Fundamental Studies of Electrodes for SOFCs

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January 27-28, 2005
Tampa, FL
Outline

• Technical Issues Addressed
• Objectives & Approach
• Recent Progress (Since May 2004)
  – QM Calculations
  – Probing and mapping gas-surface interactions
  – Cells with Patterned Electrodes: TPB width/thickness
  – Fabrication of Porous Electrodes
• Applicability to SECA
• Activities for the next 6-12 Months
1. Why one particular electrode material is better than others?
   - Origin of intrinsic catalytic properties
   - Effect of surface defects/Nano-struture
   - Role of ionic and electronic transport

2. Why a particular electrode architecture is more efficient than others?
   - Quantify microscopic features important to electrodes
   - Predictive models for design of better electrodes

3. How to fabrication FGE with desired microstructure and composition cost effectively
Objectives

• To develop novel tools for probing and mapping surface reactions
  – In-situ experimental measurements (FTIR, SERS, TERS, µ-IS) under practical conditions
  – Ex-situ measurements under well-controlled conditions (ESD/PSD)
  – Computational approaches

• To apply this tools to investigations of important reactions in SOFCs
  – Oxygen reduction, Cr-poisoning, S-poisoning
  – MIEC active regions, Bonding sites / mechanisms
  – Rate-limiting steps, surface reaction rates, bulk diffusion coefficients

• To establish scientific basis for rational design of better electrodes
Recent Progress (Since May 2004)

• QM Calculations
• Experimental: Probing and mapping gas-surface interactions
• Cells with Patterned Electrodes: TPB width/thickness
• Fabrication of Porous Electrodes
Computational Approach
QM Calculation of Gas-Surface Interactions

Quantum Mechanical (QM) methods

Geometrical Configuration for reactants, intermediates, transition states and products

Vibrations

FTIR/Raman Spectroscopy

Energetics

Reaction mechanism: Favorable reaction pathways
Modeling in Different Length Scale

Atomic-Level View

Ni Anode

LSM Cathode

Macro-level view

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Cathode: $O_2$–LSM Interactions
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Anode: \( \text{H}_2\text{S} - \text{Ni} \) Interactions
1. Cluster model: Gaussian 03 code
   a. bare-cluster model: metal

   Ni(111)

2. Slab model: VASP code
   Super cell

   Periodic Boundary Condition

   Ni(111) Bulk

   side view

   top view

b. embedded-cluster model: metal oxide ionic solid

   NiO

   - an array of point charges to represent the surrounding ions
The O-O stretching of the superoxo end-on geometry is in line with experimental IR frequencies (1040 – 1190 cm$^{-1}$).
Dissociative Adsorption of $O_2$ on Metal Oxide

- $\text{Mn(OH)}_4O_2$: A cluster model for LSM
- B3LYP/6-311+G(d)

$v(O-O^{-1}) = 1100 \text{ cm}^{-1}$

- Comparing with experimental bands using FT-IR (1124 cm$^{-1}$), it may be assigned to be superoxide ion.
Ni(111) Surface and Adsorption Sites

- atop
- bridge
- fcc hollow
- hcp hollow

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Summary – QM Calculations

• Constructed Pt, Ni, Cu, and LaMnO\textsubscript{3} surfaces for QM calculations

• Predicted some adsorbed oxygen species on cathode surfaces

• Calculated dissociative adsorption of oxygen molecules on manganese oxide

• Detailed mechanistic studies of O\textsubscript{2} reduction and S-poisoning are still in progress
Conclusions

• QM calculations provide important insight into mechanisms of fuel cell reactions: geometric configurations and energetics;

• Computations complement measurements (FTRI/Raman): experimental design and data interpretation

• Super-cell models are needed to represent real systems
Work in Progress

Extension of the small **cluster model** to a **super-cell model** to mimic real system

Cathode

Oxygen reduction on real cathode materials (LSM, LSC…)

MD: Oxygen diffusion on surfaces & across interfaces on electrodes

Oxygen or vacancy transport through lattice
Work in Progress

Super-Cell Model

Anode

H₂S interaction with Ni-YSZ surface to provide a reliable reaction mechanism

S-H-O interactions on other anode materials

Vibration frequency
Energetics
Sulfur poisoning

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Recent Progress (Since May 2004)

- Computational: QM Calculations
- **Experimental:** Probing and mapping gas-surface interactions
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In-Situ Characterization Techniques

FTIR

pd-FTIR: Electrically-induced species
Rapid Scan (120 spectra/s): Surface reaction kinetics/bulk transport properties

Raman

SERS: Dramatically enhanced sensitivity (with enhancement factor up to $10^8$) to surface species: adsorbates/intermediates
TERS (Raman+SPM): Dramatically enhanced spatial resolution (~dimension of the SPM tip size), nano-scale mapping of surfaces species

Micro-Impedance Spectroscopy:
To measure the impedance of a single grain, a grain boundary, or a TPB
FTIR-ES Setup

FTIR Spectrometer
(Liquid-N₂-Cooled MCT Detector)

Dome with KBr Window

Heating Cartridge

Gas Switching Experiment

Gas 1 (Reference) | Gas 2 | Gas 1

Time

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FTIR – Gas Switching Experiments

- 1 = Reduced surface oxygen species
- 2 = Change in bulk emissivity

![Graph showing FTIR results with wavenumber in cm⁻¹ and E₀ - E values. The graph indicates changes from 1% O₂ to Ar.](image-url)
Results – Kinetics: Superoxide peak height

- SSC has higher concentration of surface species
- Adsorption much faster than desorption
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Results – Kinetics: Baseline shift

From Ar to 1% $O_2$

From 1% $O_2$ to Ar

Material response dictated by surface + bulk kinetics
Raman Microspectroscopy

- Raman spectroscopy sensitive to composition and structure
- May be used to map the inhomogeneity of electrode materials
- In-situ under conditions similar to fuel cell operation
Phases Relevant to Cr-Poisoning

In addition to pre-/post-test analysis, possibly for in-situ probing and mapping of Cr2O3 to elucidate Cr-poisoning mechanism, providing critical info for design of Cr-tolerant cathode.
Ni-YSZ cermet was exposed to humidified hydrogen containing 100 ppm H₂S at 727°C for 5 days.

Possibly for in-situ probing and mapping (patterned sites) of NiSₓ to elucidate S-poisoning mechanism → S-tolerant anodes
Raman microspectroscopy

- Raman sensitive to carbon compounds
- Motorized stage allows for controlled surface mapping

Carbon deposition at distance from anode center

- 1583 cm⁻¹
- 1358 cm⁻¹

Button Cell
Run on CH₄
Surface Enhanced Raman Scattering (SERS)

Extremely sensitive to surface species
Spatial resolution: \(\sim \mu m\)

In-Situ SERS
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**Tip Enhanced Raman Scattering**

- Nanoscale spatial resolution
- Nanoscale chemical mapping
- Enhanced Raman signal

**Objective**

**In-situ** TERS for study of oxygen reduction/evolution processes under various practical testing conditions:

**Temperature, pO2, current/voltage**
TERS – SSC in Air

- Surface signal greatly enhanced
- Confirms FTIR data
- Additional peaks are yet to be interpreted, M-O
Ex-situ Characterization of Cr-poisoning process

Patterned LSM

Symmetrical cell

SPM head

Thermal couple

Counter electrode
In-situ characterization of Cr-poisoning process
Advantage: **simplicity**

- No complications due to sheet resistance or m.t. in gas phase
- Simple modeling and simulation
- May be directly correlated with TERS or Raman mapping, in-situ, under various conditions: T, pO2, I/V
Study of a single grain, gb, or TPB

Patterned Pt Electrode

SSC

Patterned Electrodes
SPM tip
Electrodes by FIB

Impedance Analyzer

SPM Controller

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Impedance spectra collected inside one SSC grain at 290°C, Au coated W tip
Conclusions - FTIR

- For studied MIEC cathode materials in studied operating conditions, initial adsorption and reduction of oxygen is not rate-limiting.

- SSC shows greater activity for oxygen reduction than LSF, LSC, LSCF, and LSM at lower operating temperatures.

- FTIR-ES can be used to simultaneously identify surface species and measure kinetic parameters.
Conclusions - Raman

• SERS and TERS offer extremely high sensitivity and spatial resolution in probing and mapping surface species on electrodes of SOFCs;

• Surface species associated with sulfur-poisoning, Cr-poisoning, and carbon deposition are detected by Raman spectroscopy (characteristic peaks), offering possibilities of probing and mapping these species to elucidate the poisoning mechanisms;
Recent Progress (Since May 2004)

- **Computational:** QM Calculations
- **Experimental:** Probing and mapping gas-surface interactions
- **Cells with Patterned Electrodes:** TPB width/thickness
- **Fabrication of Porous Electrodes**
The effective width of TPB is less than 1 µm → Scale of porous LSM
Effect of MIEC Electrode Thickness

Interfacial Conductance (1/Ohms) vs. Electrode Thickness (microns)

- 750°C
- 700°C
Electrode thickness dramatically influence on the catalytic properties of MIEC electrode stripes.

Impedance data demonstrate a clear peak performance (around 0.18µm at 750°C). For electrodes thicker than this critical value, the performance drops rapidly with thickness, approaching the value associated with the activity of the TPB (e.g., performance drops to less than 30% of the maximum near L=0.4 µm).

For electrodes thinner than the critical value, the performance drops as it gets thinner because of the sheet resistance of the electrode, which makes part of the electrode no longer active.

Electronic conductivity sets the minimum electrode thickness while ionic conductivity sets the upper limit of electrode thickness.
Recent Progress (Since May 2004)

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Particles of desired electrode materials are dispersed in a sol of the same electrode material.
Formation of Porous Nanocomposite Electrodes in a Particle-Solution Spraying Process

- Liquid droplet containing Sm, Sr, Co nitrates
  - SSC solid particle
  - GDC solid particle
Nanocomposite Cathodes Fabricated Using Particle-solution Spraying Process

- Sm, Sr, Co nitrates for Sm$_{0.5}$Sr$_{0.5}$CoO$_3$ (SSC) phase
- Gd$_{0.1}$Ce$_{0.9}$O$_{1.95}$ (GDC) solid powders, 0.5 µm
- Deposition temperature: 1200°C for 10 min.

Potential Applications of Particle-Solution Spraying Process for Composite Electrodes

PSSP can virtually be employed to fabricate all kinds of composite electrodes (cathodes and anodes) by minor modifications:

- Both phases are synthesized from solutions.
- To avoid formation of undesired phases, two spray nozzles are used. Each phase is formed separately and then sprayed onto the substrate.
- One phase can be introduced as solid particles while the other phase is formed from solution.
- Both phases are solid particles before spray.
Electrochemical Performance of SOFC with Fractal-structured Nanocomposite Cathodes

Porous Electrodes Created by Combustion CVD

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Applicability to SOFC Commercialization?

• Do we really understand why one electrode material is better than the other?
  – Not yet; we still do not have a complete picture of the processes. However, we do know them better.

• Benefits to the SECA team?
  – Basic understanding does have technological implications; e.g., effective TPB width and max thickness are critical to design of MIEC electrodes
  – New tools for in-situ determination of electrode properties under practical conditions
  – Mechanistic understanding may help rational design of efficient electrodes (S- and Cr-poisoning)
Activities for the Next 6-12 Months

- QM computations using super-cell models to better represent real systems
- Couple QM calculations with TERS experiments to characterize surface
- Finalize the design and construction of TERS, $\mu$-IS and TPD systems, including tip preparation for $\mu$-IS and TERS
- Identification of surface species relevant to oxygen reduction, S-poisoning, and Cr-Poisoning under various electrochemical conditions using SERS/TERS
Activities for the Next 6-12 Months

- Investigation of local impedance of a single TPB, MIEC surface, and electrolyte surface using $\mu$-IS under in-situ conditions

- FTIR: Vary thickness of cathode for gas switching experiments
  - Find sampling depth of emission spectroscopy
  - Separate surface reaction from bulk diffusion

- Resolve FTIR kinetic data with EIS data

- Characterize effect of cathode composition on surface activity and bulk properties
Acknowledgement

Lane Wilson, NETL/DoE

SECA Core Technology Program
Dept of Energy/National Energy Tech Laboratory

Equipment funded by DURIP/ARO
Center for Innovative Fuel Cell and Battery Technologies,
Georgia Tech