Gas Transport and Electrochemistry in Solid Oxide Fuel Cell Electrodes

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Overview of Research Activities

- Heat & Mass Transfer with Chemical Rxns:

  CVD Nanomaterials  Photonics  Fuel Cells

Outline

- Introduction – Energy Conversion
- Fuel Cell Background & Motivation
- Imaging & Analysis at the Pore Level
  - Pore Imaging
  - Gas Transport
  - Electrochemistry
- Electrode Microstructure and Grading
- Conclusions & Future Research Plans
Global Energy Usage
U.S. Energy Usage

Energy Conversion Efficiency

US Power Plants, 2003, in quadrillion BTU
Energy Conversion Technologies

- For Fossil Fuels:
  - SOA: Heat Engines
    - Steam Cycles
    - Gas Turbines
    - Internal Combustion
  - Fuel Cells?

  - High Electrical Efficiency
  - Fuel Flexibility
  - Scalable
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# Types of Fuel Cells

<table>
<thead>
<tr>
<th>Fuel Cells</th>
<th>Electrolyte</th>
<th>Operating Temperature ℃</th>
<th>Fuel Supply</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (AFC)</td>
<td>circulating liquid or matrix</td>
<td>50-250</td>
<td>Hydrogen or NH₃-Cracker</td>
<td>small units, up to automobiles</td>
</tr>
<tr>
<td>Proton Exchange Membrane (PEM)</td>
<td>immobilized, acidic</td>
<td>60-100</td>
<td>Hydrogen or Converter</td>
<td>small units, up to automobiles</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>concentrated acid gel</td>
<td>175-200</td>
<td>Hydrogen or Converter</td>
<td>Power Plants 50 to 200 kW</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Li/Na-carbonate melt</td>
<td>600-1000</td>
<td>Selected fuel or Converter</td>
<td>Power Plants up to 1 MW</td>
</tr>
<tr>
<td>Solid Oxide (SOFC)</td>
<td>ceramic Zr/Y-oxides</td>
<td>650-1000</td>
<td>All Fuels, direct feed</td>
<td>Small to large Power Plants</td>
</tr>
</tbody>
</table>
Solid Oxide Fuel Cell

Hydrogen (& CO) Fueled

\[
\begin{align*}
H_2 + O^2- &\rightarrow H_2O + 2e^- \\
\text{and/or} \\
CO + O^2- &\rightarrow CO_2 + 2e^- \\
\text{H}_2 &\rightarrow \\
H_2O \text{ and/or} CO_2
\end{align*}
\]

Internal Reforming

Steam Reforming

\[CH_4 + H_2O \leftrightarrow 3H_2 + CO\]

Shift Reaction

\[CO + H_2O \leftrightarrow H_2 + CO_2\]

from http://www.thirdorbitpower.com/SOFC_mech.html
How, specifically, can we design fuel cell microstructure to optimize performance and durability?

Modeling Tool needed to Determine Optimal Microstructure.
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SOFC Pore Structure Imaging

X-Ray Microtomography (XMT)

- Non-destructive tomography capable of reconstructing 3-D pore structure.
- X-rays penetrate sample, which is mounted on a rotation stage, and pass through a scintillation screen. The 2-D slice is captured by a camera.
- The sample is rotated through 180 degrees where each slice is captured at specified angle intervals and reconstructed into a 3-D volume of the pore structure.
SOFC Pore Structure Imaging – cont’d

- XMT Experiment details
  - Xradia (Concord, CA)
  - 8 keV copper source
  - 181 projections at 300 sec per projection
  - 22.6 µm field of view
  - 50 nm resolution
  - 3-D tomographic reconstruction
Imaging Processing and Modeling

Digital image file

Geometry Input file for Model

ImageJ

http://rsb.info.nih.gov/ij/

Modeling Challenges

- Gas diffusion occurs at high temperature and through micron size pores. Continuum theory is no longer valid.
- Gas particles can get adsorbed on the solid material.
- Complex structure.

Chemical reactions among gas components need to be included for the case of internal reforming and at the TPB.
A Comparison of Modeling Approaches

![Diagram showing simulation cost versus Knudsen number for different modeling approaches]

- Molecular Dynamics
- Monte Carlo
- Dusty Gas Model
- Lattice Boltzmann Method

The diagram illustrates the continuum, slip, transition, and free molecular regions for various Knudsen numbers. The simulation cost is indicated on the vertical axis, while the Knudsen number is on the horizontal axis.
Lattice Boltzmann Method (LBM)

- Historically derived from the lattice gas cellular automata
- LBM is a numerical approximation to the Boltzmann equation

- Multiple species
- Complex geometry
- Parallel algorithm
- Wall interactions
- Non-continuum regime

Basic LBM Algorithm: Stream and Collide

\[ n_{i,r}^{\sigma, n+1} = n_{i,r}^{\sigma, n} - \Omega_{i,r}^{\sigma, n} \]

- species
- old time-level
- discrete velocity
- direction
- velocity distribution function
- BGK collision term

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Multi-Component Gas Transport in a SOFC Anode

Digitized Pore Structure
\( \phi = 0.5 \)

LBM Validation

Concentration polarization [V]

Non-dimensional current density (i*)

Zhao & Virkar (2005)
Chan et al. (2001)
Present LB model
LBM Validation – cont’d.

Knudsen number (Kn)

Mole fraction ratio (X*)

Diffusivity ratio (D*)

LBM: data points  Dusty Gas: solid lines

3D LBM Analysis of a SOFC Anode

H₂, H₂O

Pore space

Electrolyte (YSZ)

Anode (Ni + YSZ)

Surface representing the interface between the solid region and pores.

Pore Structure ($\Psi, <r>, <r^2>$), Properties, $\eta_{conc}, \eta_{ohmic}$

H₂ mole fraction

Pore phase

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**Electrochemical Reaction Kinetics in a SOFC Anode**

Global Reaction: \( H_2^g + O_{\text{electrolyte}}^{2-} \rightarrow H_2O^g + 2e_{\text{Ni}}^- \)

The Gauckler Reaction Mechanism:

\[
\begin{align*}
H_2(g) + 2S &\rightleftharpoons_{k_1,k-1} 2H \cdot S \\
H_2O(g) + S &\rightleftharpoons_{k_2,k-2} H_2O \cdot S \\
O \cdot S + H \cdot S &\rightleftharpoons_{k_3,k-3} OH \cdot S + S \\
H_2O \cdot S + O \cdot S &\rightleftharpoons_{k_4,k-4} 2OH \cdot S \\
H_2O \cdot S + S &\rightleftharpoons_{k_5,k-5} OH \cdot S + H \cdot S \\
O_O^x + S &\rightleftharpoons_{k_6,k-6} O \cdot S + V_O^{--} + 2e_{\text{Ni}}^-
\end{align*}
\]

---

Electrochemical Model Rate Equations

- Traditional analysis requires selection of single rate limiting step and equilibration
  - Langmuir-Hinshelwood type rate equation
- Approach breaks down when reaction mechanisms contain steps that occur at similar rates
- For proposed mechanism requires solution to set of (4) coupled non-linear, stiff differential-equations

\[ \frac{\partial \theta_H}{\partial \theta} = \left( 2k_1\theta_V^2 - 2k_{-1}\theta_H^2 - k_3\theta_H\theta_O + k_{-3}\theta_{OH}\theta_V + k_5\theta_{H_2O}\theta_V - k_{-5}\theta_{OH}\theta_H \right) \]
\[ \frac{\partial \theta_{H_2O}}{\partial \theta} = \left( k_2\theta_V - k_{-2}\theta_{H_2O} + k_{-4}\theta_{OH} - k_5\theta_{H_2O}\theta_V - k_{-5}\theta_{OH}\theta_H \right) \]
\[ \frac{\partial \theta_{OH}}{\partial \theta} = \left( k_3\theta_H\theta_O - k_{-3}\theta_{OH}\theta_V + 2k_4\theta_{H_2O}\theta_O - 2k_{-4}\theta_{OH}^2 + k_5\theta_{H_2O}\theta_V - k_{-5}\theta_{OH}\theta_H \right) \]
\[ \frac{\partial \theta_O}{\partial \theta} = \left( -k_3\theta_H\theta_O + k_{-3}\theta_{OH}\theta_V - k_4\theta_{H_2O}\theta_O + k_{-4}\theta_{OH}^2 + k_6\theta_V + k_{-6}\theta_O \right) \]

\[ 1 = \theta_V + \theta_H + \theta_{OH} + \theta_{H_2O} + \theta_O \]

\[ \theta_i: \text{ Species Surface Coverage} \]

\[ k_6 = k_6^0 \cdot \exp \left( \frac{2F}{RT} \eta \right) \]
\[ k_{-6} = k_{-6}^0 \cdot \exp \left( (\beta - 1) \frac{2F}{RT} \eta \right) \]
\[ i = 2F \frac{N_0}{N_A} \left( k_6 \theta_V - k_{-6} \theta_O \right) \]
\[ \bar{J} \cdot \bar{n} = \frac{i}{2F} \]
Validation of Reaction Kinetics Function

\[ H_2^g + 2S \xrightleftharpoons[k_{-1} \cdot k_1]{k_2} 2H \cdot S \]
\[ H_2O^g + S \xrightleftharpoons[k_{-2} \cdot k_2]{k_{-1} \cdot k_1} H_2O \cdot S \]
\[ O \cdot S \xrightleftharpoons[k_{-3} \cdot k_3]{k_{-1} \cdot k_1} OH \cdot S + S \]

\[ H_2O \cdot S + O \cdot S \xrightleftharpoons[k_{-4} \cdot k_4]{k_5 \cdot k_{-5}} 2OH \cdot S \]
\[ H_2O \cdot S + S \xrightleftharpoons[k_{-5} \cdot k_5]{k_{-4} \cdot k_4} OH \cdot S + H \cdot S \]
\[ O_0^x \cdot S \xrightleftharpoons[k_{-6} \cdot k_6]{k_{-5} \cdot k_5} O \cdot S + V_0^- + 2e^-_{NI} \]


Electrochemistry & Gas Transport in a SOFC Anode

(a) (b)

Reifsnider et. al. 2005
TPB at Ni-YSZ interfaces

New method allows electrochemically active boundaries to be placed on obstacles in an ad hoc manner as TPB dictates in SEM (See Fig. 1c)

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Electrode Microstructure

Structure can be described by three parameters:

- $\Psi$ – Structural Parameter ($\varepsilon/\tau$)
  - Porosity: $0 \leq \varepsilon \leq 1$
  - Tortuosity: $\tau \geq 1$
  - ~10X as important upon performance as other parameters in conditions studied.

- $<r>$ – Average pore radius

- $<r^2>$ – Pore radius distribution

Pore-Level Analysis $\Rightarrow$ Properties, $\eta_{\text{act}}, \eta_{\text{ohmic}}, \eta_{\text{conc}}$
Effect of Grading Electrode Microstructure

- Performance evaluated with alternative anode designs
  - Two fuel streams
    - Diluted hydrogen - Conditions near cell outlet
      - 10% H₂ – 3% H₂O – balance inert gas
    - Partially reformed methane
      with internal reforming - Approx. cell inlet
      - 10% H₂ – 49% CH₄ –
        30% H₂O – 6% CO – 5% CO₂
  - Four microstructure cases
    - {1} - Ψ is a constant high value of 0.25
    - {2} - Ψ is a constant low value of 0.05
    - {3} - Ψ is high at the TPB and low at the gas supply channel 0.25 -> 0.05
    - {4} - Ψ is low at the TPB and high at the gas supply channel 0.05 -> 0.25
Model Validation by Experiments


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Effect of Electrode Grading on Performance

Diluted Hydrogen Feed

With Internal Reforming


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SOFC Performance Correlations

Curve Fits

\[ Da \sim d^{1.79} \]
\[ R^2 = 0.999 \]

\[ Da \sim \Psi^{0.357} \]
\[ R^2 = 0.998 \]

- Displays prevalently kinetically limited characteristics (Da<1)

- Exponent of power law fits display larger sensitivity of Da to d than \( \Psi \)

\[ Da = \frac{\tau_{\text{diffusion}}}{\tau_{\text{reaction}}} = \frac{R_{EC}d^2}{D_{H_2}C_{H_2}} \]

Conclusions

- SOFC is promising energy conversion device.
- Performance strongly dependent on electrode microstructure.
- Presented modeling/experimental approach to analyze and design SOFC electrodes.
- Optimized fuel cell electrodes can provide a durable high efficiency energy conversion technology for our society.
Acknowledgements

- Sponsors
  - Office of Naval Research
  - Army Research Office
  - University of Connecticut - Institute of Materials Science

- Collaborators
  - Naval Undersea Warfare Center
  - Adaptive Materials
  - NexTech Materials
  - Xradia
  - Advanced Photon Source, Argonne National Lab
Acknowledgements – Fuel Cell Group

- Aldo Peracchio, Visiting Scholar
- Abhijit Joshi, Post-Doctoral Researcher
- Graduate Students
  - Srinath S. Chakravarthy
  - Eric S. Greene
  - Kyle N. Grew
  - John R. Izzo
  - Andrew C. Lysaght
- Undergraduate & High School Students