

Research on SOFC Materials with Emphasis on Electrodes

Anil V. Virkar, Feng Zhao, Ramanan Ganeshanathan,
Yi Jiang and Tad J. Armstrong

Department of Materials Science & Engineering

University of Utah

Salt Lake City, UT 84112, USA

Presented at SECA Core Technology Workshop

Sacramento, CA

February 19, 2003

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. N_2) on the cathodic reaction.
- 2) The measurement of transport parameters, which govern cathodic polarization.

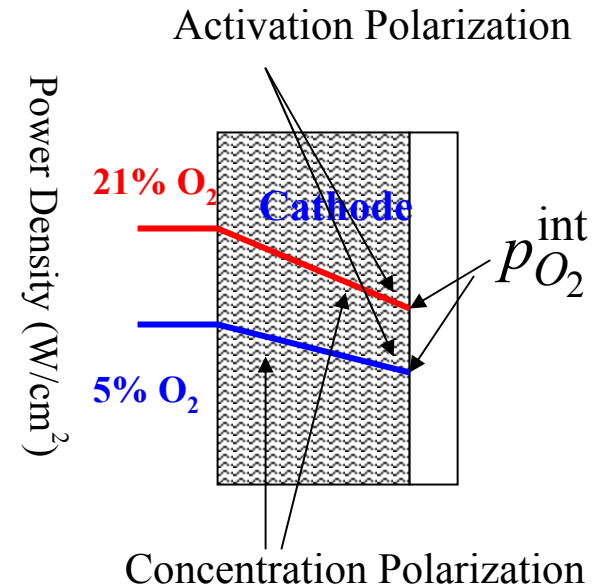
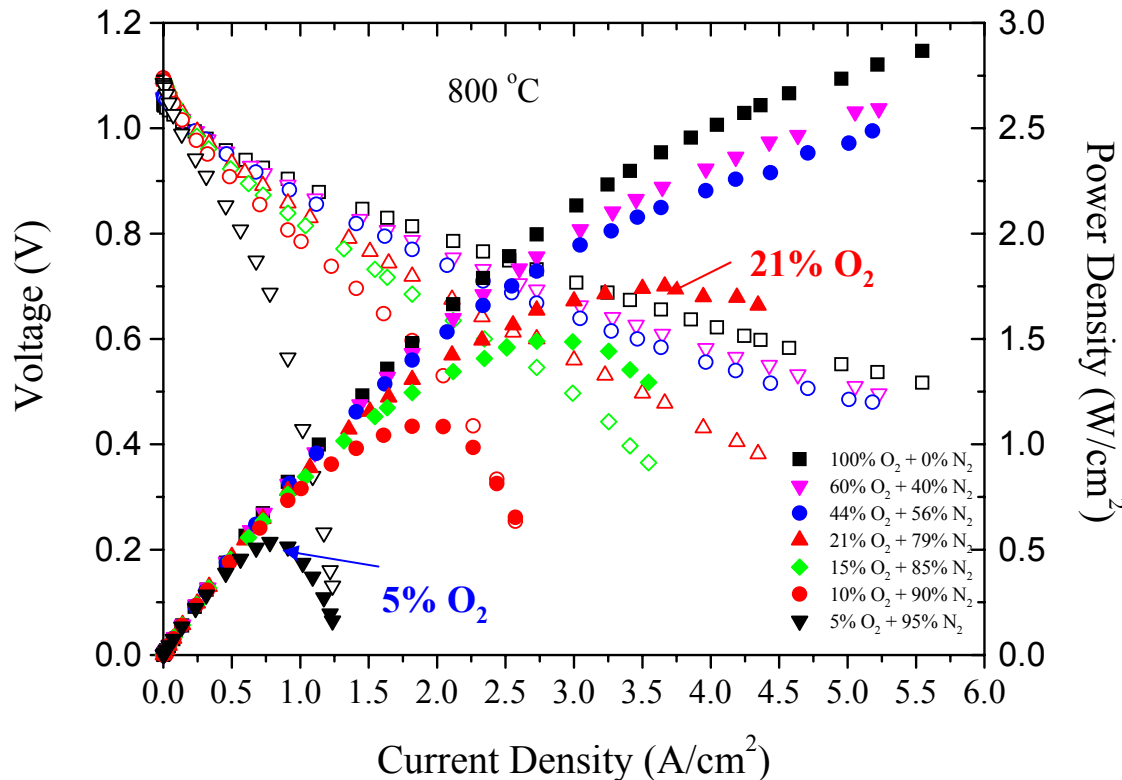
R & D Objectives and Approach

- 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

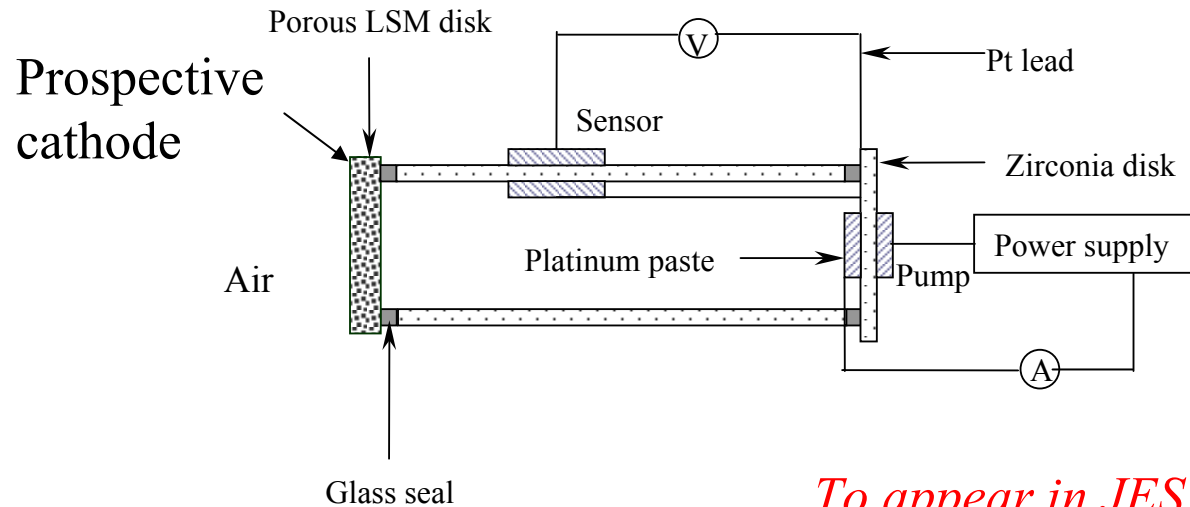
- Cathode Polarization – important parameters
Concentration and Activation polarization
- Estimation of Relevant Parameters from V-I curves.
- Experimental work on the characterization of MIEC materials for cathodes
Surface exchange and diffusion
- Investigation of Cathodes in Cells
- Summary

Effect of Oxygen Concentration



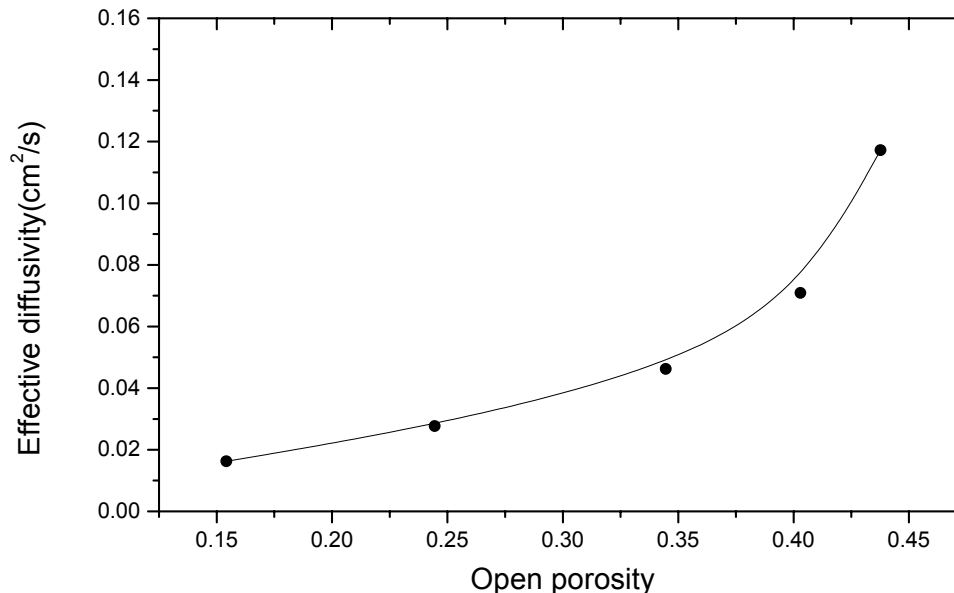
Cathode Thickness ~ 100 microns
Anode Thickness ~ 1 mm

Effective O₂-N₂ Diffusivity through Porous Cathode



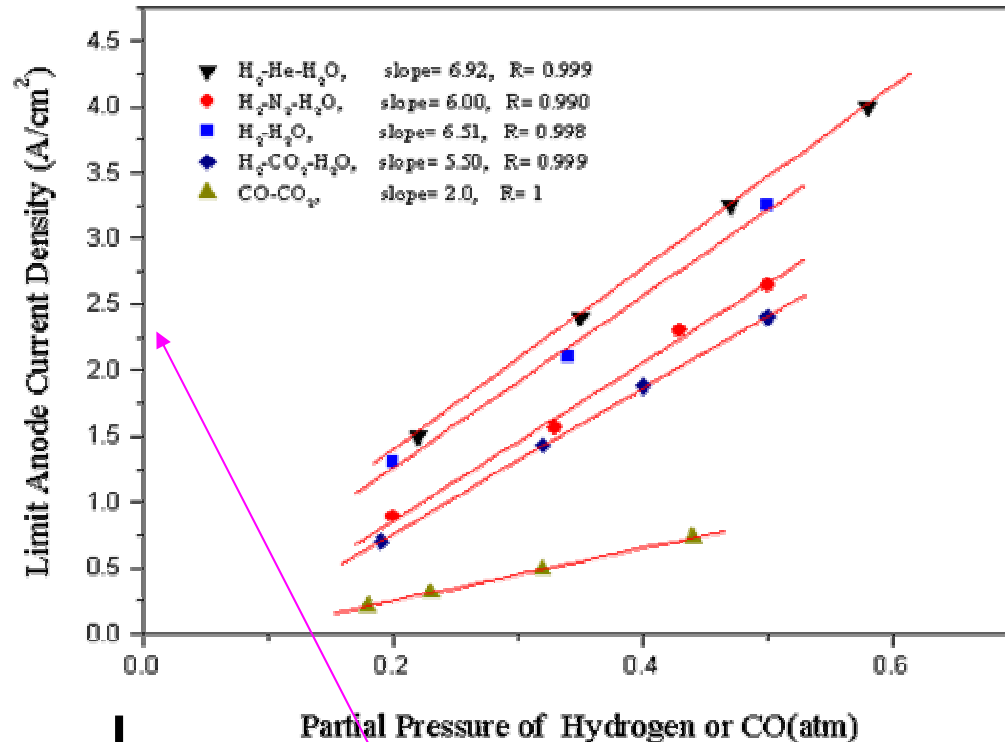
Required for estimating cathode concentration polarization.

To appear in JES, March 2003

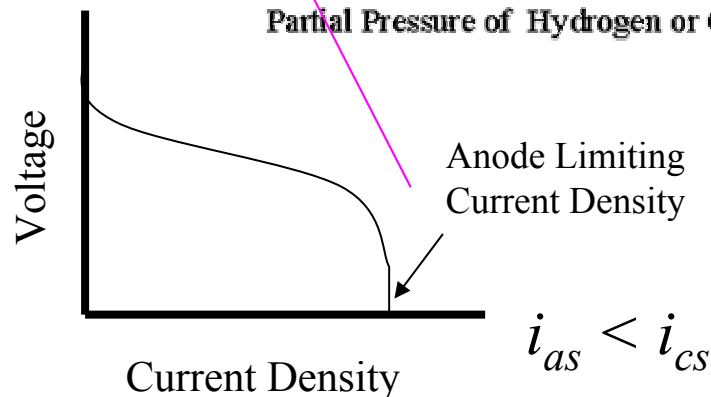


$$D_{O_2-N_2}^{eff} \sim 0.1 \text{ cm}^2/\text{s}$$

Anode Limiting Current Density: Slope gives (approximately) Effective Fuel Diffusivity



Fuel	Effective Diffusivity (cm^2/s)
H_2 - H_2O	~ 0.5
H_2 -He- H_2O	~ 0.55
H_2 - N_2 - H_2O	~ 0.35
H_2 - CO_2 - H_2O	~ 0.3
CO- CO_2	~ 0.075



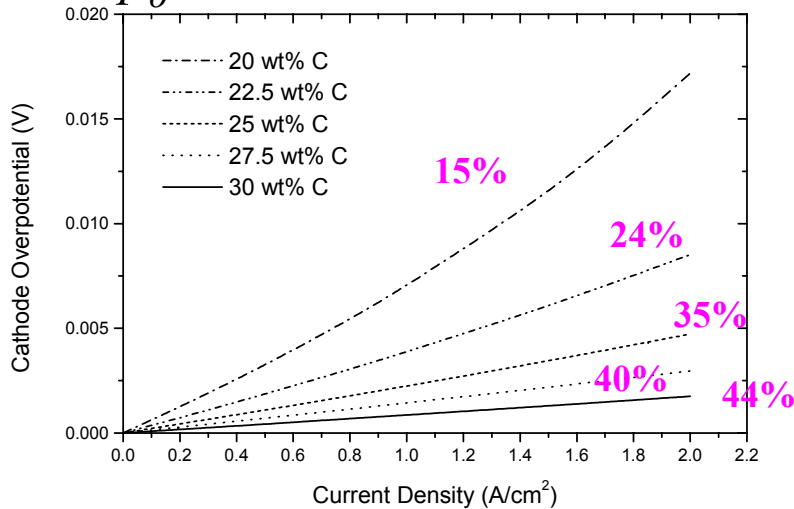
To appear in JES, 2003

Cathodic Concentration Polarization

Cathodic Short Circuit Current Density

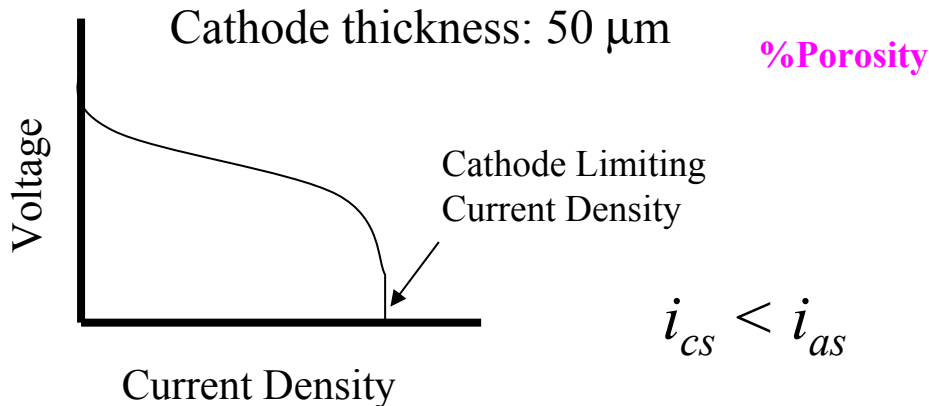
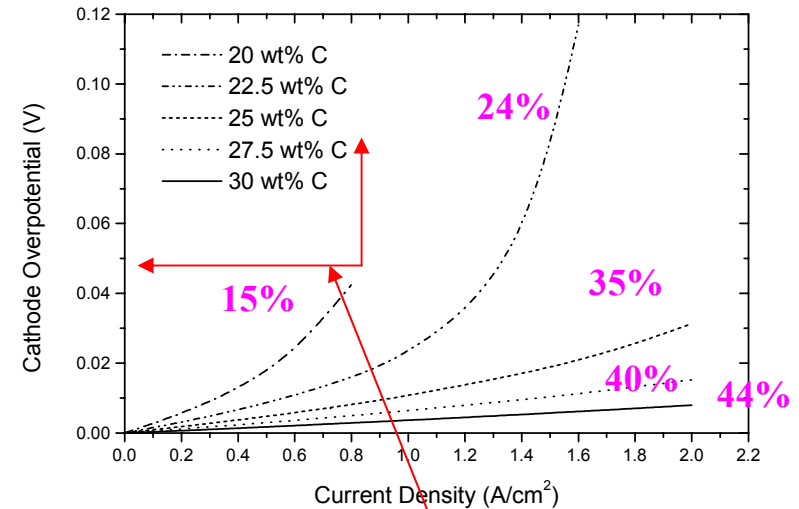
$$i_{cs} \approx \left[\frac{4FD_{O_2-N_2}^{eff}}{RTl_c} \right] p \ln \left(\frac{p}{p - p_o} \right)$$

p_o - partial pressure of O_2 in the oxidant stream



Concentration Polarization

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



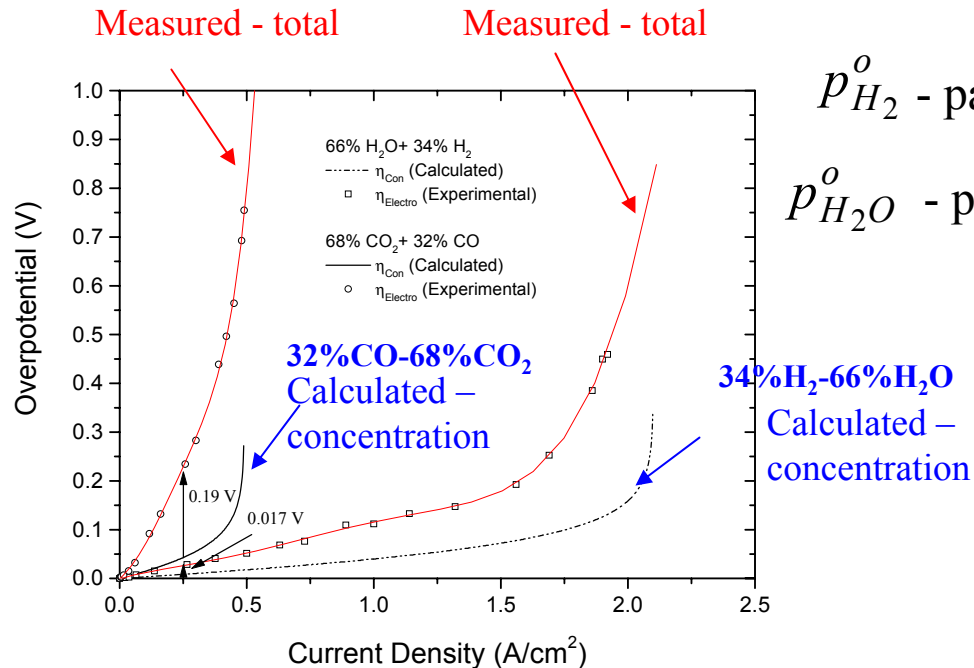
Cathode thickness: 200 μm

Point to note: At $\sim 0.8 \text{ A/cm}^2$, the conc. pol. is $\sim 50 \text{ mV}$. But the short circuit current density is only about $\sim 0.9 \text{ A/cm}^2$.

Anodic Concentration Polarization: Comparison of H₂-H₂O with CO-CO₂

$$i_{as} \approx \left[\frac{2FD_{H_2-H_2O}^{eff}}{RTl_a} \right] p_{H_2}^o \quad \eta_{conc(a)} = -\frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}} \right) + \frac{RT}{2F} \ln \left(1 + \frac{p_{H_2}^o i}{p_{H_2O}^o i_{as}} \right)$$

For CO-CO₂, replace $p_{H_2}^o$ by p_{CO}^o and $p_{H_2O}^o$ by $p_{CO_2}^o$



$p_{H_2}^o$ - partial pressure of H₂ in the fuel stream

$p_{H_2O}^o$ - partial pressure of H₂O in the fuel stream

Activation Polarization

Assume Tafel Limit

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

where

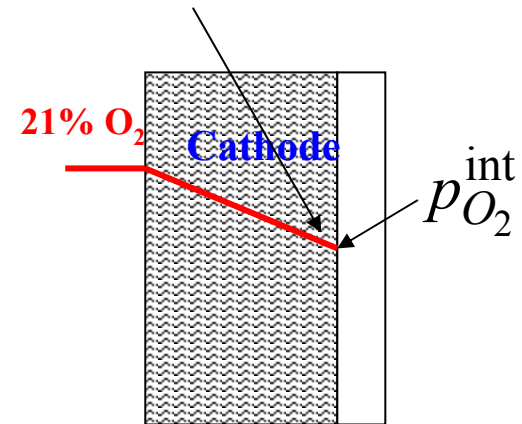
$$a \approx -\frac{RT}{4\alpha F} \ln i_o^c$$

i_o^c = 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.

Activation Polarization



$p_{O_2}^{int}$ depends
on $D_{O_2-N_2}^{eff}$
and other
parameters

Thus, activation polarization is not independent of
concentration polarization.

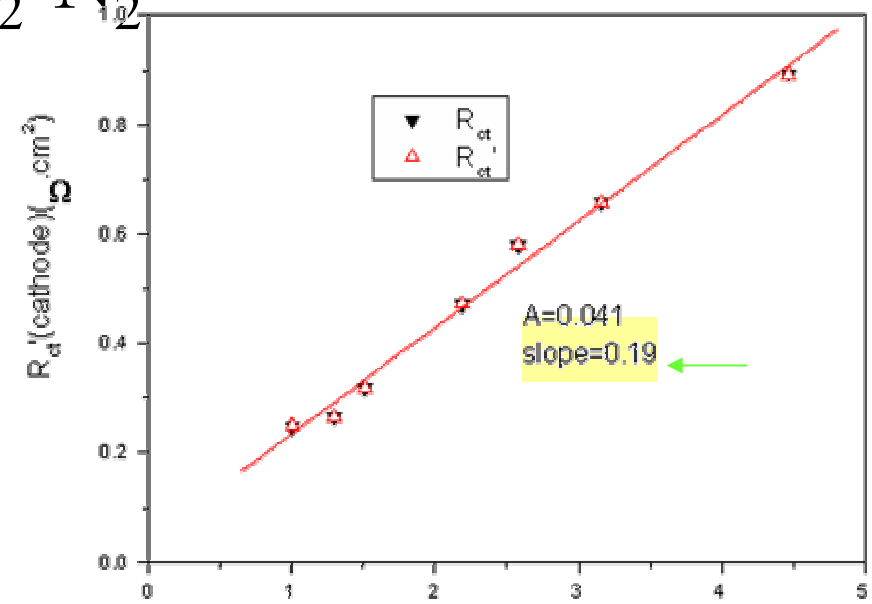
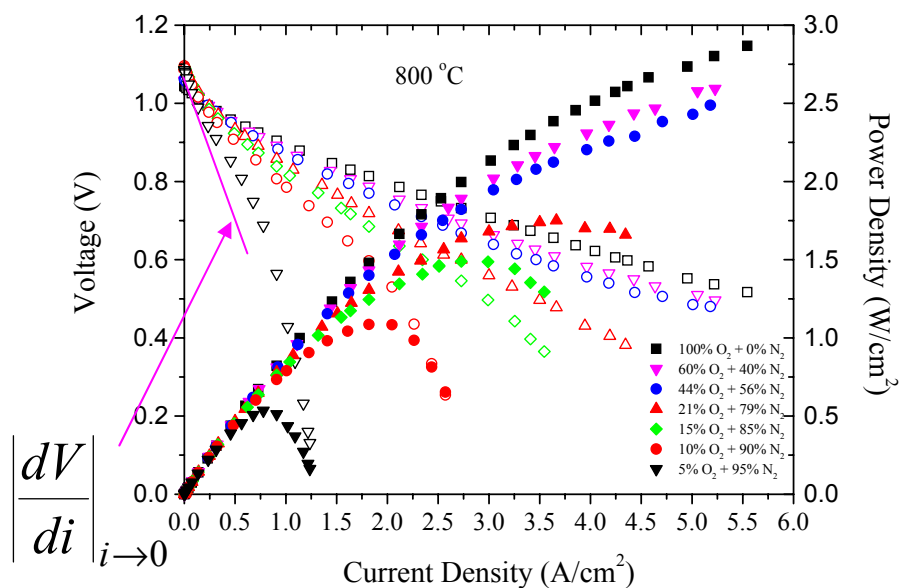
Activation Polarization (Contd.)

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



$$R_{ct(eff)}^{cathode} = \underbrace{\left. \frac{dV}{di} \right|_{i \rightarrow 0}}_{\text{Cathode } pO_2 \text{ Dependent}} - \underbrace{R_i - \left. \frac{d\eta_{act}^{anode}}{di} \right|_{i \rightarrow 0} - \left. \frac{d\eta_{conc}^{anode}}{di} \right|_{i \rightarrow 0}}_{\text{Cathode } pO_2 \text{ Independent}} - \underbrace{\left. \frac{d\eta_{conc}^{cathode}}{di} \right|_{i \rightarrow 0}}_{\text{Cathode } pO_2 \text{ Dependent}}$$

Plot $\left. \frac{dV}{di} \right|_{i \rightarrow 0} - \left. \frac{d\eta_{conc}^{cathode}}{di} \right|_{i \rightarrow 0}$

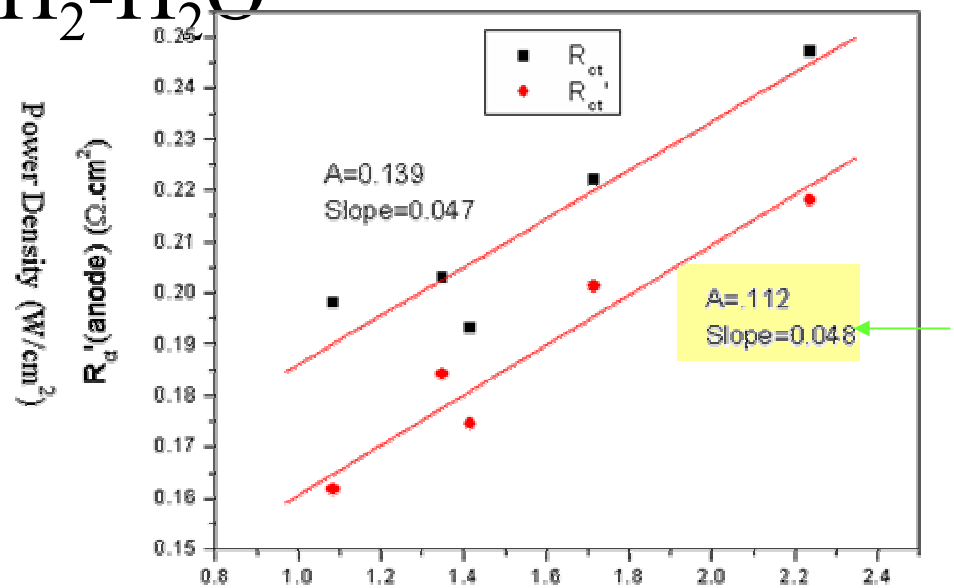
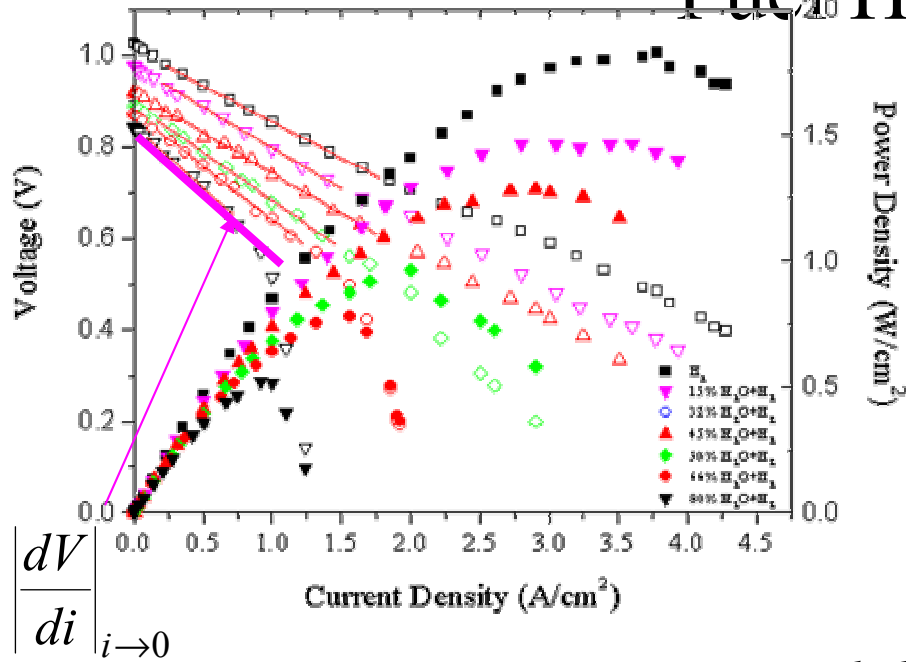
↑ Measured ↑ Calculated

as a function of cathode pO₂

$$i_o^c \propto \frac{1}{R_{ct(eff)}^{cathode}}$$

The slope is a measure of $R_{ct(eff)}^{cathode}$

Activation Polarization using Polarization Curves: Fuel H₂-H₂O



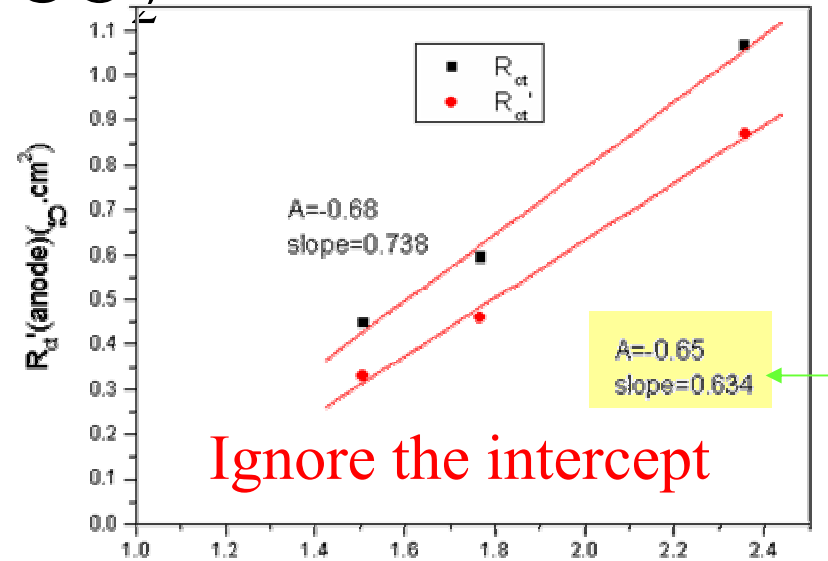
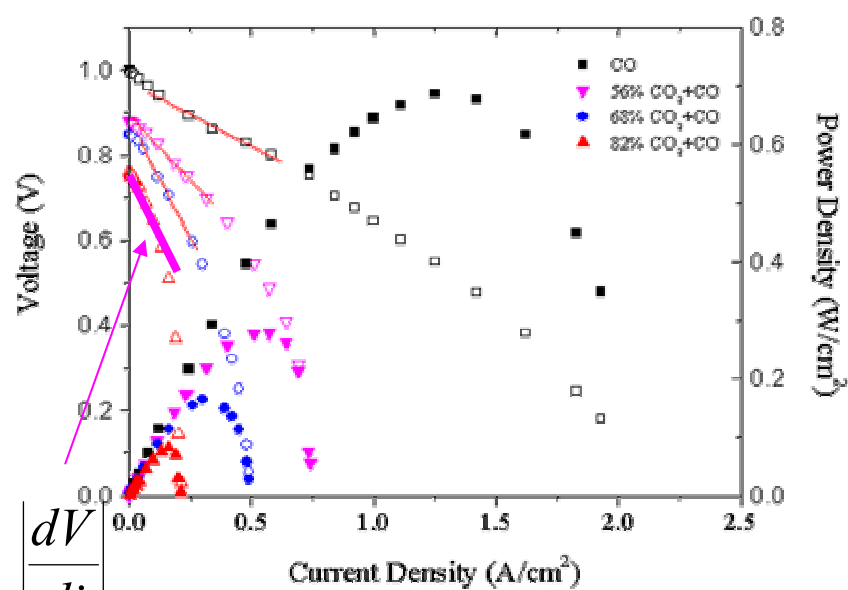
$$R_{ct(eff)}^{anode} = \underbrace{\left. \frac{dV}{di} \right|_{i \rightarrow 0}}_{\text{Measured}} - \underbrace{R_i - \left. \frac{d\eta_{act}^{cathode}}{di} \right|_{i \rightarrow 0} - \left. \frac{d\eta_{conc}^{cathode}}{di} \right|_{i \rightarrow 0}}_{\text{Anode } p_{H_2} \text{ Independent}} - \underbrace{\left. \frac{d\eta_{conc}^{anode}}{di} \right|_{i \rightarrow 0}}_{\text{Anode } p_{H_2} \text{ Dependent}}$$

Plot $\left. \frac{dV}{di} \right|_{i \rightarrow 0} - \left. \frac{d\eta_{conc}^{anode}}{di} \right|_{i \rightarrow 0}$ as a function of p_{H_2}

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

Measured (green arrow) Calculated (green arrow)

Activation Polarization using Polarization Curves: Fuel CO-CO₂



$$R_{ct(eff)}^{anode} = \underbrace{\left| \frac{dV}{di} \right|_{i \rightarrow 0}}_{\text{Anode pCO Dependent}} - \underbrace{R_i - \left| \frac{d\eta_{act}^{cathode}}{di} \right|_{i \rightarrow 0} - \left| \frac{d\eta_{conc}^{cathode}}{di} \right|_{i \rightarrow 0}}_{\text{Anode pCO Independent}} - \underbrace{\left| \frac{d\eta_{conc}^{anode}}{di} \right|_{i \rightarrow 0}}_{\text{Anode pCO Dependent}}$$

Plot $\left| \frac{dV}{di} \right|_{i \rightarrow 0} - \left| \frac{d\eta_{conc}^{anode}}{di} \right|_{i \rightarrow 0}$

Measured

Calculated

as a function of pCO

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

Activation Polarization: Slope of $R_{ct(eff)}$ vs. $p^{-0.5}$

Electrode	Gas Mixture	Slope
Cathode	O ₂ -N ₂	0.19
Anode	H ₂ -H ₂ O	0.048
Anode	CO-CO ₂	0.63

- 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 H₂ as the fuel, and O₂ as the oxidant, the anode ‘activity’ is about four times the cathode activity.
- 4) Nickel-based anode is very good with H₂ as a fuel – but not with CO as a fuel.

Conductivity Relaxation Technique

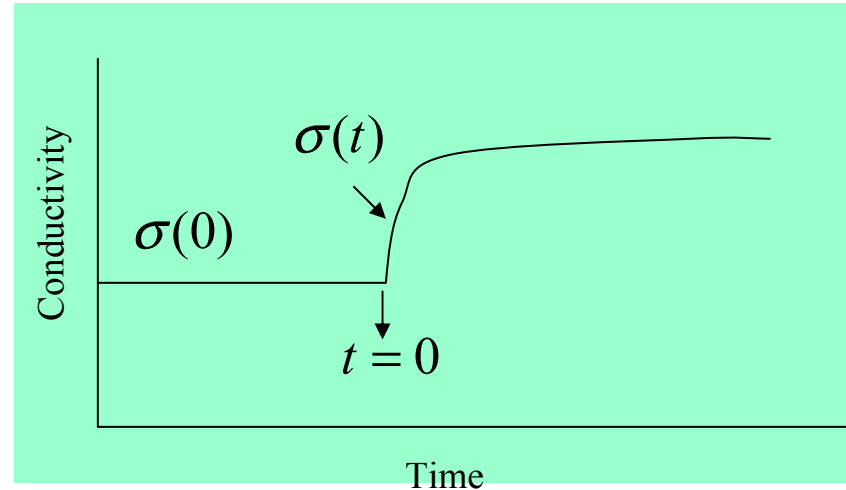
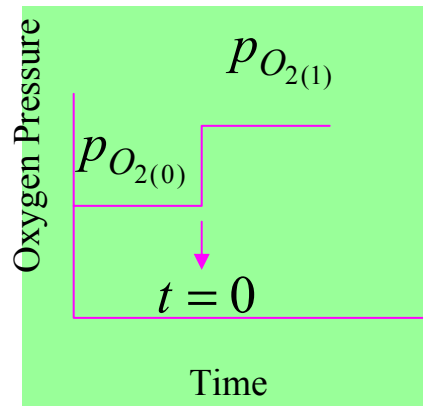
Objective: To estimate the surface exchange coefficient and chemical diffusion coefficient of oxygen for prospective MIEC cathode materials.

- 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_{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.

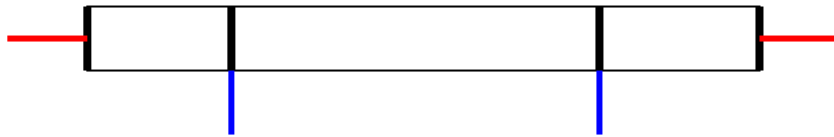
$$R_{ct(eff)}^c \propto \frac{1}{\sqrt{\tilde{D}k_{exc}}} \quad \text{or} \quad i_o^c \propto \sqrt{\tilde{D}k_{exc}}$$

Conductivity Relaxation Technique for Surface Exchange and Diffusion

MIEC conductivity depends upon oxygen partial pressure



Current leads



Voltage probes

\tilde{D} = Chemical diffusion coefficient of oxygen
(cm²/s)

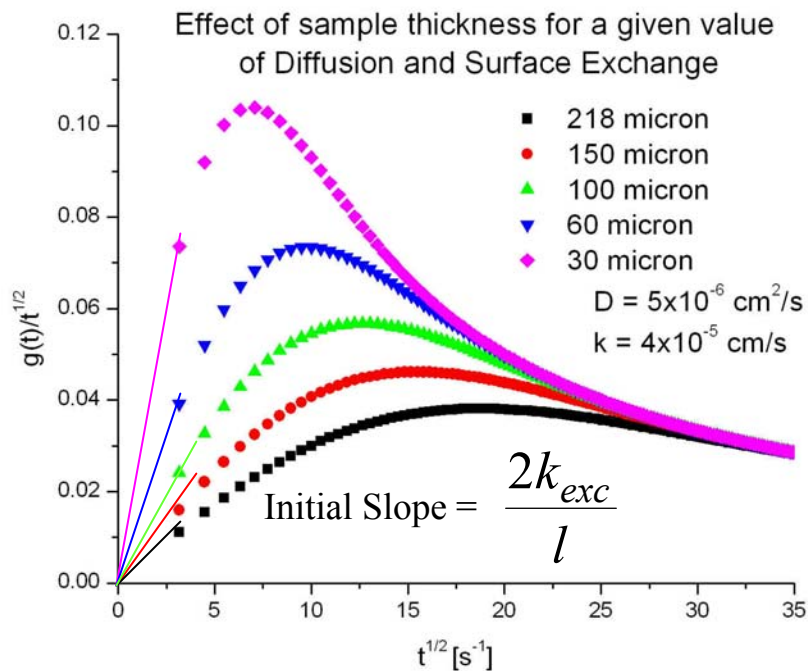
k_{exc} = Surface exchange parameter (cm/s)

$g(t)$ is a normalized conductivity function

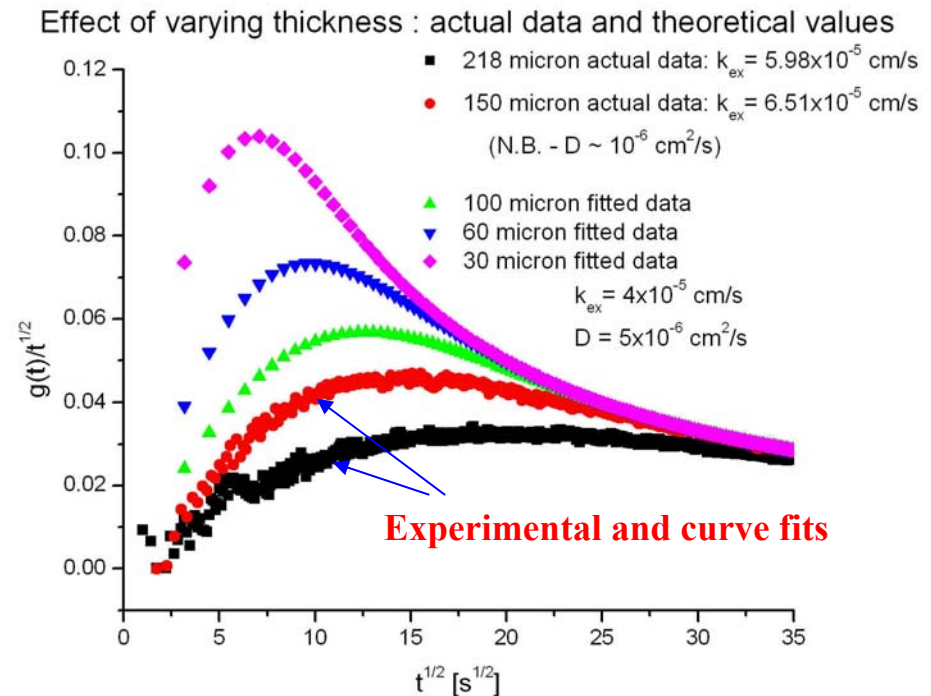
Plot $\frac{g(t)}{\sqrt{t}}$ vs. \sqrt{t}

Initial Slope ($t \rightarrow 0$) = $\frac{2k_{exc}}{l}$

Examples of $g(t)/t^{0.5}$ vs. $t^{0.5}$ Plots: Effect of Thickness

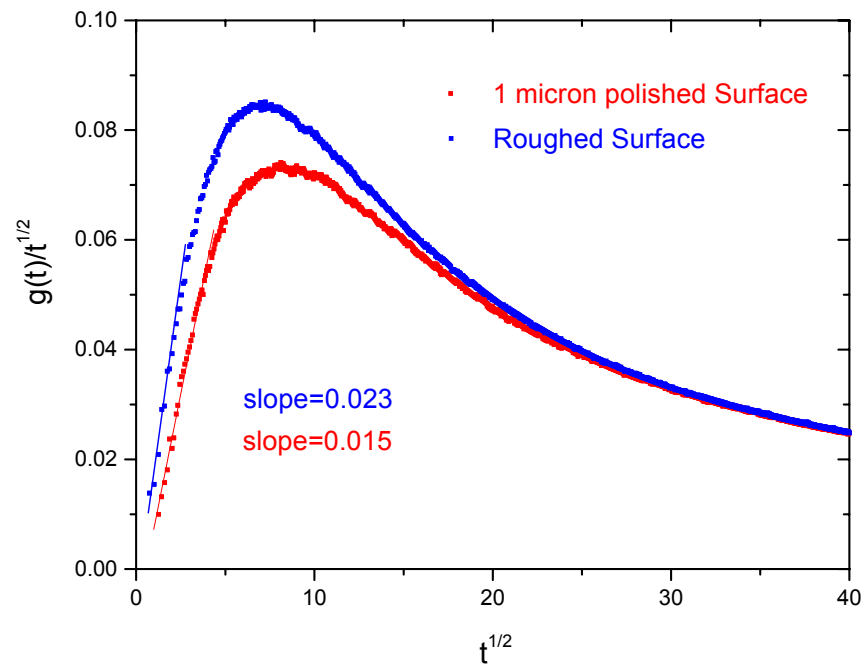


Effect of thickness: Calculations



Comparison with Experiments

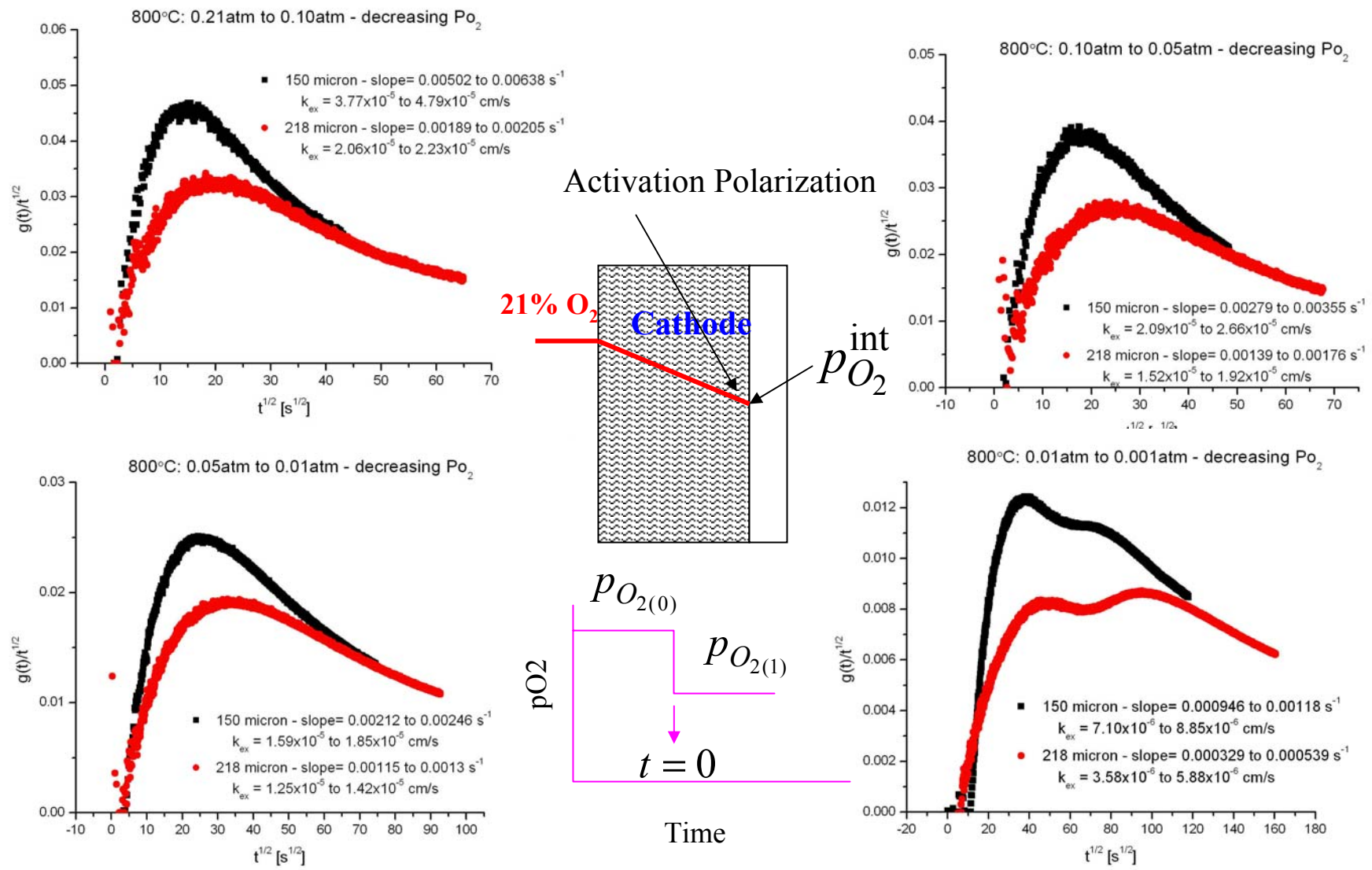
An Example of a Plot: Comparison between Polished and Rough Surfaces



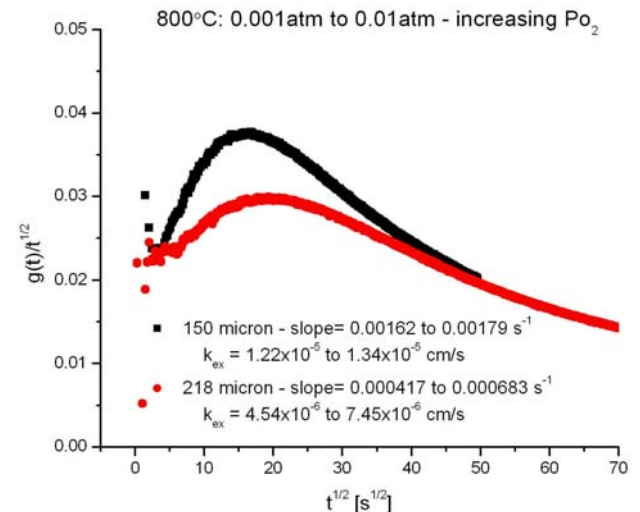
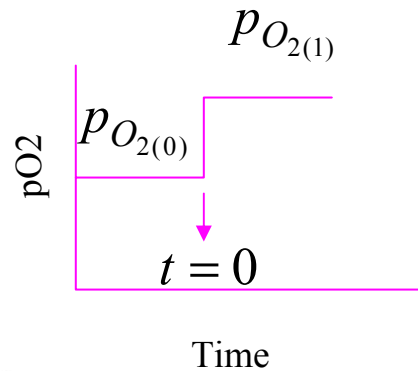
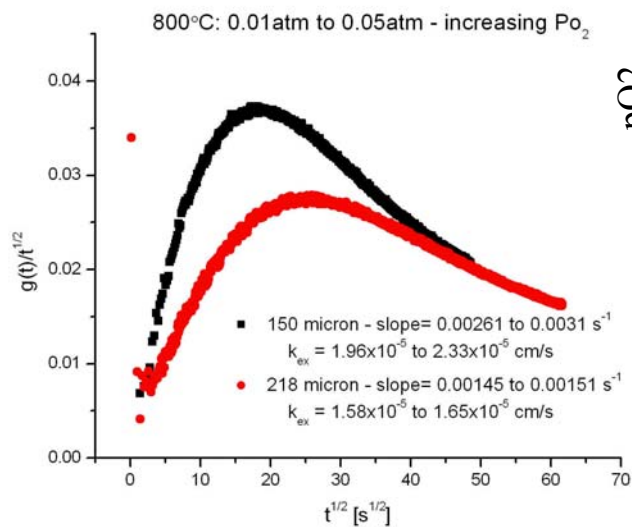
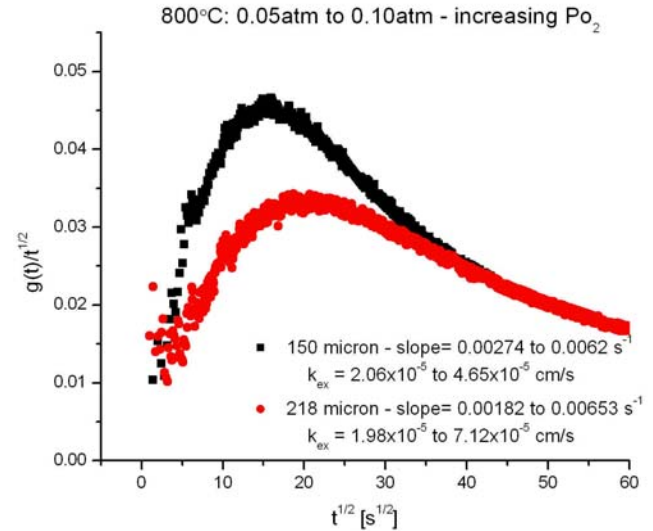
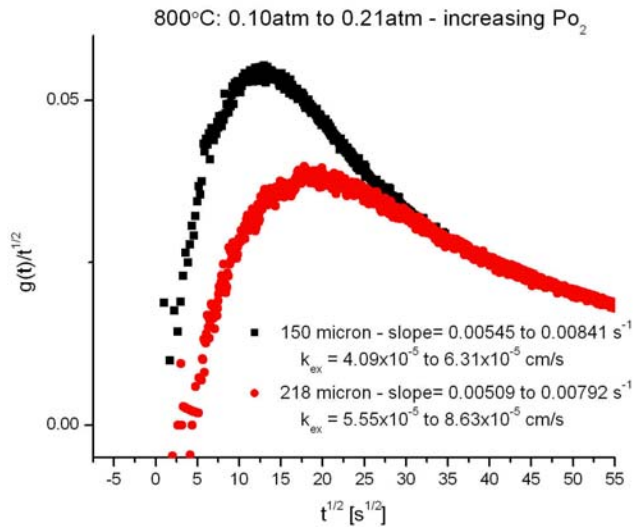
$$\text{Initial slope} = \frac{2k_{exc}}{l}$$

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

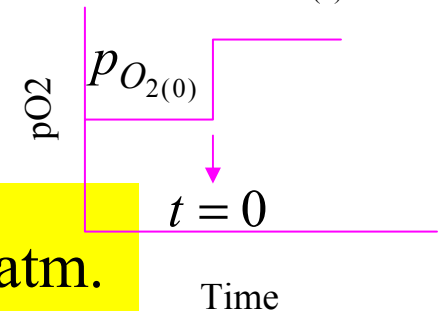
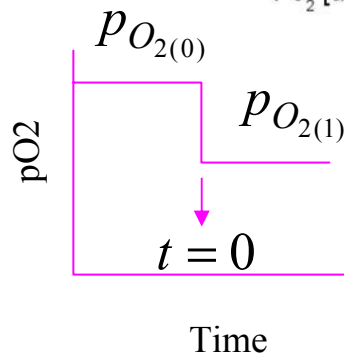
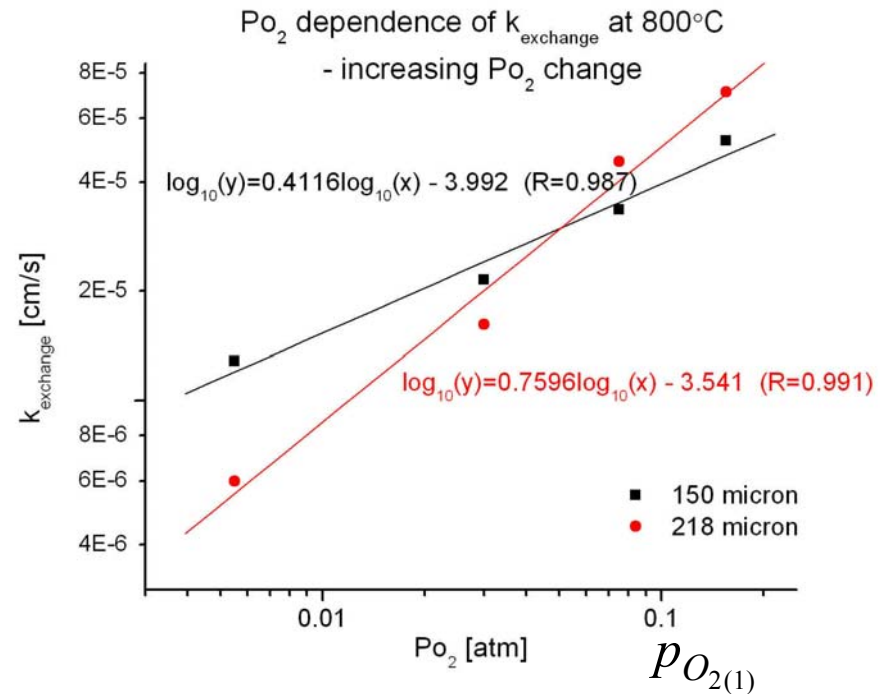
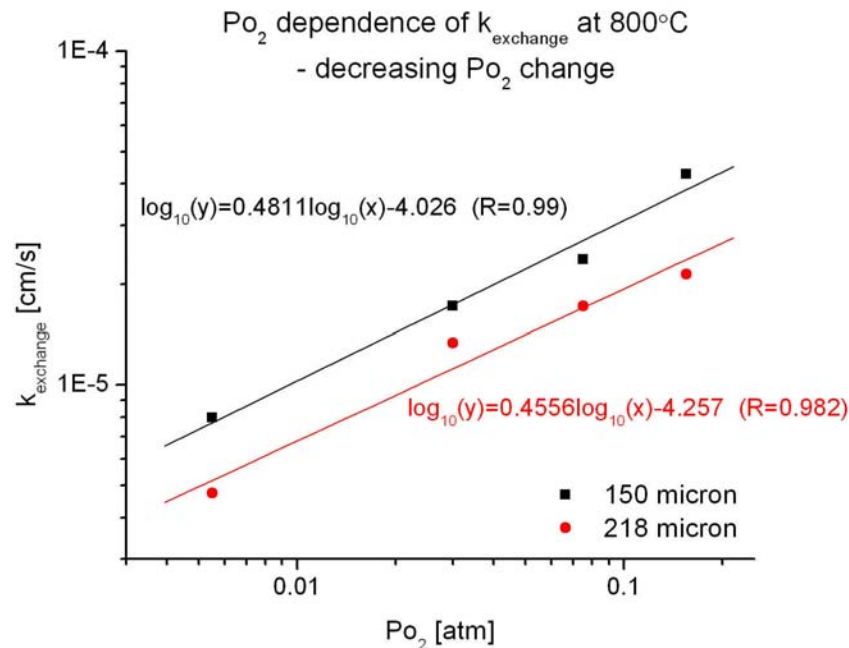
Plots of $g(t)/t^{0.5}$ vs. $t^{0.5}$: Samples of Two Thicknesses: Effect of Oxygen Partial Pressure (Decreasing)



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

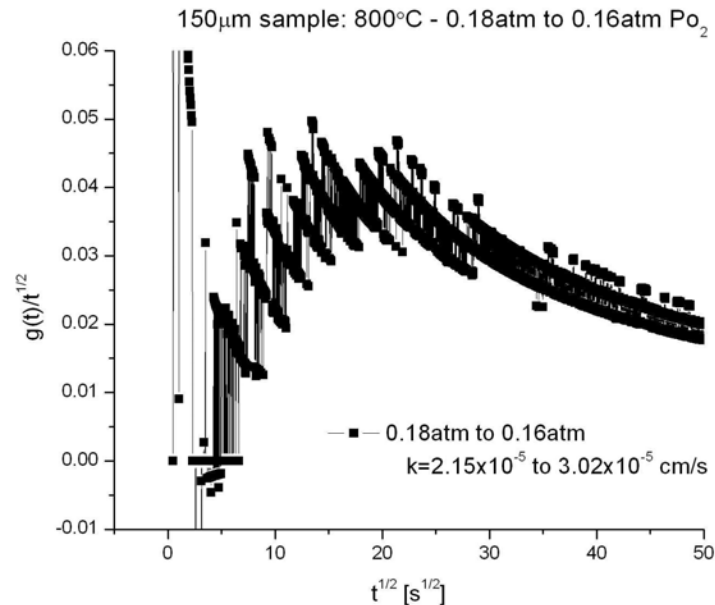
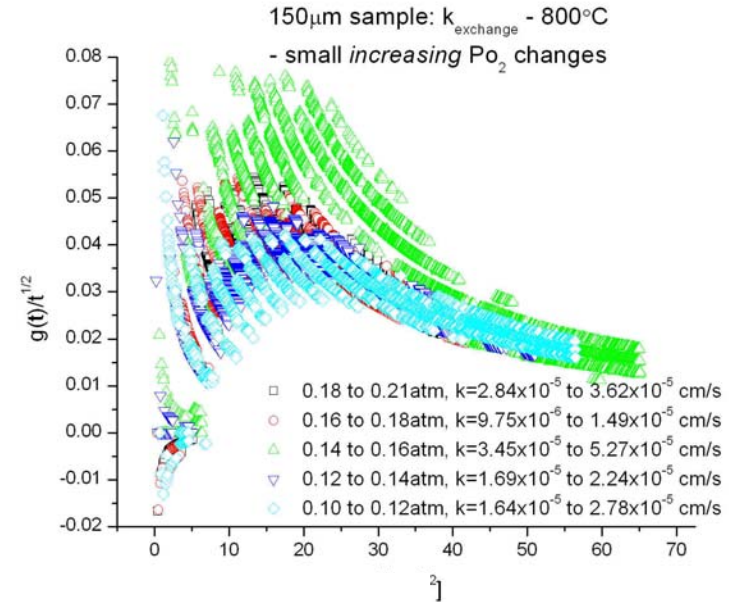
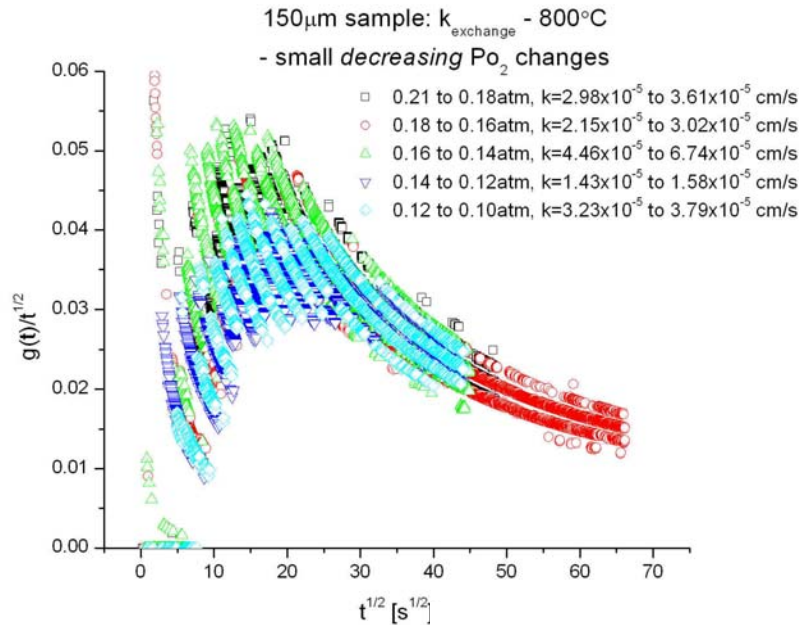


$$k_{exc} = 2.26 \times 10^{-4} \text{ cm/s for } p_{O_2} = 1 \text{ atm.}$$

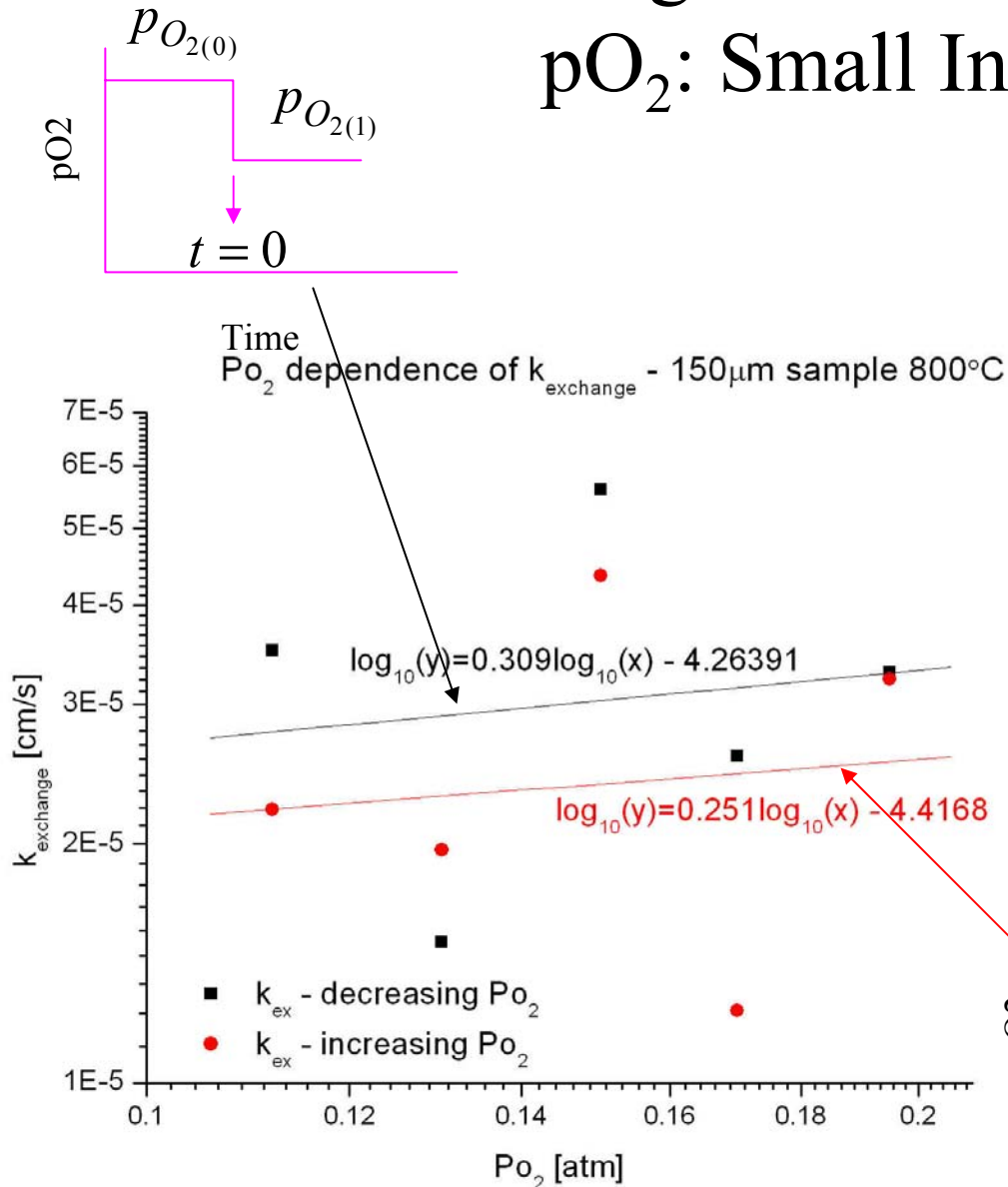
$$k_{exc} = 7.64 \times 10^{-5} \text{ cm/s for } p_{O_2} = 0.21 \text{ atm}$$

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

Oxygen Exchange Studies in Small Intervals of pO_2

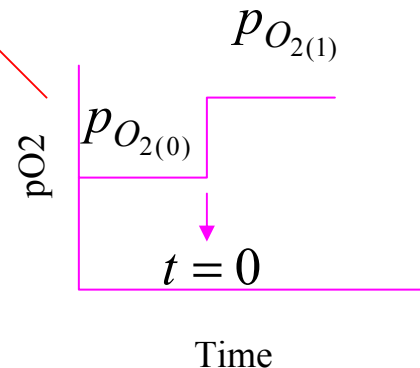


Surface Exchange Parameter as a Function of pO_2 : Small Intervals



Note that k_{exc} decreases with decreasing pO_2 . Thus, i_o^c 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

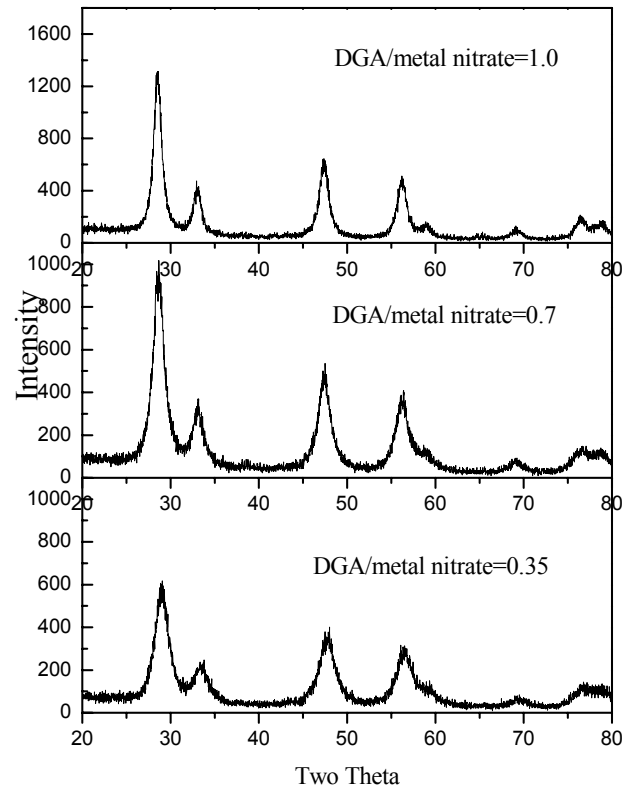
Rationale:

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

Combustion Synthesis

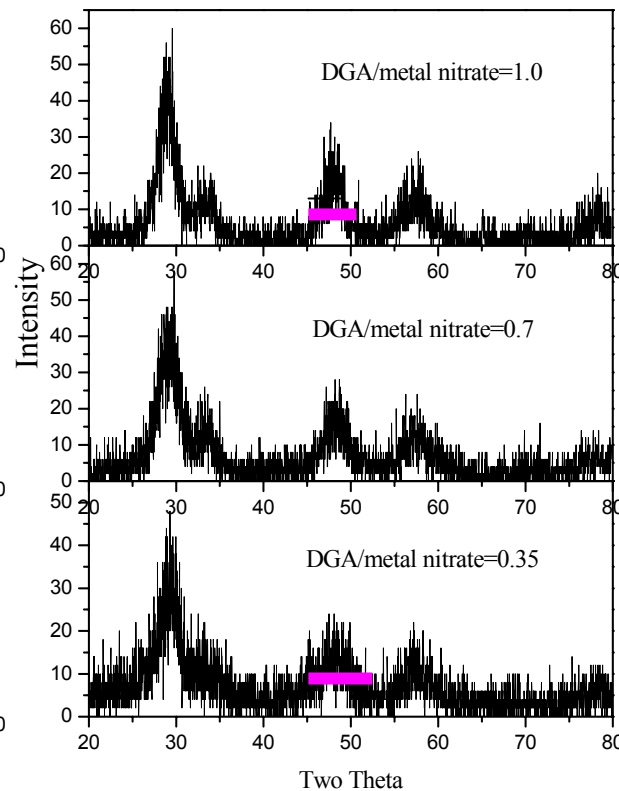
- 1) Fine (nanosize) powders.
- 2) The lower the amount of DGA, the finer the size.

CeO₂(Samaria-doped)

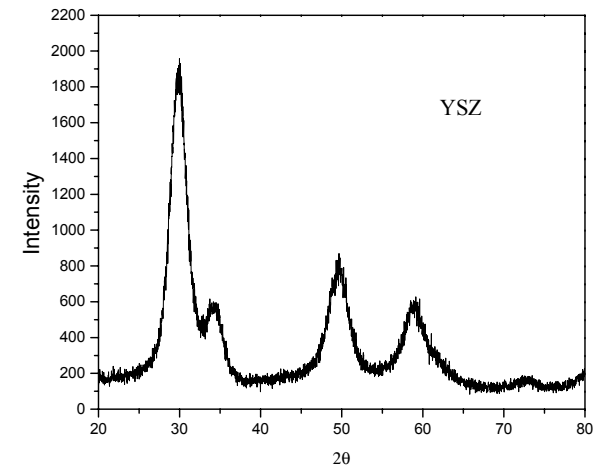


DGA=D-gluconic acid

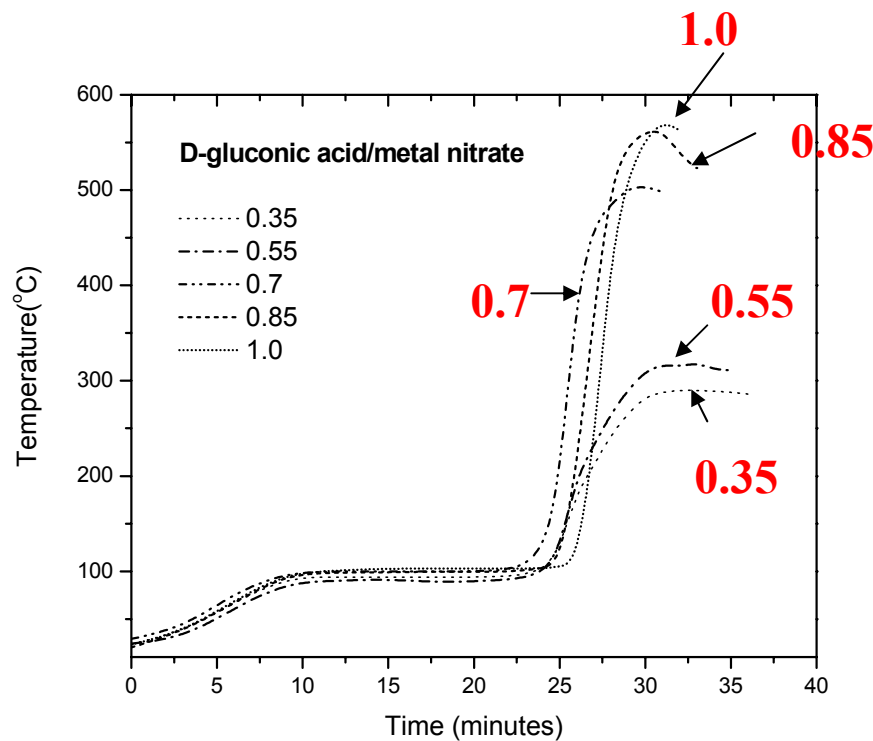
CeO₂(Scandia-doped)



DGA=D-gluconic acid

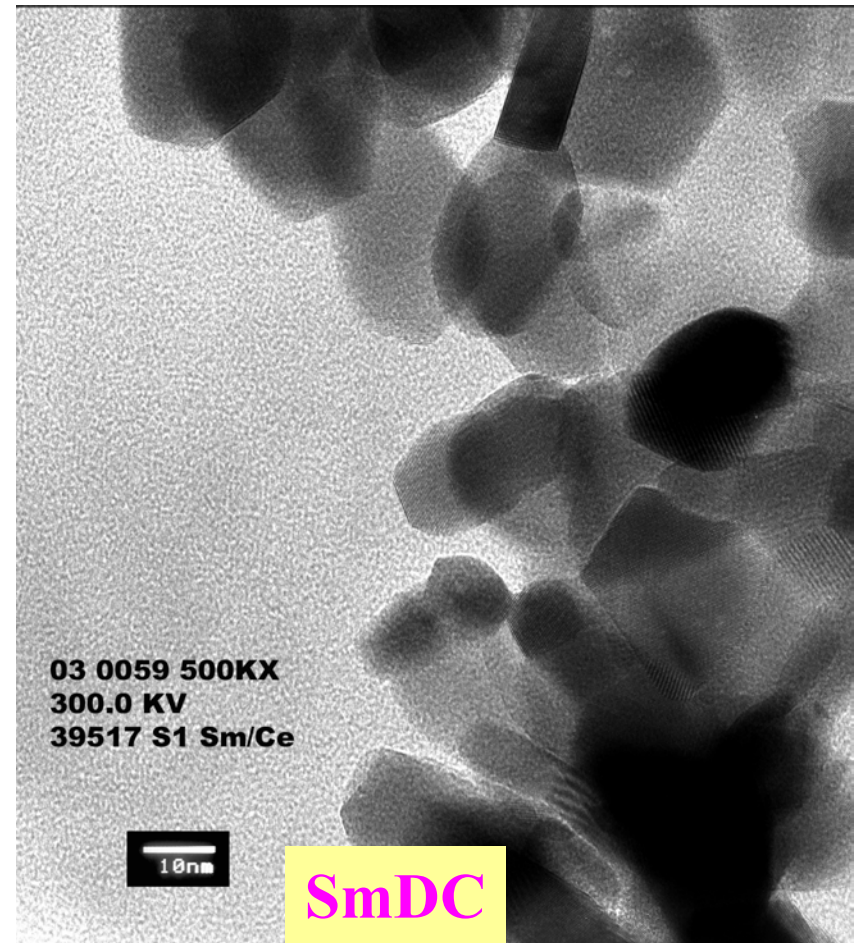
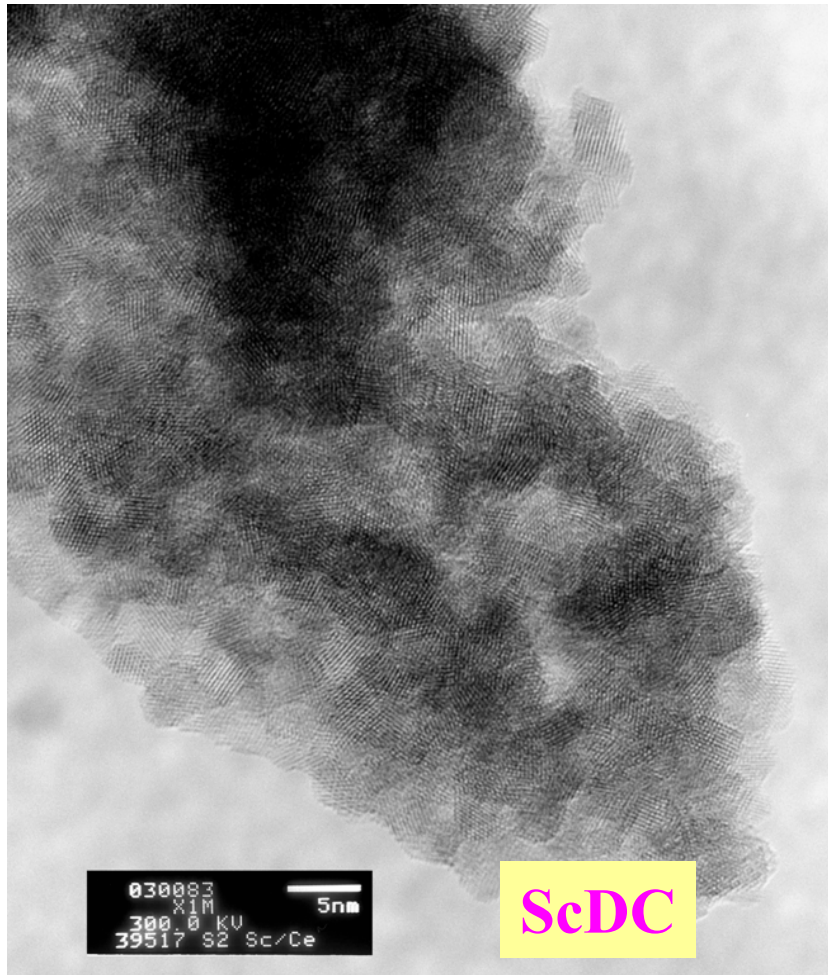


Combustion Synthesis of Sm-CeO₂ (SmDC)

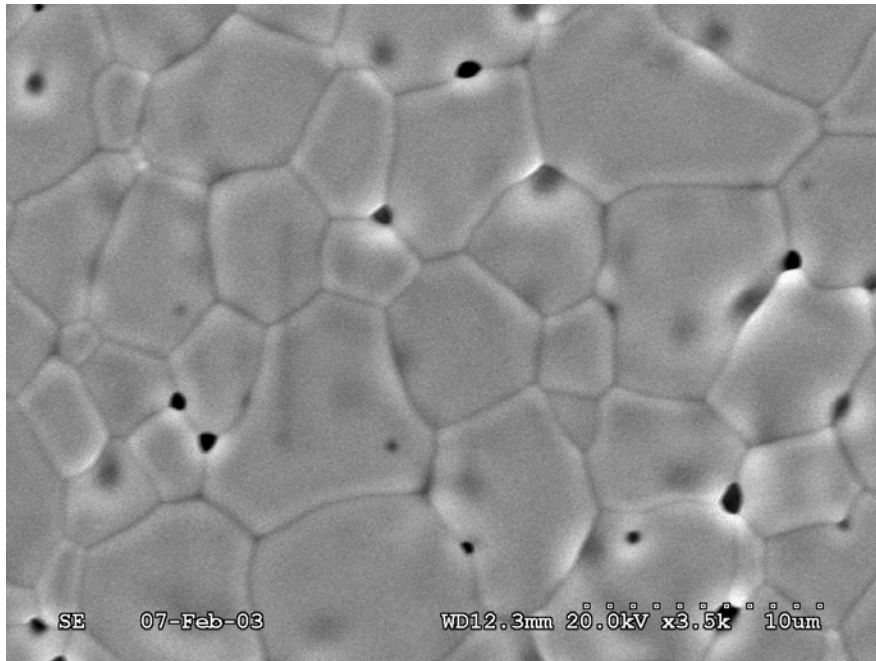


Plot of the measured temperature vs. time for various amounts of DGA. The estimated adiabatic temperature is much higher.

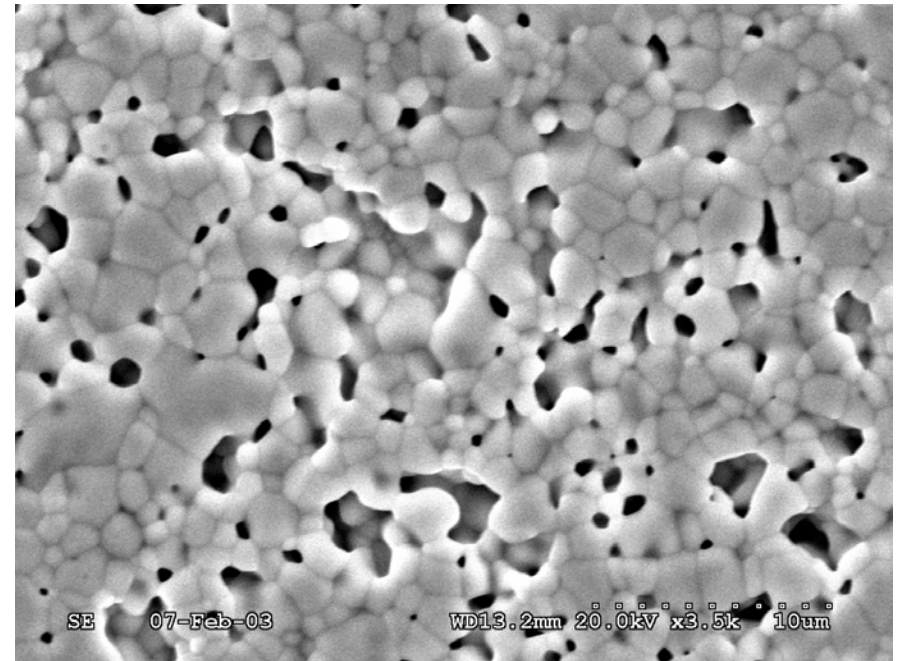
Transmission Electron Micrographs of ScDC and SmDC Powders



Microstructures of Dense and Porous ScDC

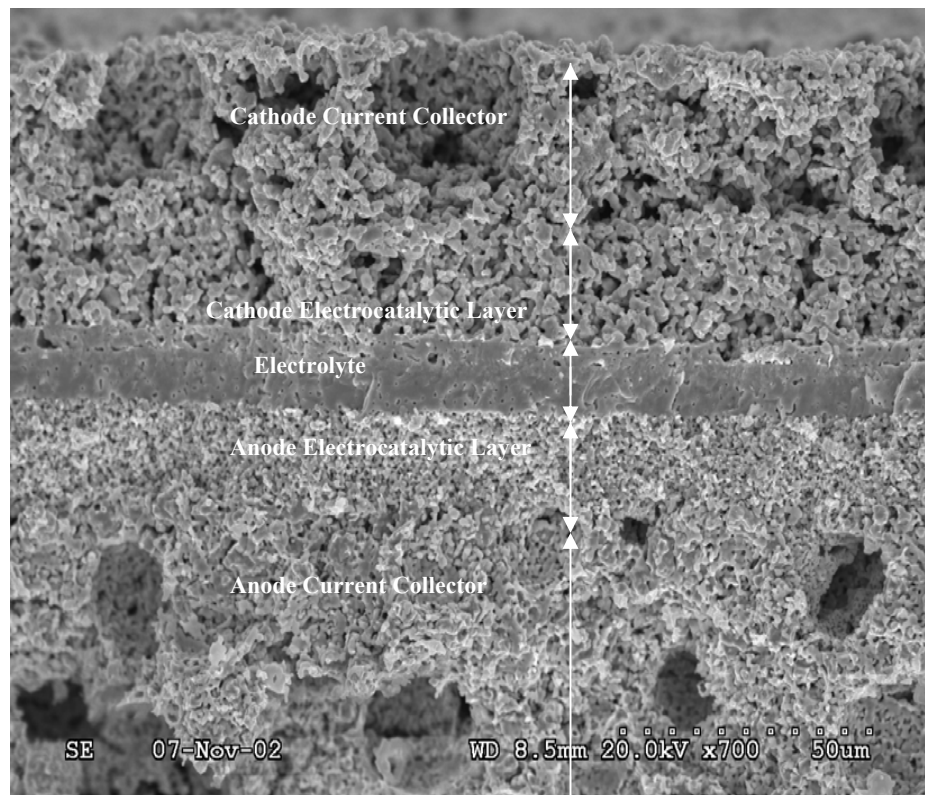


Dense ScDC (Sc:Ce = 20:80)
Porosity ~3.8%: Coarse grained

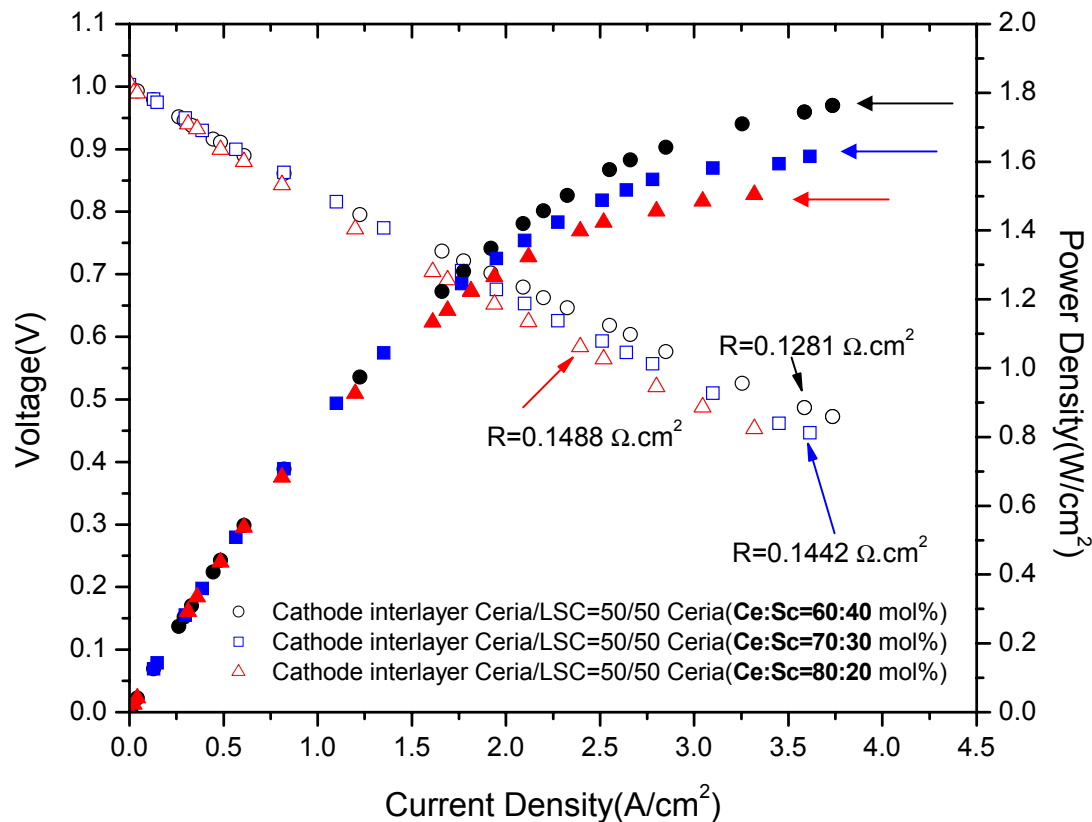


Porous ScDC:
Porosity ~24.3%: Fine grained

Cell Microstructure



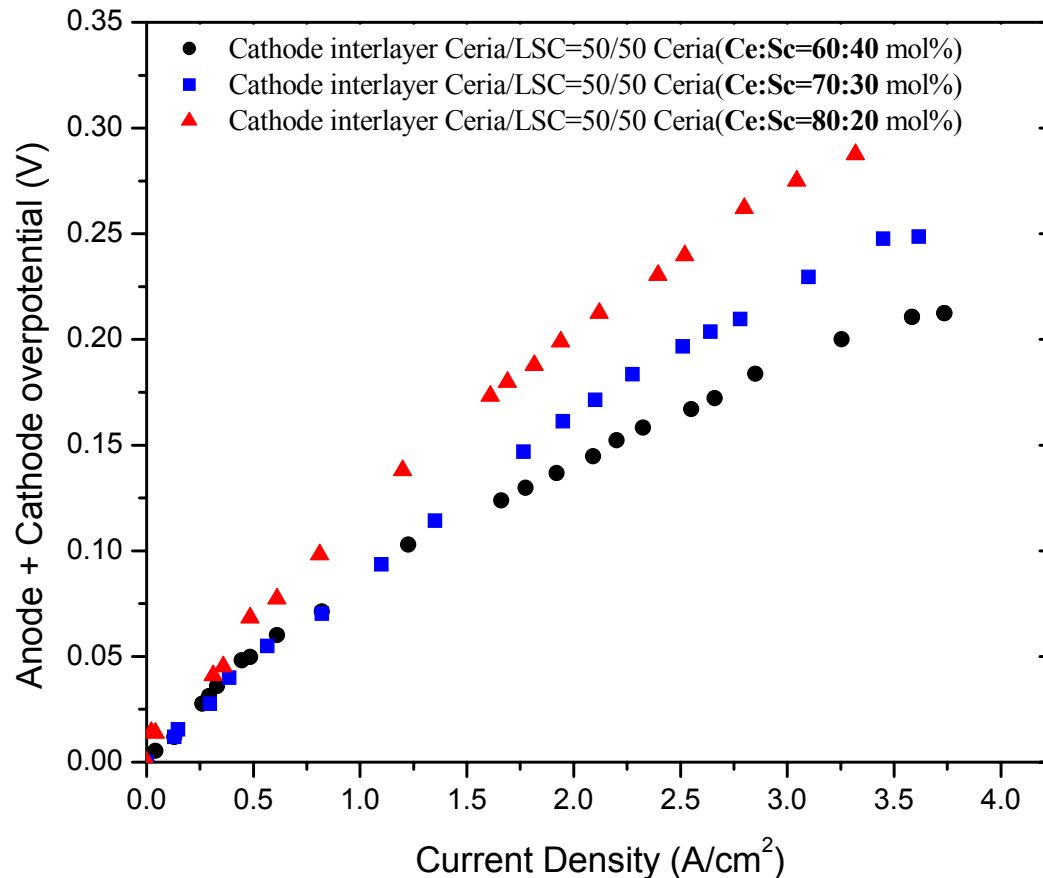
Effect of ScDC Composition in the Cathode Interlayer on Performance



Cathode Active
Area = 2 cm²

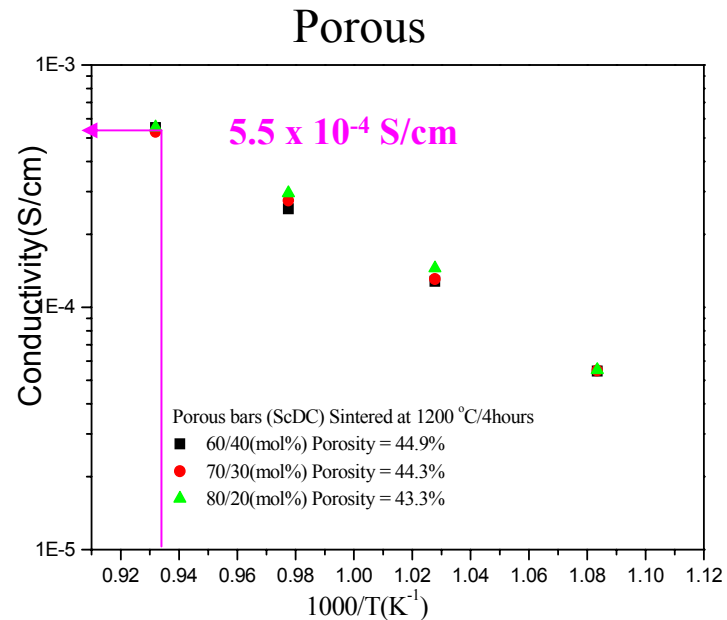
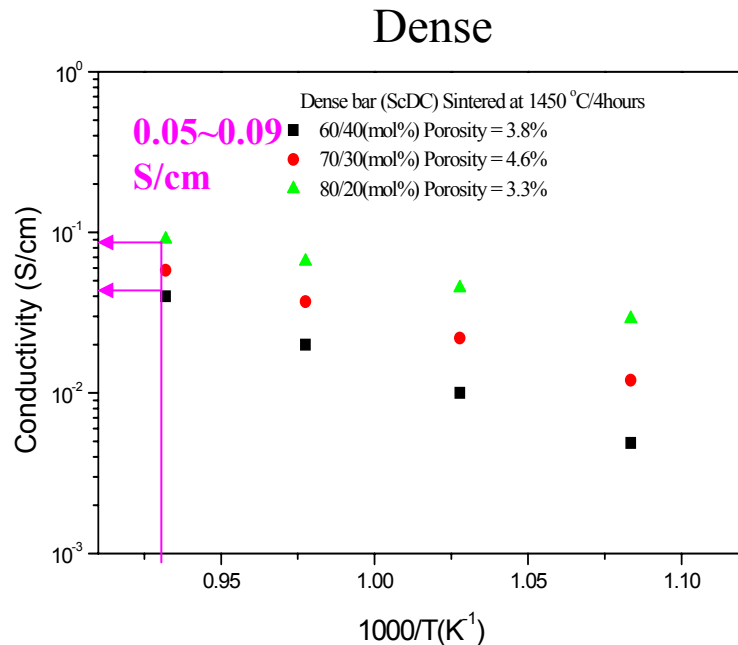
The greater the scandia (Sc₂O₃) content, the greater is the oxygen vacancy concentration. Other dopants will be tried soon.

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



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.