Research on SOFC Materials with Emphasis on Electrodes

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**Project Title:** Cathodes for Low Temperature SOFC: Issues Concerning Interference from Inert Gas Adsorption and Charge Transfer

**Technical Issues Addressed:**
1) The effect of inert gas (e.g. N₂) on the cathodic reaction.
2) The measurement of transport parameters, which govern cathodic polarization.
R & D Objectives and Approach

• To synthesize dense samples of perovskite MIEC including LSM (which is predominantly an electronic conductor with negligible ionic conductivity), LSC and LSF.
• To investigate the oxygen incorporation reaction using mixtures of $O_2$ and $N_2$, as well as of $O_2$ and Ar.
• To fabricate anode-supported cells with MIEC + YSZ or MIEC + SDC composite cathodes.
• To investigate cell performance and cathodic polarization as a function of temperature and the composition of the oxidant.
Results to Date

• Cathode Polarization – important parameters
  Concentration and Activation polarization
• Estimation of Relevant Parameters from V-I curves.
• Experimental work on the characterization of MIEC materials for cathodes
  Surface exchange and diffusion
• Investigation of Cathodes in Cells
• Summary
Effect of Oxygen Concentration

- Voltage (V)
- Current Density (A/cm²)
- Power Density (W/cm²)
- 21% O₂
- 5% O₂

Cathode Thickness ~100 microns
Anode Thickness ~ 1mm
Effective $O_2$-$N_2$ Diffusivity through Porous Cathode

Prospective cathode

$D_{O_2-N_2}^{\text{eff}} \sim 0.1 \text{ cm}^2/\text{s}$

To appear in JES, March 2003
Anode Limiting Current Density: Slope gives (approximately) Effective Fuel Diffusivity

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Effective Diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂-H₂O</td>
<td>~0.5</td>
</tr>
<tr>
<td>H₂-He-H₂O</td>
<td>~0.55</td>
</tr>
<tr>
<td>H₂-N₂-H₂O</td>
<td>~0.35</td>
</tr>
<tr>
<td>H₂-CO₂-H₂O</td>
<td>~0.3</td>
</tr>
<tr>
<td>CO-CO₂</td>
<td>~0.075</td>
</tr>
</tbody>
</table>

To appear in JES, 2003

iₘₐₗ < iₖₑₜ
Cathodic Concentration Polarization

Cathodic Short Circuit Current Density

\[ i_{cs} \approx \frac{4FD_{O_2-N_2}^{eff}}{RTl_c} p \ln \left( \frac{p}{p - p_o} \right) \]

\( p_o \) - partial pressure of \( O_2 \) in the oxidant stream

Concentration Polarization

\[ \eta_{conc(c)} = -\frac{RT}{4F} \ln \left( 1 - \frac{i}{i_{cs}} \right) \]

Cathode Overpotential (V)

Current Density (A/cm\(^2\))

Cathodic Limiting Current Density

\( i_{cs} < i_{as} \)

Cathode thickness: 50 µm

%Porosity

Cathode thickness: 200 µm

Point to note: At ~0.8 A/cm\(^2\), the conc. pol. is ~50 mV. But the short circuit current density is only about ~0.9 A/cm\(^2\).
Anodic Concentration Polarization: Comparison of H₂-H₂O with CO-CO₂

\[ i_{as} = n \left[ \frac{2FD_{eff}^{H₂-H₂O}}{RTl_a} \right] p_{H₂}^o \]

\[ \eta_{conc(a)} = \frac{RT}{2F} \ln \left( 1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left( 1 + \frac{p_{H₂}^o i}{p_{H₂O}^o i_{as}} \right) \]

For CO-CO₂, replace \( p_{H₂}^o \) by \( p_{CO}^o \) and \( p_{H₂O}^o \) by \( p_{CO₂}^o \)

\( p_{H₂}^o \) - partial pressure of H₂ in the fuel stream

\( p_{H₂O}^o \) - partial pressure of H₂O in the fuel stream

![Graph showing overpotential vs. current density with data points for different compositions: 66% H₂O + 34% H₂ and 68% CO₂ + 32% CO.]
Activation Polarization

Assume Tafel Limit

$$\eta_{act} \approx a + b \ln i$$

where

$$a \approx -\frac{RT}{4\alpha F} \ln i_o^c \quad i_o^c = \text{Exchange current density}$$

$$i_o^c$$ is a function of $$p_{O_2}^{int}$$ The higher the $$p_{O_2}^{int}$$, the higher is the $$i_o^c$$

The $$i_o^c$$ also depends upon the electrocatalyst, and microstructure.

Thus, activation polarization is not independent of concentration polarization.
Activation Polarization (Contd.)

Exchange current density, $i_o^c$, depends upon a number of parameters.

1) The higher the surface exchange parameter, $k_{exc}$, the higher is the $i_o^c$.
2) The higher the oxygen vacancy concentration of the cathode, the higher is the $i_o^c$.
3) The higher the oxygen ion conductivity (or oxygen diffusivity), the higher is $i_o^c$.
4) The finer the microstructure, (generally) the higher is the $i_o^c$.
5) The higher the temperature, the higher is the $i_o^c$.
6) The higher the pO$_2$, the higher is the $i_o^c$.

The above is for the cathode. Similar is the case for the anode, with pO$_2$ replaced by pH$_2$, for example.
Activation Polarization using Polarization Curves: Oxidant O₂-N₂

\[ R_{ct}^{\text{eff}} = \lim_{i \to 0} \frac{dV}{di} - R_i - \frac{d\eta_{\text{act}}^\text{anode}}{di} \bigg|_{i \to 0} - \frac{d\eta_{\text{conc}}^\text{anode}}{di} \bigg|_{i \to 0} - \frac{d\eta_{\text{conc}}^\text{cathode}}{di} \bigg|_{i \to 0} \]

- Cathode pO₂ Dependent
- Cathode pO₂ Independent
- Cathode pO₂ Dependent

Plot \( \left| \frac{dV}{di} \right|_{i \to 0} - \frac{d\eta_{\text{conc}}^\text{cathode}}{di} \bigg|_{i \to 0} \) as a function of cathode pO₂

The slope is a measure of \( \frac{1}{R_{ct}^{\text{eff}}} \).

\[ i_o^c \propto \frac{1}{R_{ct}^{\text{eff}}} \]
Activation Polarization using Polarization Curves:

Fuel H₂-H₂O

\[ R^{\text{anode}}_{\text{ct}(\text{eff})} = \left| \frac{dV}{di} \right|_{i \to 0} - R_i - \frac{d\eta^{\text{cathode}}_{\text{act}}}{di} \bigg|_{i \to 0} - \frac{d\eta^{\text{cathode}}_{\text{conc}}}{di} \bigg|_{i \to 0} - \frac{d\eta^{\text{anode}}_{\text{conc}}}{di} \bigg|_{i \to 0} \]

Plot \[ \left| \frac{dV}{di} \right|_{i \to 0} - \frac{d\eta^{\text{anode}}_{\text{conc}}}{di} \bigg|_{i \to 0} \]
as a function of pH₂

The slope is a measure of \[ R^{\text{anode}}_{\text{ct}(\text{eff})} \]
Activation Polarization using Polarization Curves:
Fuel CO-CO<sub>2</sub>

\[
\frac{dV}{di} \Bigg|_{i \to 0} = R_{ct(\text{eff})}^{\text{anode}} = \left. \frac{dV}{di} \right|_{i \to 0} - R_i - \frac{d\eta_{\text{act}}^{\text{cathode}}}{di} \Bigg|_{i \to 0} - \frac{d\eta_{\text{conc}}^{\text{cathode}}}{di} \Bigg|_{i \to 0} - \frac{d\eta_{\text{conc}}^{\text{anode}}}{di} \Bigg|_{i \to 0}
\]

Plot \[
\left| \frac{dV}{di} \right|_{i \to 0} - \frac{d\eta_{\text{conc}}^{\text{anode}}}{di} \Bigg|_{i \to 0}
\]
as a function of pCO

The slope is a measure of \( R_{ct(\text{eff})}^{\text{anode}} \)

Ignore the intercept
### Activation Polarization: Slope of $R_{ct(\text{eff})}$ vs. $p^{-0.5}$

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Gas Mixture</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>O$_2$-N$_2$</td>
<td>0.19</td>
</tr>
<tr>
<td>Anode</td>
<td>H$_2$-H$_2$O</td>
<td>0.048</td>
</tr>
<tr>
<td>Anode</td>
<td>CO-CO$_2$</td>
<td>0.63</td>
</tr>
</tbody>
</table>

1) The slope is a measure of activation polarization. The higher the slope, the lower is the exchange current density, the higher is the activation polarization.

2) Inverse of the slope includes many parameters, including parameters that describe the ease of adsorption of the electroactive gaseous species.

3) With H$_2$ as the fuel, and O$_2$ as the oxidant, the anode ‘activity’ is about four times the cathode activity.

4) Nickel-based anode is very good with H$_2$ as a fuel – but not with CO as a fuel.
Conductivity Relaxation Technique

**Objective:** To estimate the surface exchange coefficient and chemical diffusion coefficient of oxygen for prospective MIEC cathode materials.

- The technique consists of measuring the time dependence of total conductivity of an MIEC at temperature after an abrupt change of atmosphere.
- The technique can yield information on the surface exchange coefficient, $k_{\text{exc}}$, and the chemical diffusion coefficient of oxygen, $\tilde{D}$.
- The technique has been used in our work on LSC.
- An improved method of analysis is being developed, which facilitates the estimation of the two transport parameters.

$$R_{ct(\text{eff})}^c \propto \frac{1}{\sqrt{\tilde{D}k_{\text{exc}}}}$$

or

$$i_o^c \propto \sqrt{\tilde{D}k_{\text{exc}}}$$
Conductivity Relaxation Technique for Surface Exchange and Diffusion

MIEC conductivity depends upon oxygen partial pressure

\[ \text{Initial Slope (} t \to 0\text{)} = \frac{2k_{exc}}{l} \]

\[ \sigma(t) \] is a normalized conductivity function

\[ \tilde{D} = \text{Chemical diffusion coefficient of oxygen} \]
\[ (\text{cm}^2/\text{s}) \]

\[ k_{exc} = \text{Surface exchange parameter (cm/s)} \]

\[ g(t) \text{ is a normalized conductivity function} \]

\[ \text{Plot } \frac{g(t)}{\sqrt{t}} \text{ vs. } \sqrt{t} \]
Examples of $g(t)/t^{0.5}$ vs. $t^{0.5}$ Plots: Effect of Thickness

Effect of sample thickness for a given value of Diffusion and Surface Exchange

- 218 micron
- 150 micron
- 100 micron
- 60 micron
- 30 micron

$D = 5 \times 10^{-6}$ cm$^2$/s
$k = 4 \times 10^{-5}$ cm/s

Initial Slope = $\frac{2k_{ex}}{l}$

Effect of varying thickness: actual data and theoretical values

- 218 micron actual data: $k_{ex} = 5.98 \times 10^{-5}$ cm/s
- 150 micron actual data: $k_{ex} = 6.51 \times 10^{-5}$ cm/s
(N.B. - $D \sim 10^{-6}$ cm$^2$/s)

- 100 micron fitted data
- 60 micron fitted data
- 30 micron fitted data

$k_{ex} = 4 \times 10^{-5}$ cm/s
$D = 5 \times 10^{-6}$ cm$^2$/s

Experimental and curve fits

Effect of thickness: Calculations

Comparison with Experiments
An Example of a Plot: Comparison between Polished and Rough Surfaces

![Graph showing comparison between polished and rough surfaces](image)

Roughened surface exhibits greater surface exchange. Emphasizes the importance of a fine microstructure.

Initial slope = \[\frac{2k_{\text{exc}}}{l}\]
Plots of $g(t)/t^{0.5}$ vs. $t^{0.5}$: Samples of Two Thicknesses: Effect of Oxygen Partial Pressure (Decreasing)

800°C: 0.21atm to 0.10atm - decreasing $P_{O_2}$

- 150 micron - slope = 0.00502 to 0.006638 s\(^{-1}\)
  - $k_{ew} = 3.77 \times 10^{-5}$ to $4.79 \times 10^{-5}$ cm/s
- 218 micron - slope = 0.00189 to 0.00205 s\(^{-1}\)
  - $k_{ew} = 2.06 \times 10^{-5}$ to $2.23 \times 10^{-5}$ cm/s

800°C: 0.10atm to 0.05atm - decreasing $P_{O_2}$

- 150 micron - slope = 0.00279 to 0.00355 s\(^{-1}\)
  - $k_{ew} = 2.09 \times 10^{-5}$ to $2.66 \times 10^{-5}$ cm/s
- 218 micron - slope = 0.00139 to 0.00176 s\(^{-1}\)
  - $k_{ew} = 1.52 \times 10^{-5}$ to $1.92 \times 10^{-5}$ cm/s

Activation Polarization

$p_{O_2}$

$21\%\ O_2$

Cathode

$p_{O_2(0)}$

$t = 0$

$p_{O_2(1)}$

Time
Plots of $g(t)/t^{0.5}$ vs. $t^{0.5}$: Samples of Two Thicknesses: Effect of Oxygen Partial Pressure (Increasing)
Surface Exchange Parameter as a Function of Oxygen Partial Pressure

Note: Exchange current density, $i_o^c$, is a monotonically increasing function of the surface exchange parameter, $k_{exc}$. 

$k_{exc} = 2.26 \times 10^{-4}$ cm/s for $pO_2 = 1$ atm.

$k_{exc} = 7.64 \times 10^{-5}$ cm/s for $pO_2 = 0.21$ atm
Oxygen Exchange Studies in Small Intervals of $pO_2$

150µm sample: $k_{\text{exchange}}$ - 800°C
- small decreasing $pO_2$ changes

150µm sample: $k_{\text{exchange}}$ - 800°C
- small increasing $pO_2$ changes

150µm sample: 800°C - 0.18atm to 0.16atm $pO_2$
Surface Exchange Parameter as a Function of pO$_2$: Small Intervals

Note that $k_{exc}$ decreases with decreasing pO$_2$. Thus, $i^c_0$ decreases with decreasing pO$_2$.

Need MIEC materials with high $k_{exc}$ even at low pO$_2$.
Synthesis and Characterization of Cathode Interlayer Materials

• Synthesis of rare earth oxide doped ceria powders.
• Fabrication of dense and porous ceria.
• Conductivity measurements.
• Evaluation in cells.
Cathode Interlayer Powders made using Combustion Synthesis

Rationale:
1) Fine particle size
2) Uniform composition
3) Synthesis of two phase materials

1) Fine (nanosize) powders.
2) The lower the amount of DGA, the finer the size.

\[ \text{DGA} = \text{D-gluconic acid} \]

\[ \text{CeO}_2 (\text{Samaria-doped}) \]

\[ \text{CeO}_2 (\text{Scandia-doped}) \]

\[ \text{YSZ} \]
Combustion Synthesis of Sm-CeO$_2$ (SmDC)

Plot of the measured temperature vs. time for various amounts of DGA. The estimated adiabatic temperature is much higher.
Transmission Electron Micrographs of ScDC and SmDC Powders
Microstructures of Dense and Porous ScDC

Dense ScDC (Sc:Ce = 20:80)
Porosity ~3.8%: Coarse grained

Porous ScDC:
Porosity ~24.3%: Fine grained
Cell Microstructure
Effect of ScDC Composition in the Cathode Interlayer on Performance

The greater the scandia ($\text{Sc}_2\text{O}_3$) content, the greater is the oxygen vacancy concentration. Other dopants will be tried soon.
Anode + Cathode Overpotential as a Function of ScDC Composition in the Cathode Interlayer

The only variable is the composition of ScDC in the cathode interlayer. Thus, differences are due to differences in ScDC composition.
Conductivity of Dense and Porous ScDC as a Function of Composition and Temperature

Dense bar (ScDC) Sintered at 1450 °C/4hours
- 60/40 (mol%) Porosity = 3.8%
- 70/30 (mol%) Porosity = 4.6%
- 80/20 (mol%) Porosity = 3.3%

Porous bars (ScDC) Sintered at 1200 °C/4hours
- 60/40 (mol%) Porosity = 44.9%
- 70/30 (mol%) Porosity = 44.3%
- 80/20 (mol%) Porosity = 43.3%

Ionic conductivity of the highly porous material is two orders of magnitude smaller.

Points to note:
1. The conductivity of the porous material is two orders of magnitude lower. This has implications concerning performance as a cathode.
2. For dense samples, note that conductivity (mostly ionic) is the highest in Ce:Sc 80:20, and the lowest in 60:40. Part of this may well be related to microstructure (e.g. grain size). However, the cathode performance is better with 60:40 than with 80:20 – may in part be due to the higher oxygen vacancy concentration in 60:40 compared to 80:20.
Summary

• Using V-I polarization curves, effective activation polarization resistances were estimated.
• The polarization resistance increases in the following order: Anode (for H2) < Cathode < Anode (for CO).
• Surface exchange parameter was measured for LSC using conductivity relaxation method. The higher the pO2, the higher is the surface exchange parameter.
• Fine powders of doped ceria were prepared by combustion synthesis.
Summary (contd.)

- Ionic conductivity of highly porous ceria is much lower than that of sintered ceria – implications concerning electrode behavior.
Applicability to SOFC Commercialization

- Identification of suitable cathodes with high electrocatalytic activity at low temperatures and low oxygen pressures will facilitate SOFC commercialization by
  1) Lowering the SOFC operating temperature, preferably below 700°C.
  2) Enhancing performance at high oxidant utilizations.
Activities for the next 6-12 Months

• Investigation of the transport properties of other MIEC materials.
• Investigation of the effect of oxygen partial pressure and temperature.
• Studies on porous MIEC – estimation of the surface exchange parameter.
• Evaluation of prospective materials in single cells.
• Modeling studies on cathodic polarization.