new tools for in-situ determination of electrode properties under practical conditions

• Developed new architectures/microstructures of porous MIEC electrodes using combustion CVD and templated synthesis
Activities for the Next 6-12 Months

- Fabrication and evaluation of patterned MIEC electrodes with active phase and **finer features**
  → Reaction sites, pathway, and mechanism

- **Refine Macroscopic and Microscopic Models**
  → Optimum Microstructure/Architecture

- Optimization of templated synthesis and combustion CVD for fabrication of FGEs

- Development of new in-situ characterization tools for investigation of SOFC reactions
  → AFM/STM integrated with Raman spectro-microscope to achieve chemical mapping at nano-scale
  → AFM/STM integrated impedance spectroscopy to acquire impedance spectra of individual grains and individual grain boundaries between dissimilar materials
Acknowledgement

Lane Wilson, NETL/DoE

SECA Core Technology Program
Dept of Energy/National Energy Tech Laboratory
DARPA/DSO-Palm Power Program
Army Research Office/DURIP

Center for Innovative Fuel Cell and Battery Technologies,
Georgia Tech