Chemical and Microstructural Effects in Electrode Polarization

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Outline

- A relative comparison of contributions of the various polarizations in anode-supported cells. Comparison of experimental results with a model.
- Concentration polarization in Anode-Supported Cells: Electrode thickness and microstructure effects.
- Effect of Morphology on Ion Transport through Porous Bodies and Activation Polarization.
- Cathode Activation Polarization: Charge Transfer Studies using Patterned Electrodes: LSM/YSZ and Pt/YSZ. Effect of oxygen partial pressure and temperature.
- Patterned Electrodes for the Study of Cathode Poisoning by chromium.
- Surface exchange coefficient measurements on porous MIEC samples.
- Summary.

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Chemical and Microstructural Effects

- Chemical
  - a) Material Composition
  - b) Defect Chemistry
  - c) Gas/Solid Interactions
  - d) Charge Transfer
  - e) Transport
- Microstructural
  - a) Porosity
  - b) Pore Size
  - c) Tortuosity
  - d) Thickness
  - e) Three-Phase Boundary
  - f) Specific Surface Area
  - g) Particle Size
  - h) Inter-Particle Neck Size

Approximate Values of the Various Polarizations η in Anode-Supported Cells

Various contributions at 800°C, at 1 A/cm^2, low fuel utilization
For a standard, medium performance anode-supported cell

η_{ohmic} ~150 mV

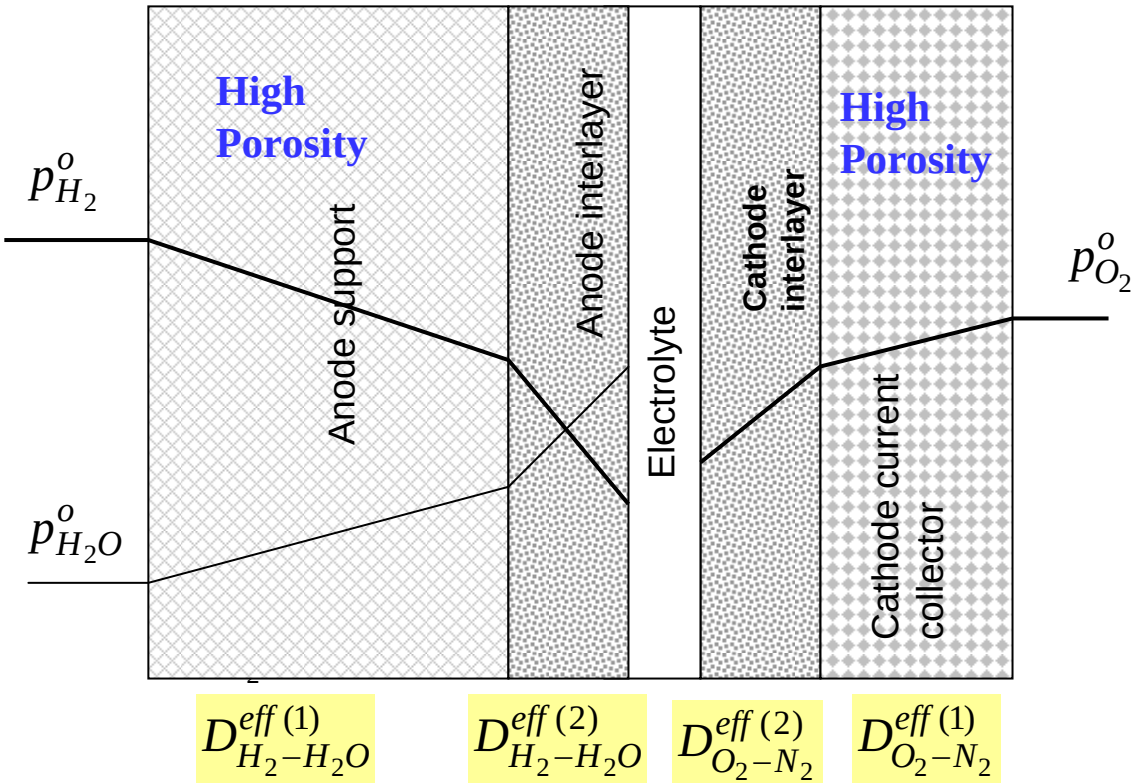
$\eta_{anode-concentration}$ ~125 mV

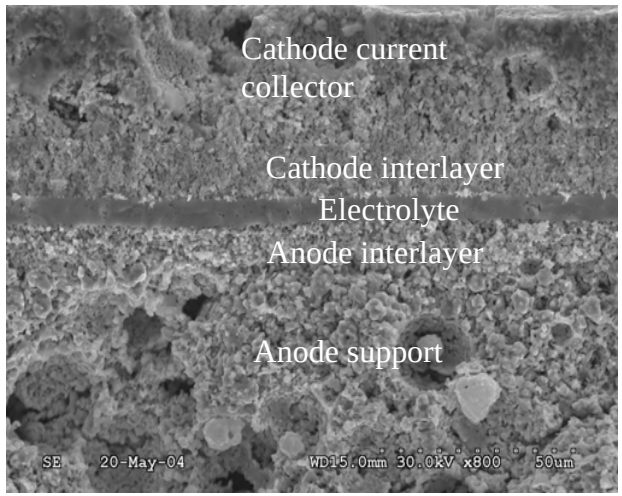
$\eta_{cathode-concentration}$ ~10 mV

$\eta_{activation}$ ~100 mV

The corresponding cell performance at ~0.7 V is ~0.7 W/cm^2

A Five Layer Anode-Supported Cell





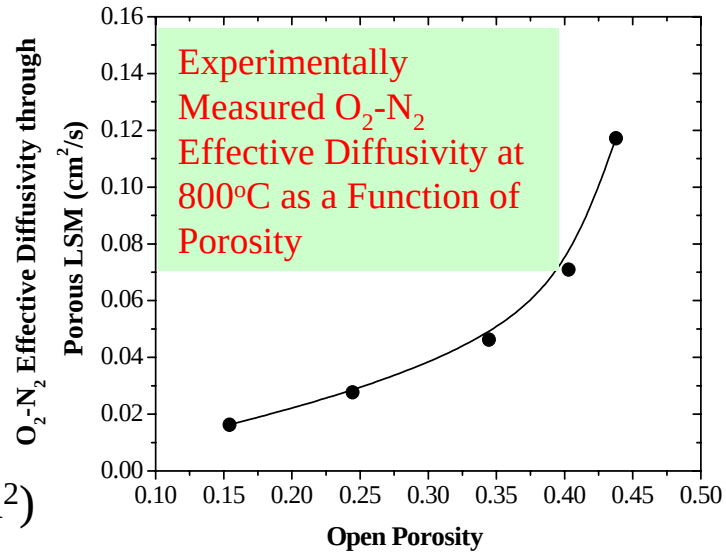
Cell performance almost identical in H_2 and H_2 + CO mixtures if pCO < pH_2

Parameters which dictate Concentration Polarization (typical values)

1) Electrode porosity (25 to 60%)
2) Electrode pore size (a few microns)
3) Electrode tortuosity (3 to 15 – high values include Knudsen diffusion)
4) Gas phase diffusivities (1 to 5 cm^2/s)
5) Electrode thickness (50 microns to 2 mm)

A Simple, Phenomenological Polarization Equation in Terms of Experimentally Measurable Parameters

$$V(i) = E_0 - iR_i - a - b\ln i + \frac{RT}{2F}\ln\left(\frac{p'_{H_2(i)}(i)\,p^o_{H_2O}}{p^o_{H_2}\,p'_{H_2O(i)}(i)}\right) + \frac{RT}{4F}\ln\left(\frac{p'_{O_2(i)}(i)}{p^o_{O_2}}\right)$$



E_0 = Nernst Voltage

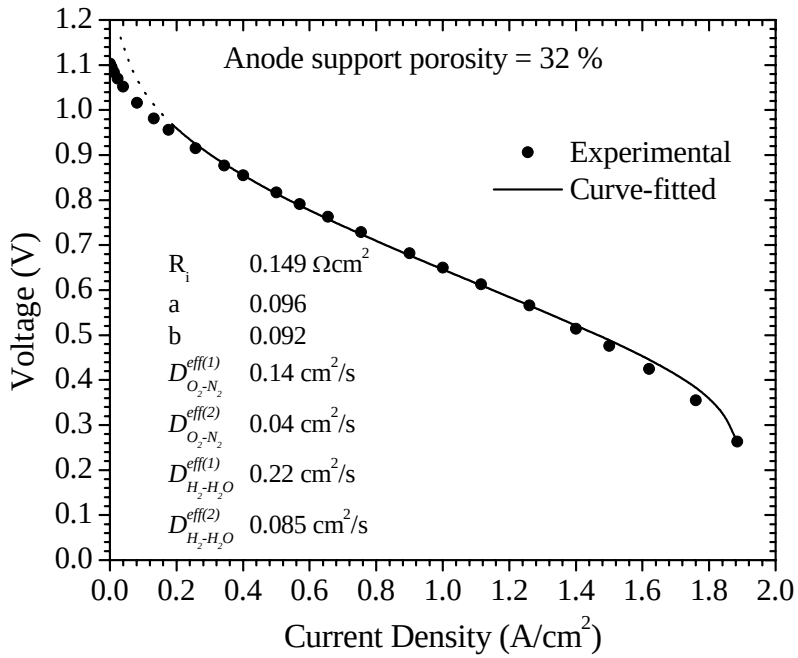
R_i = Ohmic Area Specific Resistance (Ωcm^2)

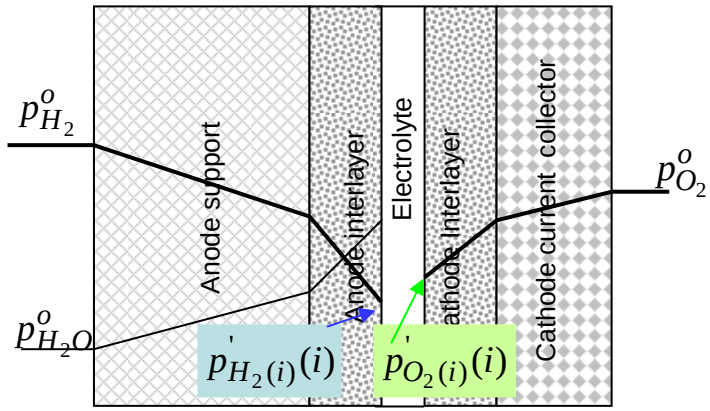
a, b = Tafel Coefficients

$p'_{H_2(i)}(i)$ = Partial pressure of hydrogen at anode/electrolyte interface. Depends on Measurable Effective Diffusivity through porous anode

$p'_{O_2(i)}(i)$ = Partial pressure of oxygen at cathode/electrolyte interface. Depends on Measurable Effective Diffusivity through porous cathode

Fitting the Model to Experimental Results





$D^{eff\,(1)}_{H_2-H_2O}$	$D^{eff\,(2)}_{H_2-H_2O}$	$D^{eff\,(2)}_{O_2-N_2}$	$D^{eff\,(1)}_{O_2-N_2}$	
0.22	**0.085**	**0.04**	**0.14**	**cm²/s**

activation

cathode concentration

$$V(i) = E_0 - iR_i - a - b\ln i + \frac{RT}{2F}\ln\left(\frac{p'_{H_2(i)}(i)\,p^o_{H_2O}}{p^o_{H_2}\,p'_{H_2O(i)}(i)}\right) + \frac{RT}{4F}\ln\left(\frac{p'_{O_2(i)}(i)}{p^o_{O_2}}\right)$$

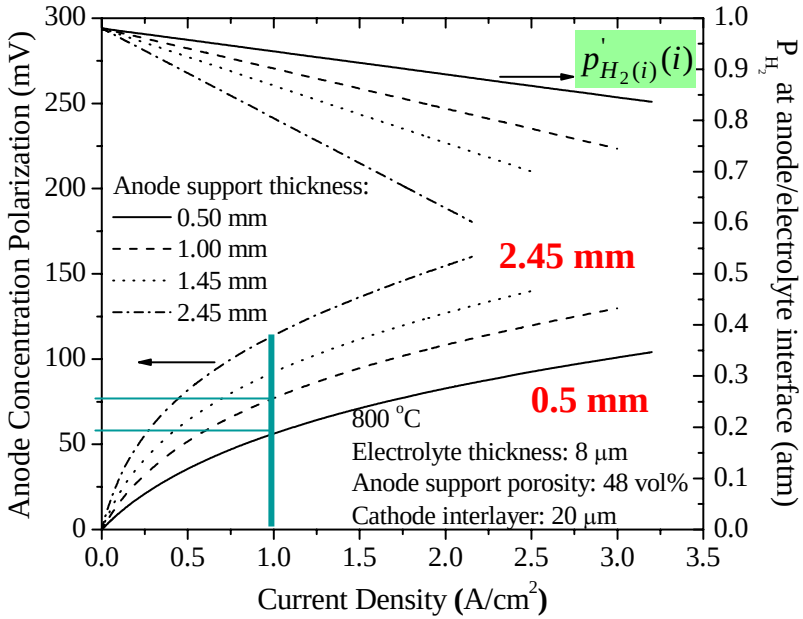
ohmic

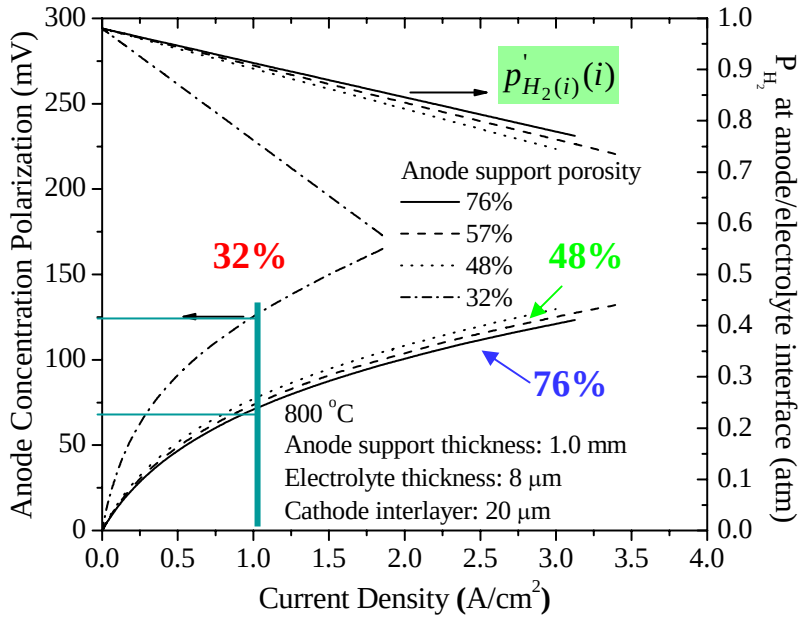
anode concentration

$p'_{H_{2(i)}}(i)$ and $p'_{H_2O(i)}(i)$ depend on $D^{eff\,(1)}_{H_2-H_2O}$ and $D^{eff\,(2)}_{H_2-H_2O}$ and thicknesses

$p'_{O_2(i)}(i)$ depends on $D^{eff\,(1)}_{O_2-N_2}$ and $D^{eff\,(2)}_{O_2-N_2}$ and thicknesses

Anode Concentration Polarization: Effect of Porosity and Thickness



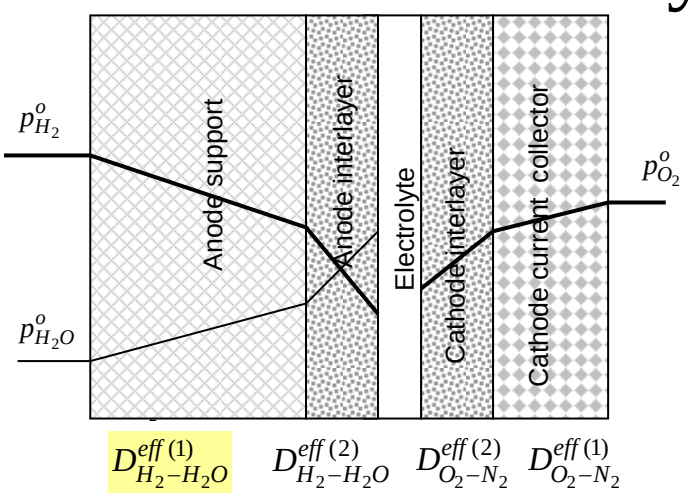


Anode Porosity **48%** Thickness Varied	Anode (0% Fuel Utl.) Concentration Polarization at 1 A/cm^2
0.5 mm	55 mV
1.0 mm	75 mV
1.45 mm	90 mV
2.45 mm	115 mV

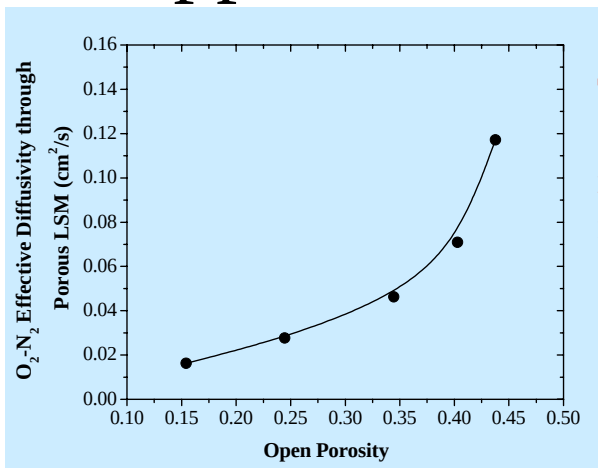
Anode Thickness **1 mm** Porosity Varied	Anode (0% Fuel Utl.) Concentration Polarization at 1 A/cm^2
32%	125 mV
48%	75 mV
57%	72 mV
76%	70 mV

Higher Polarization at Higher Fuel Utilization

Anode Concentration Polarization: Effective Diffusivity vs. Anode Support Porosity



Experimentally Measured O_2-N_2 Effective Diffusivity



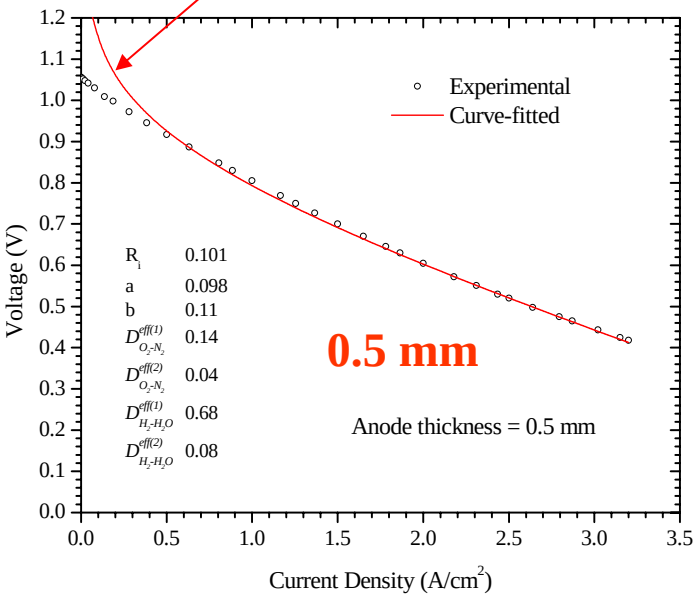
These are out-of-cell, independent measurements

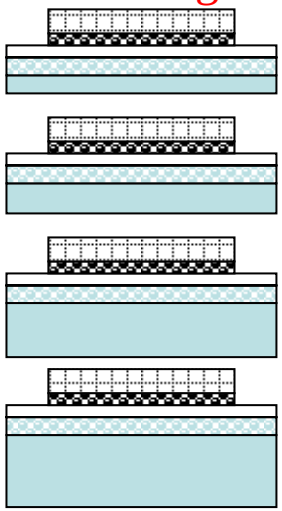
Diffusivities calculated by fitting to experimental data

Anode Support Porosity	$D^{eff\,(1)}_{O_2-N_2}$ cm^2/s	$D^{eff\,(2)}_{O_2-N_2}$ cm^2/s	$D^{eff\,(1)}_{H_2-H_2O}$ cm^2/s	$D^{eff\,(2)}_{H_2-H_2O}$ cm^2/s	Conc. Pola. At 1 A/cm² (1 mm)
32%	0.14	0.04	0.22	0.085	125 mV
48%	0.14	0.04	0.68	0.08	75 mV
57%	0.14	0.04	0.75	0.08	72 mV
76%	0.14	0.04	0.82	0.08	70 mV

Curve Fitting: Anode Support Thickness Varied

Deviation due to the assumption of Tafel equation over the whole range



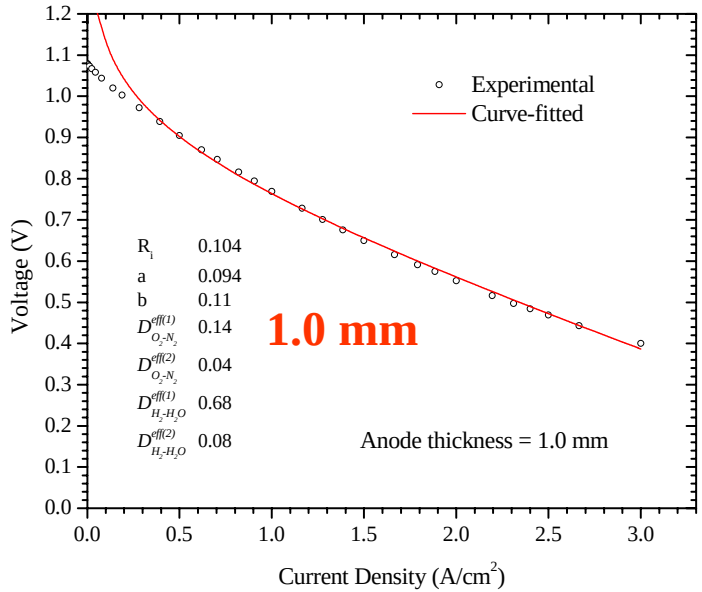


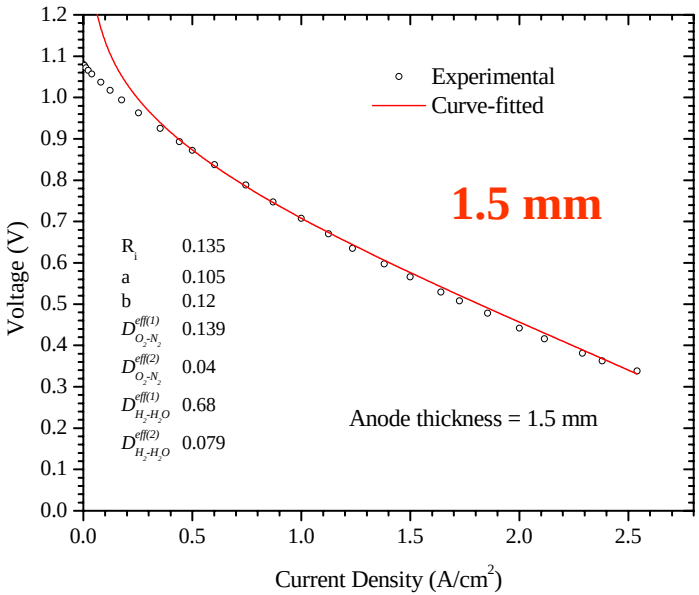
0.5 mm

1.0 mm

1.45 mm

2.45 mm





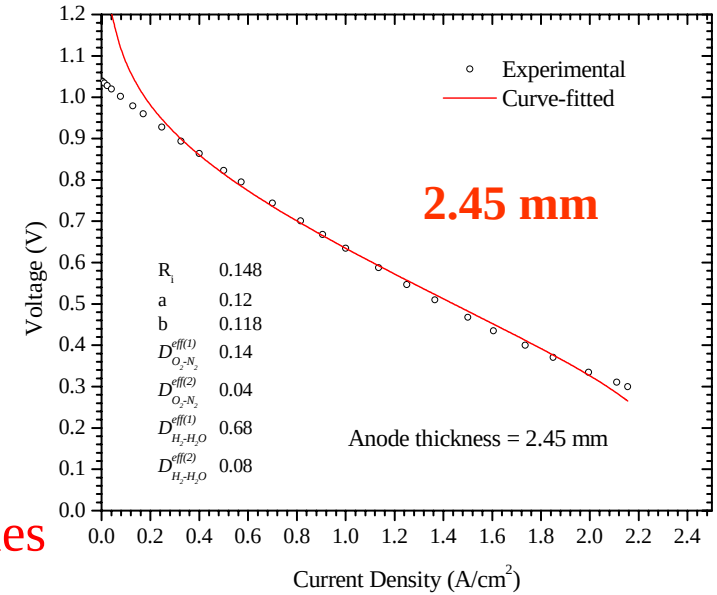
$D^{eff\,(1)}_{H_2-H_2O}$ = 0.68 cm²/s

$D^{eff\,(2)}_{H_2-H_2O}$ = 0.08 cm²/s

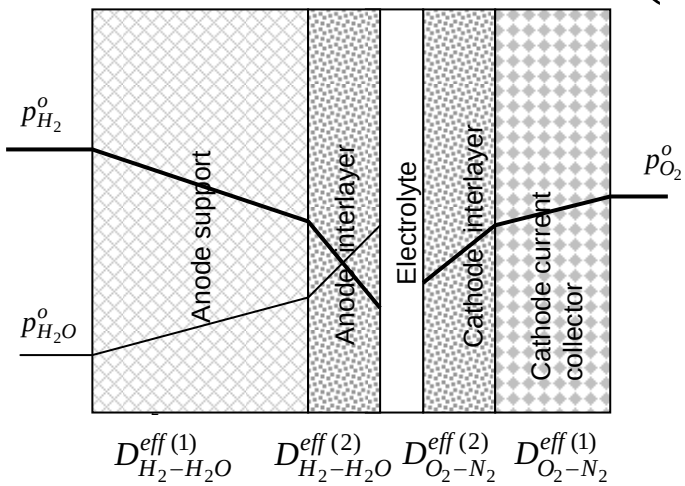
$D^{eff\,(1)}_{O_2-N_2}$ = 0.14 cm²/s

$D^{eff\,(2)}_{O_2-N_2}$ = 0.04 cm²/s

All data could be fitted with above effective diffusivities



Effective Diffusivities from Fitting to Experimental Cell Data: Anode Thickness Varied (Porosity ~48%)



Anode Support Thickness	$D^{eff\,(1)}_{O_2-N_2}$ cm²/s	$D^{eff\,(2)}_{O_2-N_2}$ cm²/s	$D^{eff\,(1)}_{H_2-H_2O}$ cm²/s	$D^{eff\,(2)}_{H_2-H_2O}$ cm²/s	Conc. Pola. At 1 A/cm²
0.5 mm	0.14	0.04	0.68	0.08	55 mV
1.0 mm	0.14	0.04	0.68	0.08	75 mV
1.5 mm	0.14	0.04	0.68	0.08	90 mV
2.45 mm	0.14	0.04	0.68	0.08	115 mV

Anode Support Thickness Varied: Conclusions

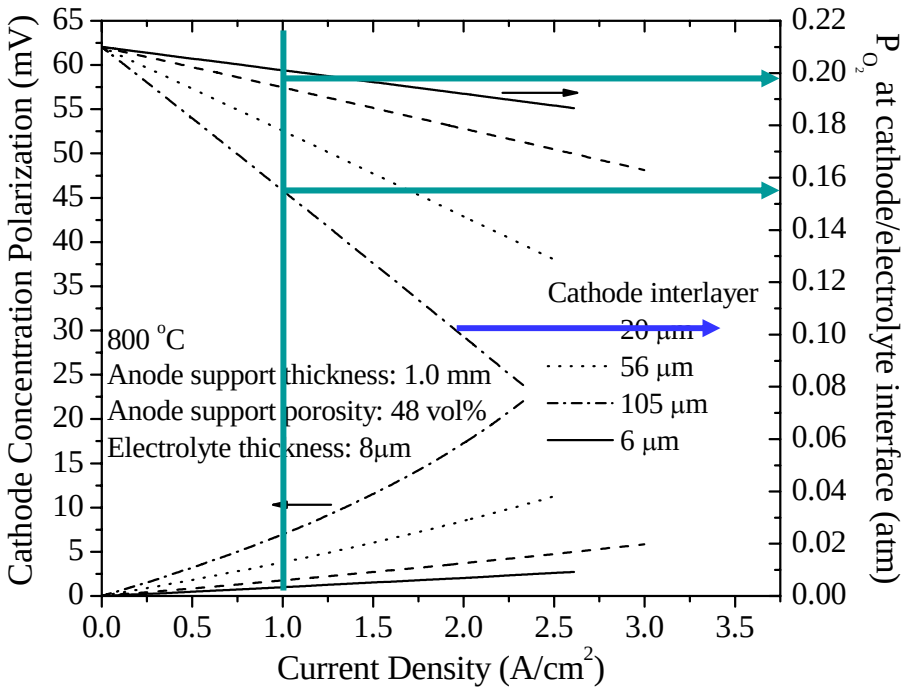
1) The thicker the anode support, the lower the performance.
2) All of the voltage vs. current density plots could be fitted to one set of effective diffusivities.
3) The main contribution is from anode concentration polarization – but not entirely.
4) Other contributions from: (a) Ohmic (b) Activation polarization.

The thicker the anode support, the lower the interface hydrogen pressure at a given current density, the poorer the electrocatalysis.

Anode Support Thickness	Ohmic (Ωcm^2)	Tafel Parameter 'a'	Tafel Parameter 'b'	Exchange Current Density (mA/cm^2)
0.5 mm	0.101	0.098	0.11	~410
1.0 mm	0.104	0.094	0.11	~425
1.5 mm	0.135	0.105	0.12	~417
2.45 mm	0.148	0.12	0.118	**~362**

The above for low fuel utilization. At higher fuel utilization, both concentration and activation polarization are higher.

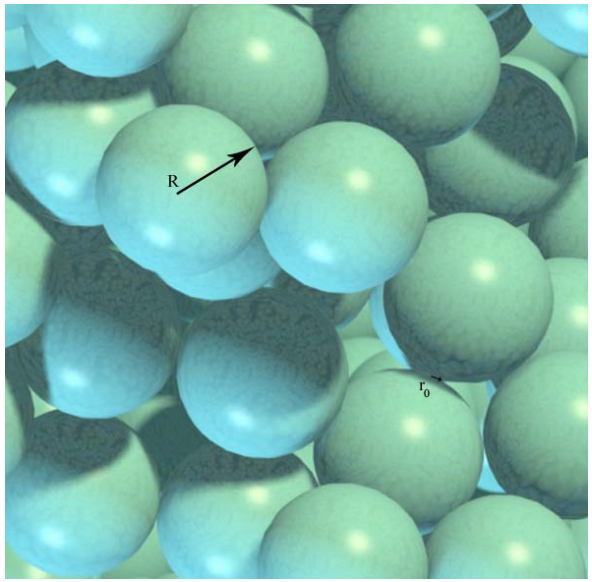
Cathode Concentration Polarization: Effect of Cathode Interlayer Thickness



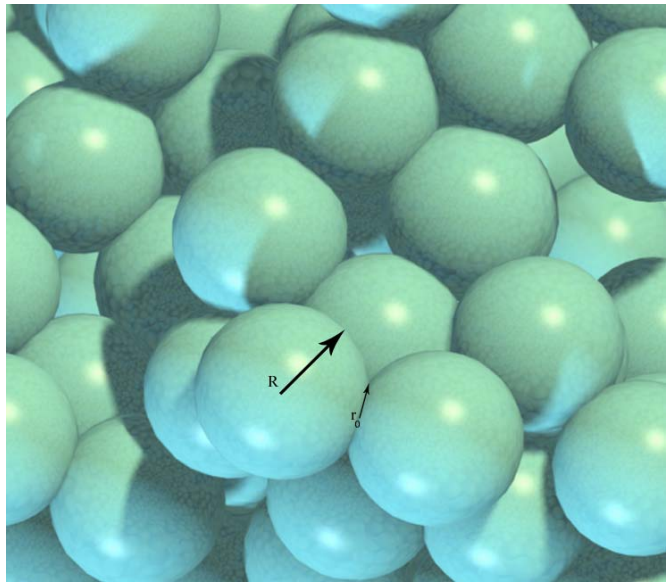
At high cathode interlayer thicknesses and/or high current densities, oxygen partial pressure at the cathode/electrolyte interface can be quite low -Implications concerning cathodic activation polarization

Estimated maximum cathode concentration polarization at 1 A/cm^2 is <10 mV

Transport Properties of Porous Bodies: Implications Concerning Electrode Activation Polarization

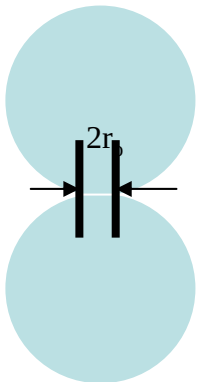


Narrow Necks



Wide Necks

Morphology



Relative Neck Size

$$\alpha = r_o / R$$

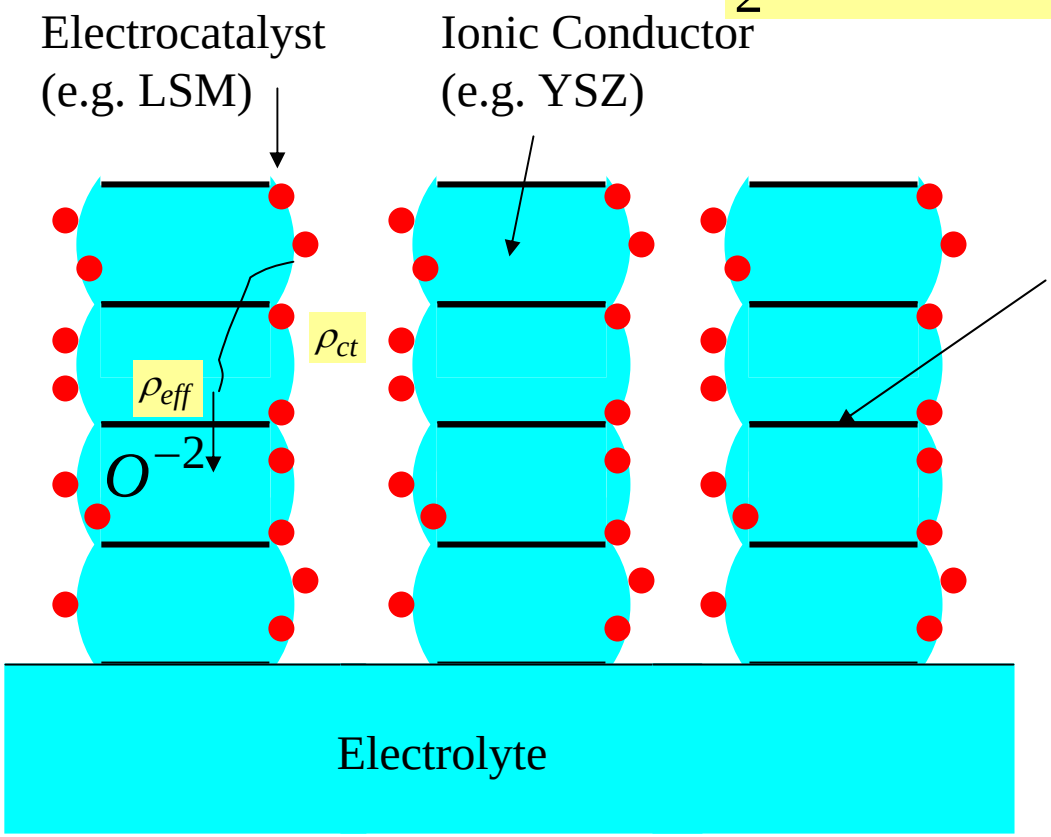
Low Conductivity
High Resistivity

High Conductivity
Low Resistivity

A Composite Cathode: Electrode Morphology

Cathodic Reaction

$$\frac{1}{2}O_2 + 2e' \rightarrow O^{-2}$$



Effective Activation Polarization Resistance of Composite Electrodes

$$R_p \approx \sqrt{\frac{\rho_{eff}\,\rho_{ct}\,d}{(1-V_v)\ell_{TPB}}}$$

ρ_{eff} Effective Resistivity

ρ_{ct} Charge Transfer Resistivity

Narrow Necks
High ρ_{eff}

Wide Necks
Low ρ_{eff}

LSM phase is contiguous –

appears noncontiguous on a two-dimensional cut

The same effect of morphology in the anode.

The same effect of morphology in

Single phase MIEC cathodes (LSC, LSF, LSCF)

Effective Resistivity of Porous Bodies: No Space Charge Effect Included

$$\rho_{eff} \approx \frac{\rho_g}{2\sqrt{1-\alpha^2}} \ln\left\{\frac{1+\sqrt{1-\alpha^2}}{1-\sqrt{1-\alpha^2}}\right\} + \frac{\rho_{gb}\delta_{gb}}{2R\alpha^2\sqrt{1-\alpha^2}}$$

ρ_g = Grain Resistivity

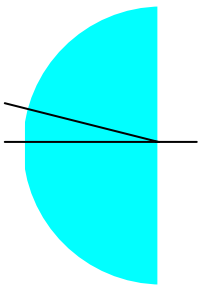
ρ_{gb} = Grain Boundary Resistivity

δ_{gb} = Grain Boundary Thickness

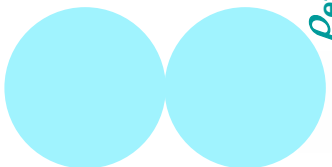
α = Neck radius/Particle radius

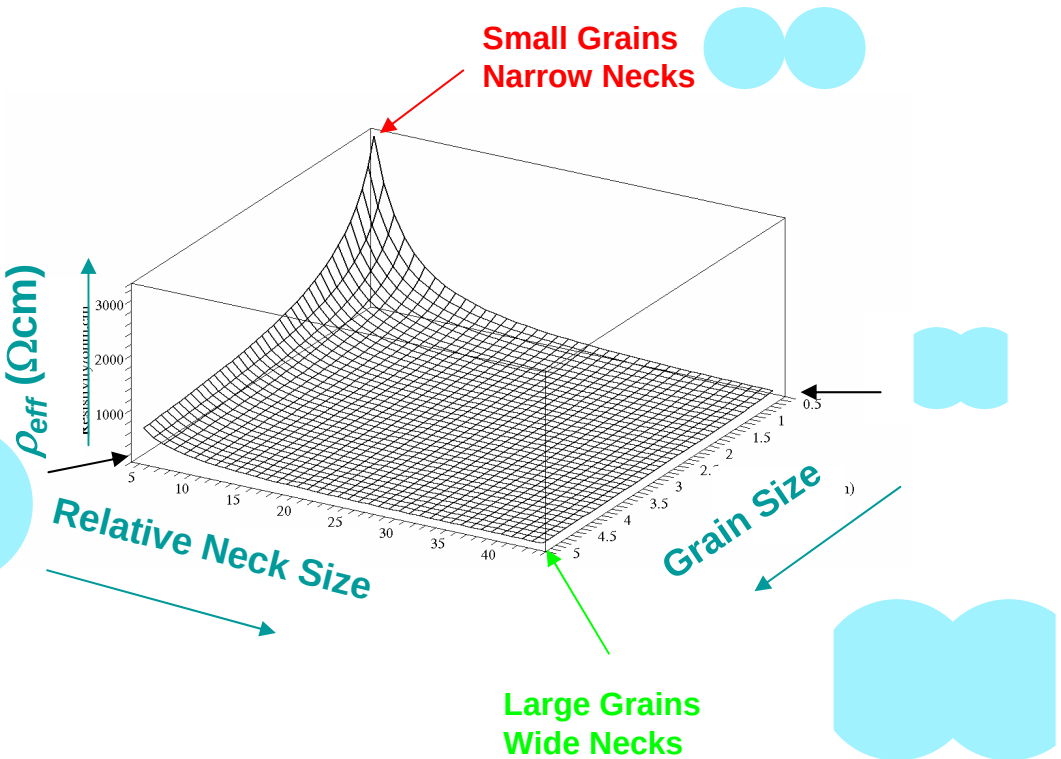
Note that as $\alpha \to 0$, both terms become singular

$$\rho_{eff} \approx \rho_g \ln\left\{\frac{2}{\alpha}\right\} + \frac{\rho_{gb}\delta_{gb}}{2R\alpha^2}$$



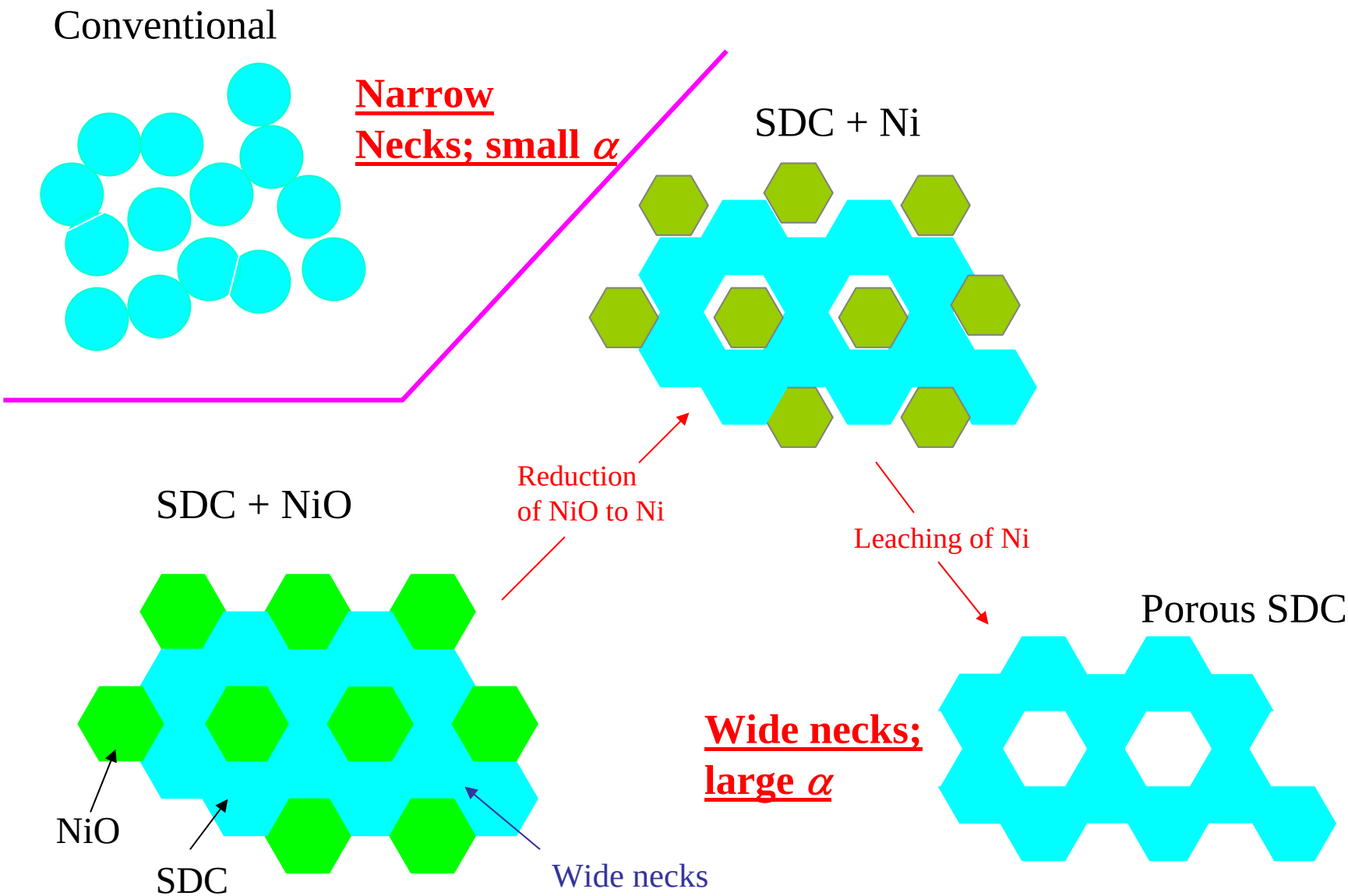
Angle



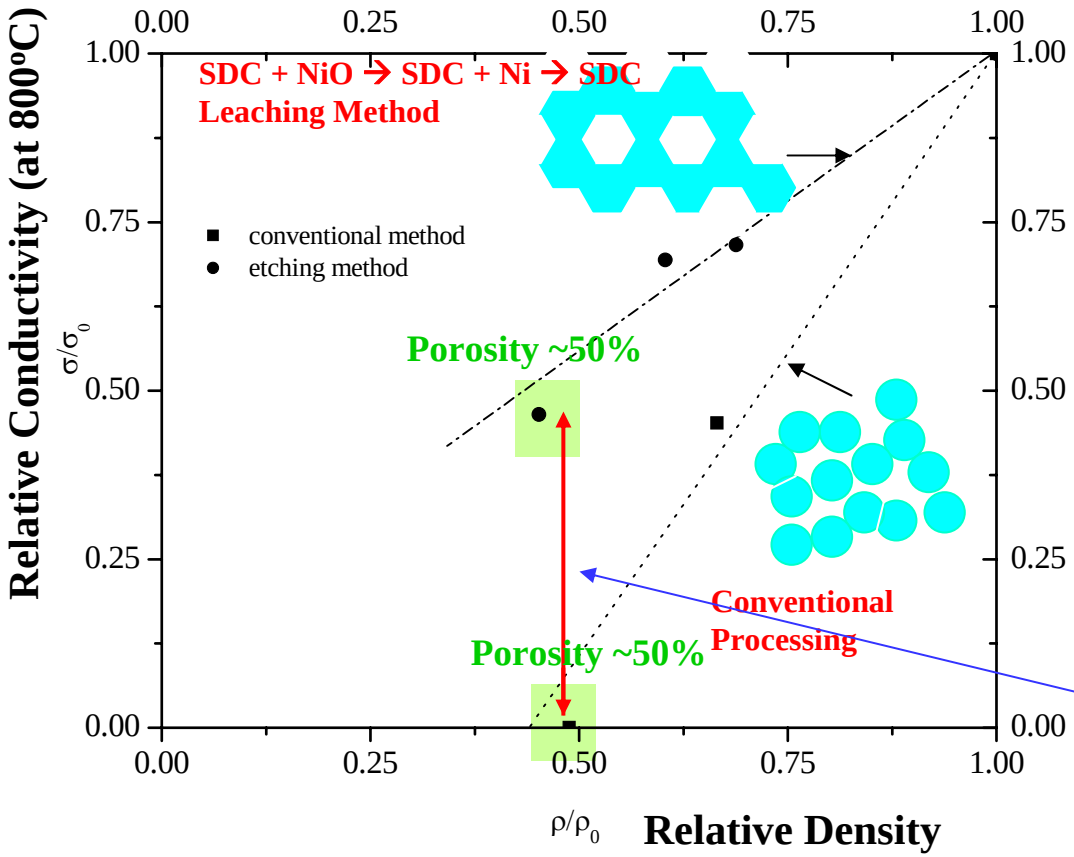


Implications: Narrow neck size has a profoundly adverse effect on conduction – and on electrocatalytic activity of porous electrodes.

Fabrication of Porous Sm_2O_3-doped CeO_2 (SDC) or Sc_2O_3-doped CeO_2 (ScDC): Fabrication of Electrode Structures with Wide Necks



Conductivity of Porous Bodies: Effect of Neck Radius: Experimental Results



$$\frac{\sigma(\text{wide necks})}{\sigma(\text{narrow necks})} \approx 76$$

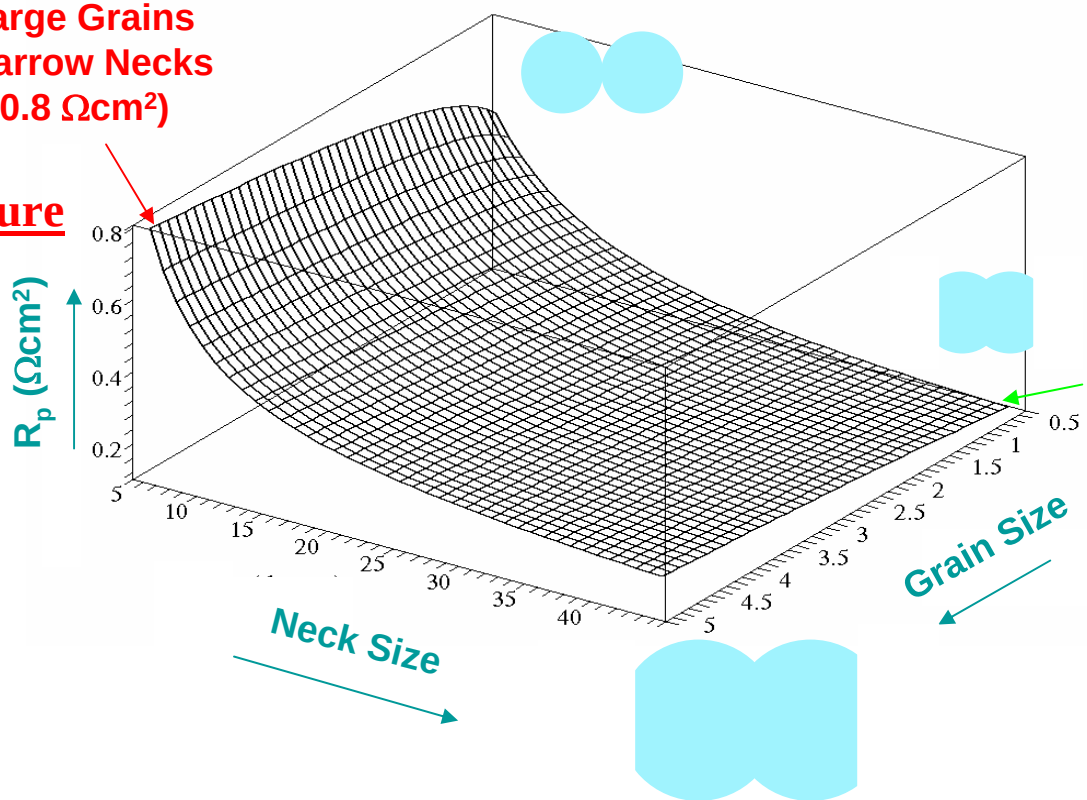
(at ~50% porosity)

Calculated Activation Polarization Resistance

Large Grains
Narrow Necks
(~0.8 Ωcm²)

Undesired Microstructure

$$R_p \approx \sqrt{\frac{\rho_{eff}\, d\rho_{ct}}{(1-V_v)\ell_{TPB}}}$$

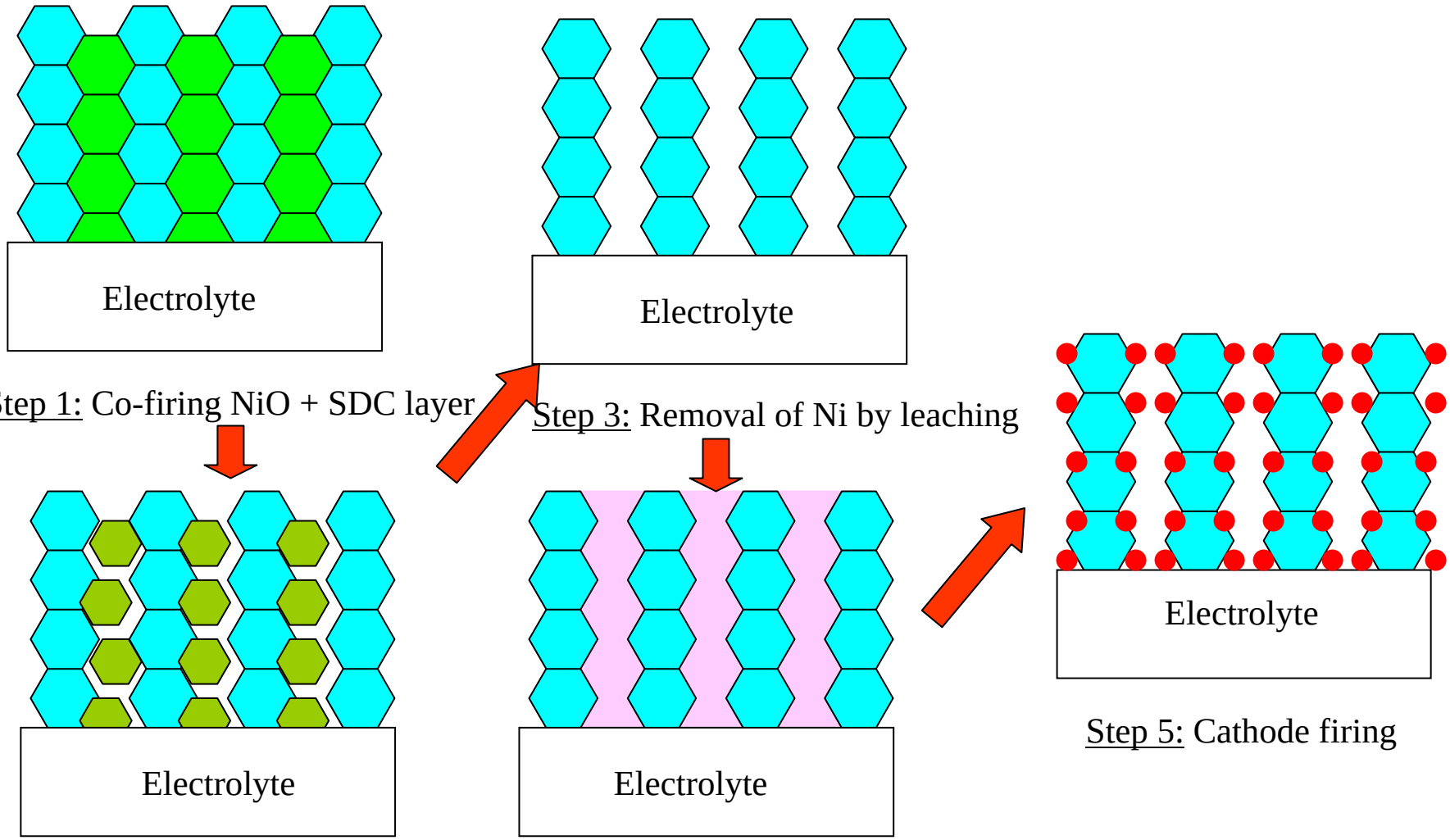


Small Grains
Wide Necks
(~0.1 Ωcm²)

Preferred Microstructure

Conclusion: Electrode particles should be fine with wide inter-particle necks.

Cathodes with Wide Inter-particle Necks
Cathode Preparation by Reduction and Infiltration



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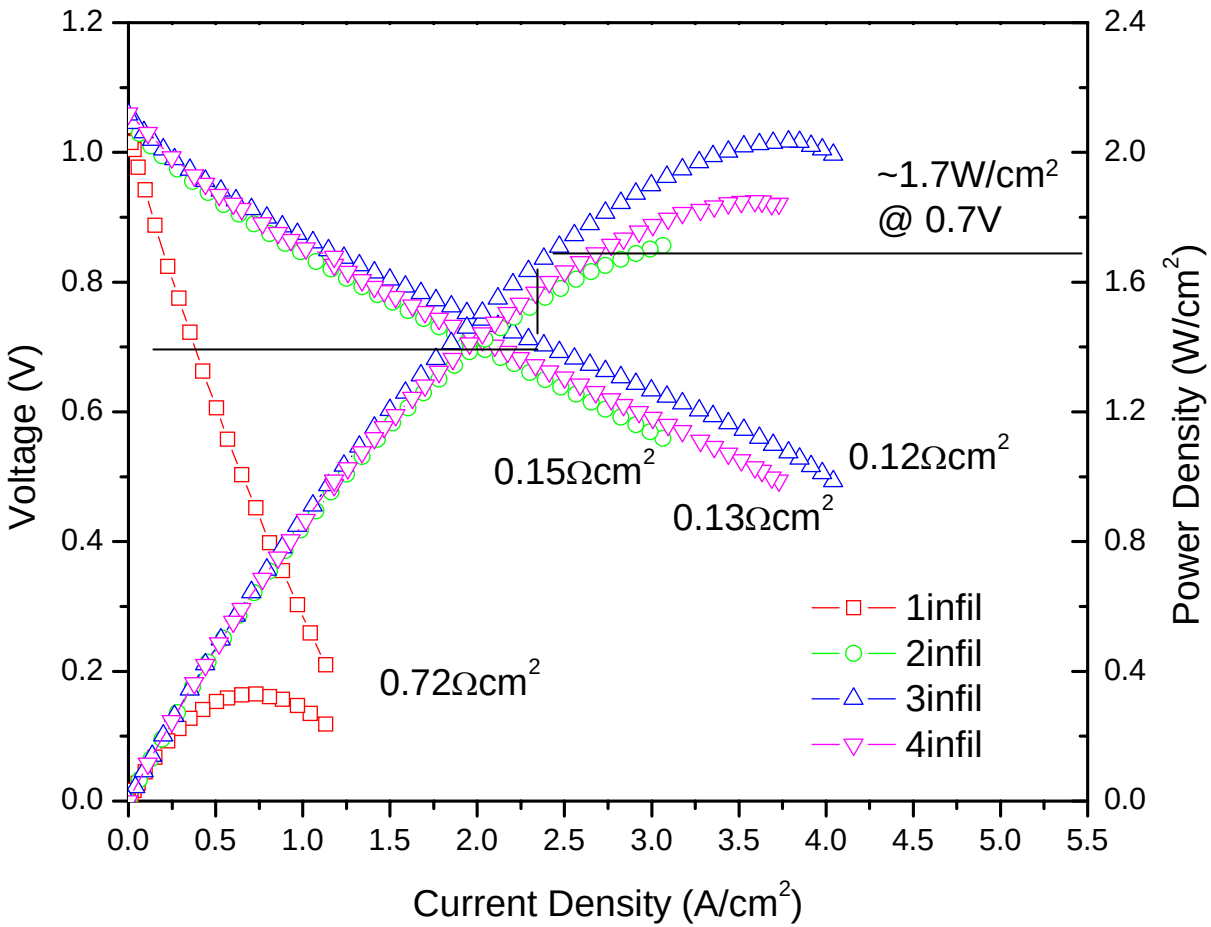
Some Results on Cells with LSC + YSZ Cathodes Made by Infiltration



H_2-Air, 800°C, low fuel utilization: 2 cm^2 active area

Rest of the Parameters Standard (not necessarily optimized)

Anode Thickness ~1 mm

Chemical Effects in Activation Polarization

Composite (Electrocatalyst, e.g. LSM + Ionic Conductor, e.g. YSZ) Cathodes

- Type of Electrocatalyst (material, composition).
- Electrolyte (e.g. YSZ. Ceria).
- Effect of atmosphere (e.g. oxygen partial pressure).
- Temperature

$$R_p \approx \sqrt{\frac{\rho_{eff} d \rho_{ct}}{(1-V_v)\ell_{TPB}}}$$

ℓ_{TPB} Three Phase Boundary Length (cm^{-1})

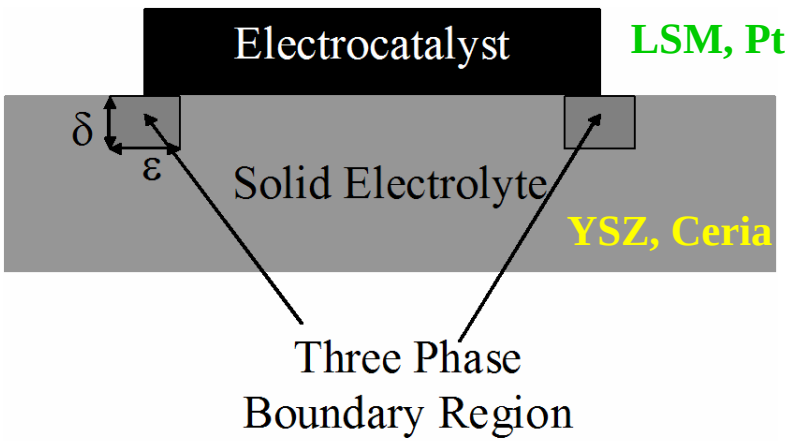
Charge Transfer Resistance

$$R_{ct} = \frac{\rho_{ct}^{'}\delta}{\varepsilon \ell_{TPB}} = \frac{\rho_{ct}}{\ell_{TPB}}$$

Charge Transfer Resistivity

$$\rho_{ct} = \frac{\rho_{ct}^{'}\delta}{\varepsilon}$$

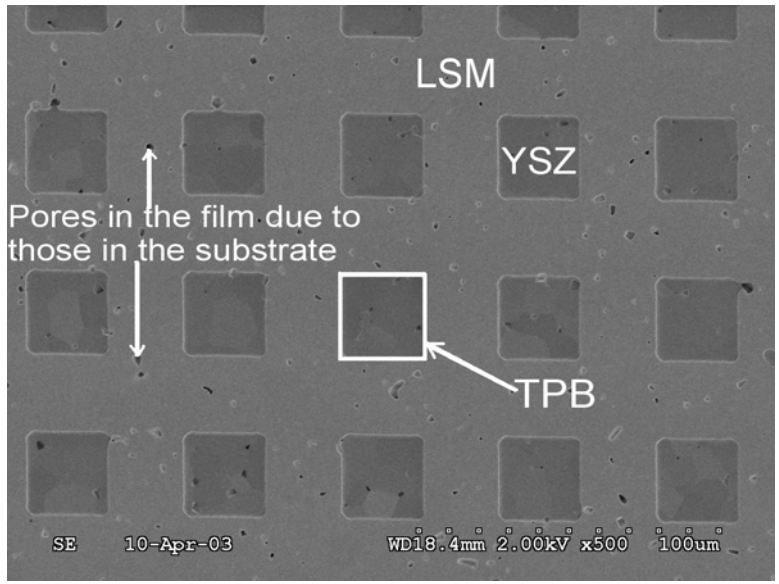
ρ_{ct} Depends on
1) Materials
2) Atmosphere
3) Temperature



Patterned Electrodes for the Measurement of Charge Transfer Resistivity

ρ_{ct}

- Use of photomicrolithography for the deposition of patterned electrodes of known TPB length.
- Patterned electrodes for the measurement of charge transfer resistivity of LSM and Pt on YSZ.
- Effect of oxygen partial pressure.
- Effect of temperature.



1) **Deposit patterned electrodes on an electrolyte disc.**
2) **Heat to the desired temperature.**
3) **Expose to the desired oxygen partial pressure.**
4) **Measure impedance spectra under zero bias.**

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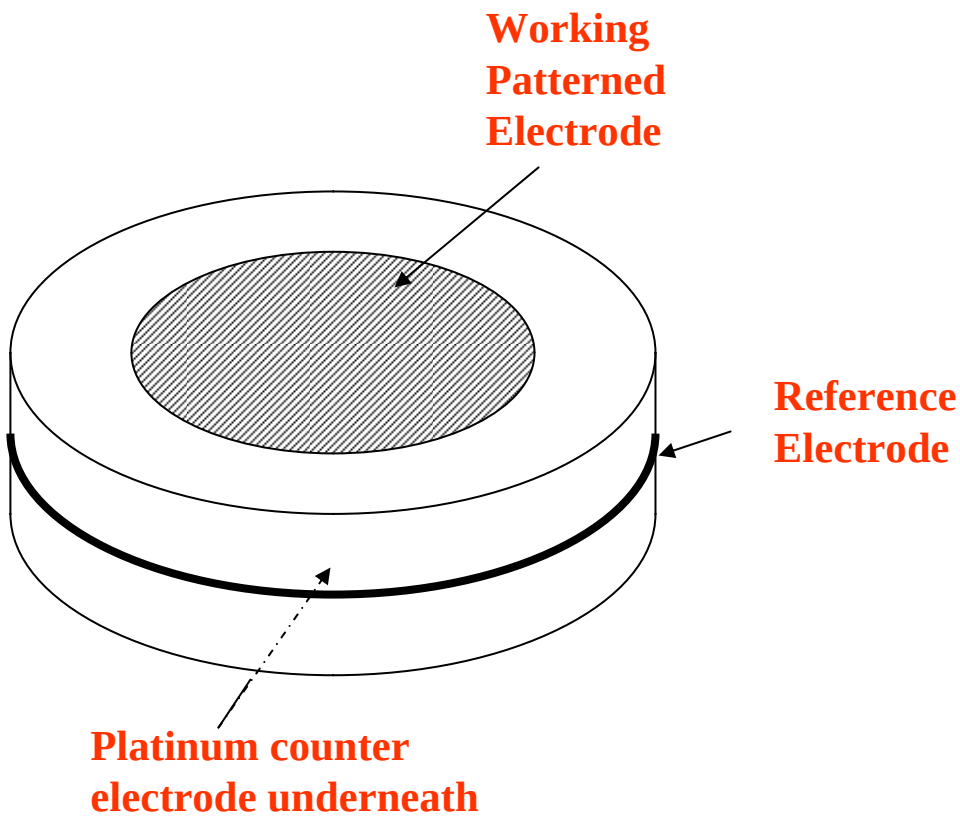
Testing Geometry



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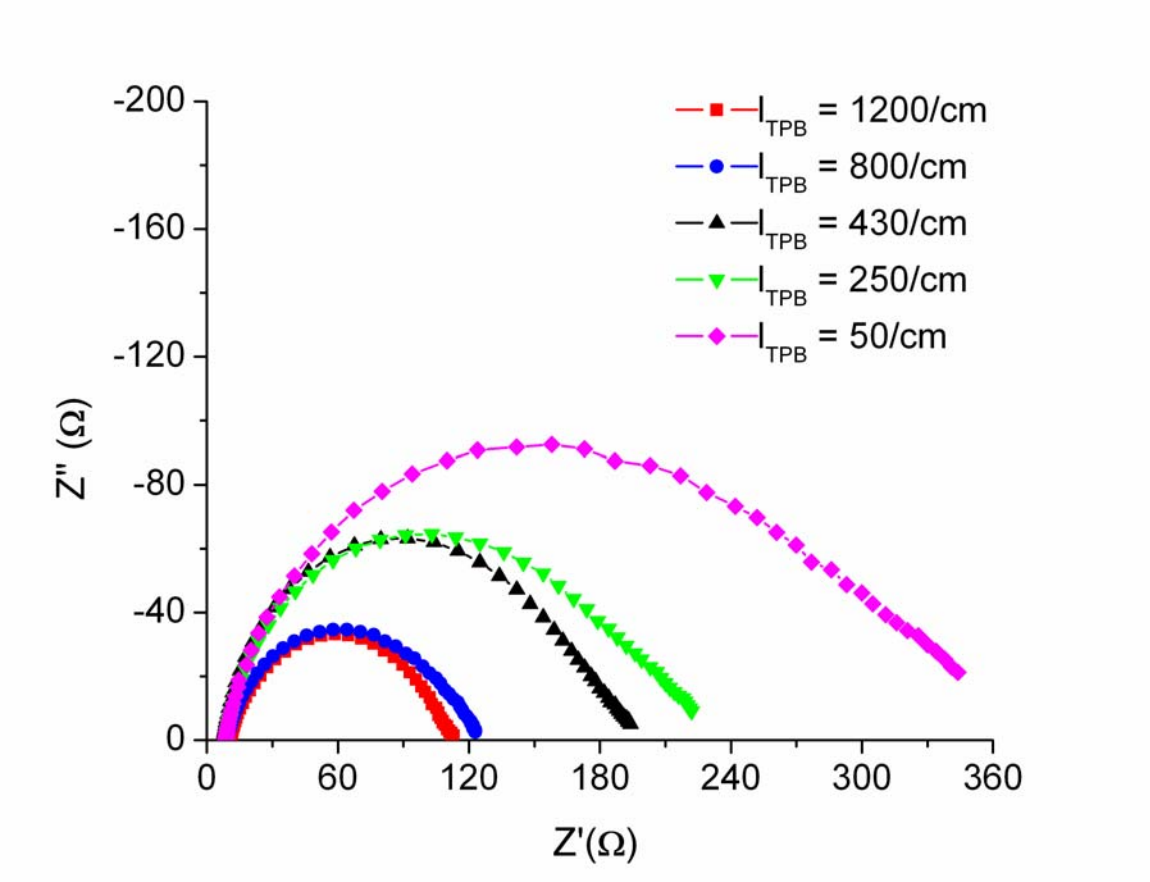
Impedance Spectra at 800°C in Air for LSM/YSZ for Several TPB Length



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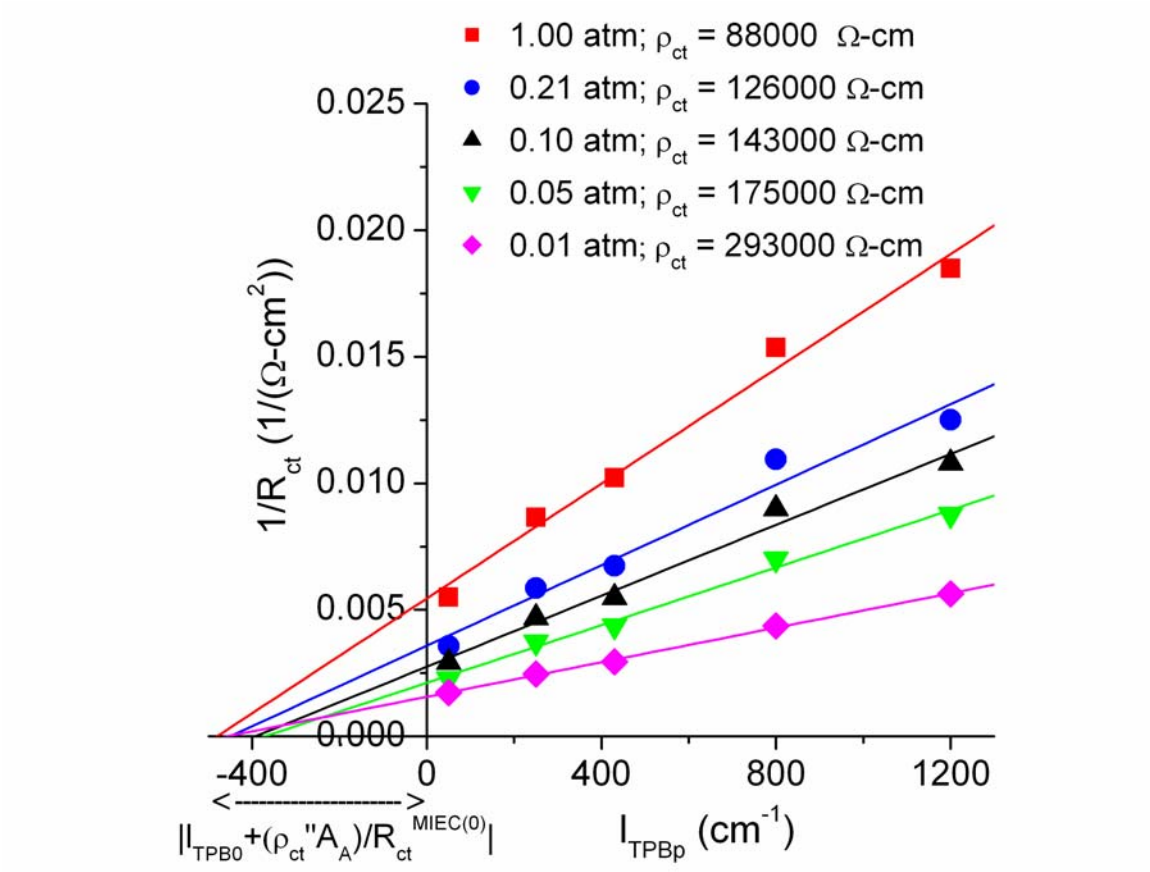
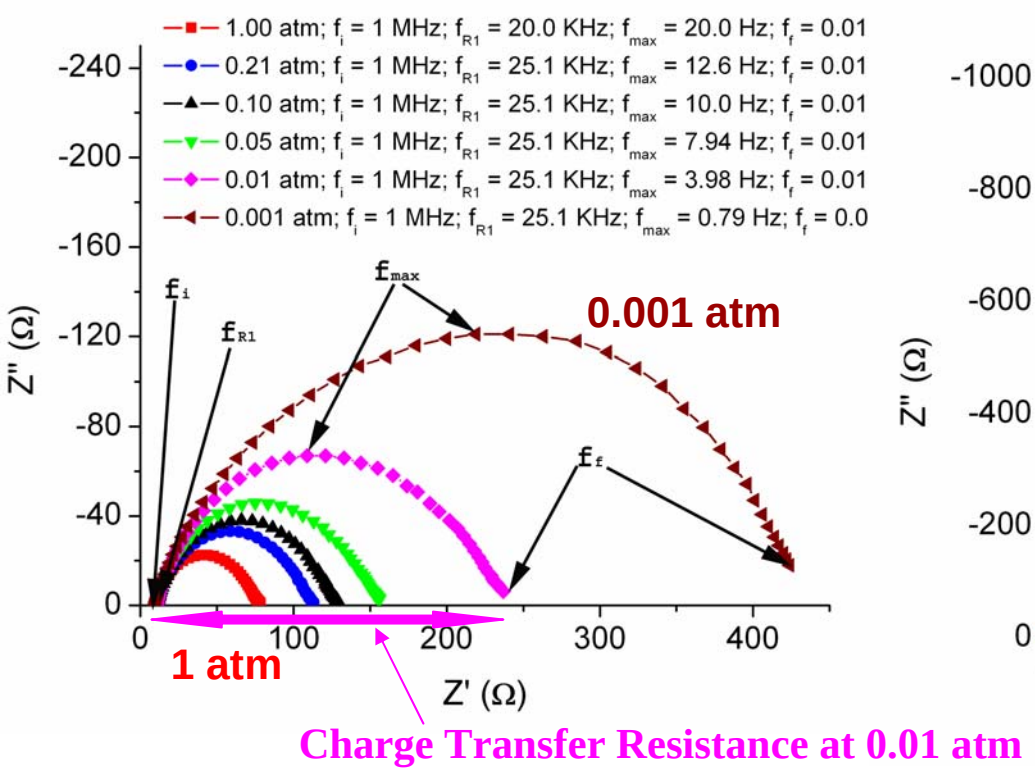
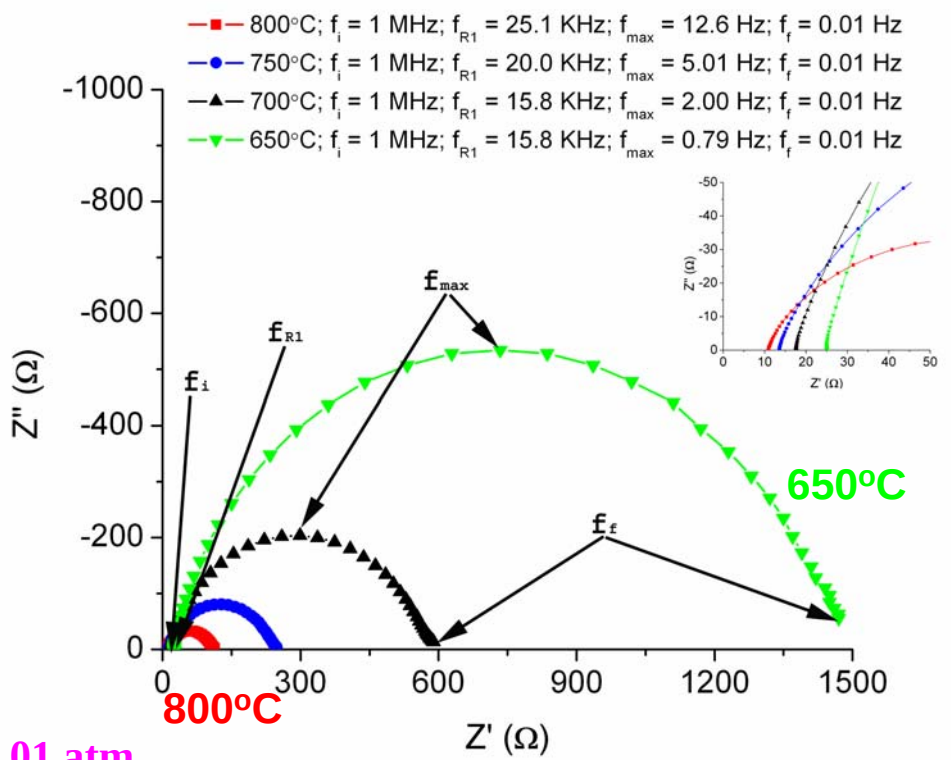
$1/R_{ct}$ vs. l_{TPB}



$1/R_{ct}$ vs. l_{TPB} is linear; thus, most of the charge transfer occurs at TPB. Nonzero intercept mainly due to unintended TPB due to pores in the film.

Effect of Oxygen Partial Pressure and Temperature on the Polarization Resistance of LSM on YSZ



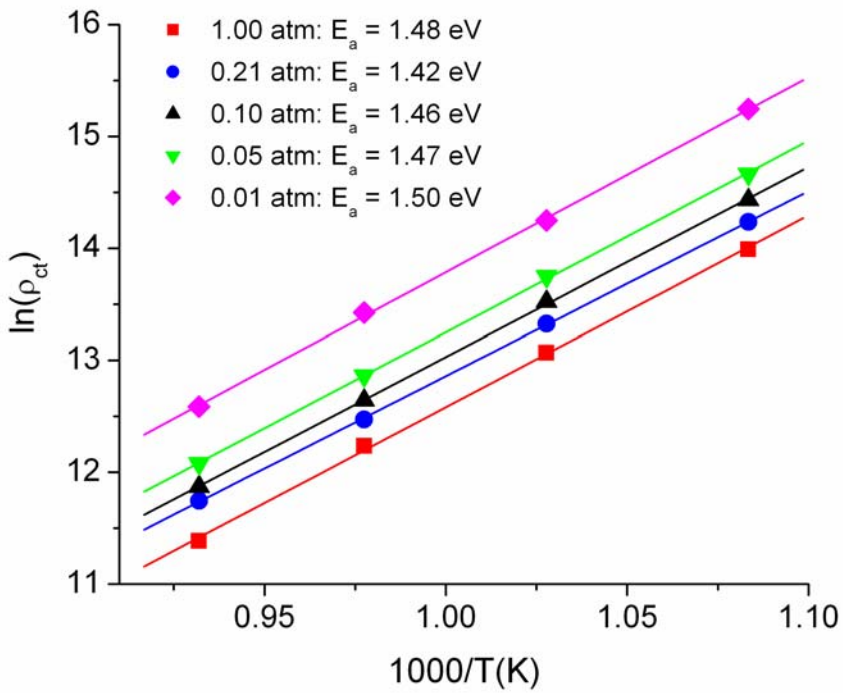


The higher the oxygen partial pressure, the lower the polarization resistance

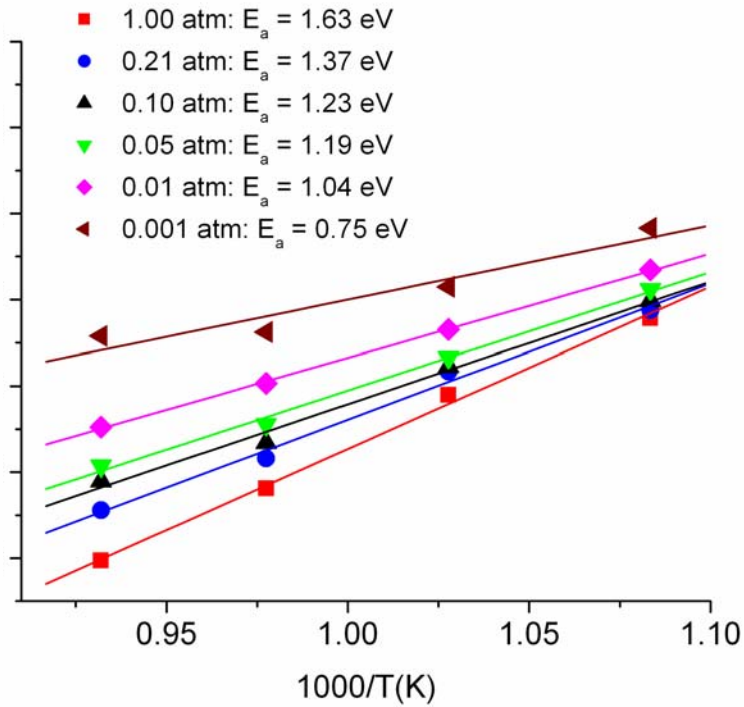
The higher the temperature, the lower the polarization resistance

Arrhenius Plots of ρ_{ct} for LSM/YSZ and Pt/YSZ at Various pO_2

LSM/YSZ



Pt/YSZ



Activation Energy independent of pO_2: Weak adsorption

Activation Energy decreases with decreasing pO_2: Stronger adsorption

Charge Transfer Resistivity, ρ_{ct}, of LSM and Pt on YSZ as a Function of pO_2 and Temperature

$$\frac{\rho_{ct}(\text{LSM/YSZ})}{\rho_{ct}(\text{Pt/YSZ})} \approx 24$$

At 800°C

$$\frac{\rho_{ct}(\text{LSM/YSZ})}{\rho_{ct}(\text{Pt/YSZ})} \approx 29$$

At 650°C

Conclusion:

1) Pt is 25 to 30 times better than LSM
2) Strong pO_2 dependence for both
3) Strong temperature dependence for both

LSM/YSZ

Temp \ p_{O2}	1 atm	**0.21 atm**	0.1 atm	0.05 atm	0.01 atm
800°C	88000	**126000**	143000	176000	293000
750°C	206000	**261000**	310000	386000	676000
700°C	474000	**613000**	746000	935000	1540000
650°C	1190000	**1520000**	1850000	2330000	4170000

Pt/YSZ

Temp \ p_{O2}	1 atm	**0.21 atm**	0.1 atm	0.05 atm	0.01 atm	0.001 atm
800°C	2900	**5200**	7300	8700	13700	39200
750°C	6700	**9500**	11400	14100	22700	41100
700°C	19900	**26100**	27600	30600	42400	69400
650°C	48200	**52900**	59000	67300	84400	137500

Calculation of The Polarization Resistance of LSM/YSZ Composite Cathodes in air at 800°C

$$R_p \approx \sqrt{\frac{\rho_{eff}\, d\rho_{ct}}{(1-V_v)\ell_{TPB}}} \qquad R_p \approx \sqrt{\frac{\rho_{eff}\, dR_{ct}}{(1-V_v)}} \qquad \text{where} \qquad R_{ct} = \frac{\rho_{ct}}{\ell_{TPB}}$$

Effective Exchange Current Density $i_o = \dfrac{RT}{4FR_p}$

d ~ 1 μm

V_v ~0.25

ℓ_{TPB} ~10,000 cm^{-1}

ρ_{eff} ~ 30 Ωcm

ρ_{ct} ~126,000 Ωcm

R_{ct} ~12.6 Ωcm^2

A decrease by a factor of 40

R_p ~0.224 Ωcm^2

i_o ~103 mA/cm^2

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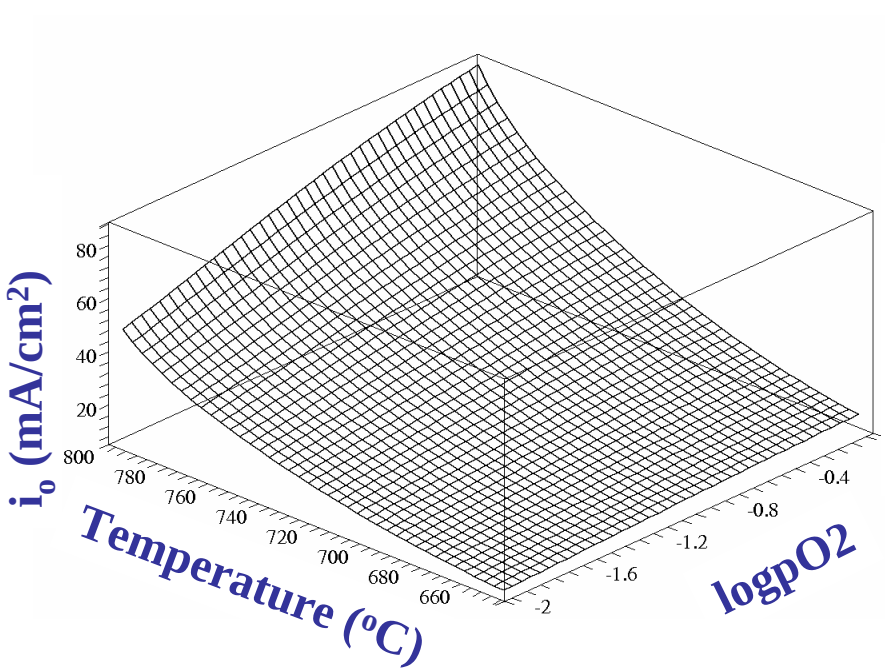
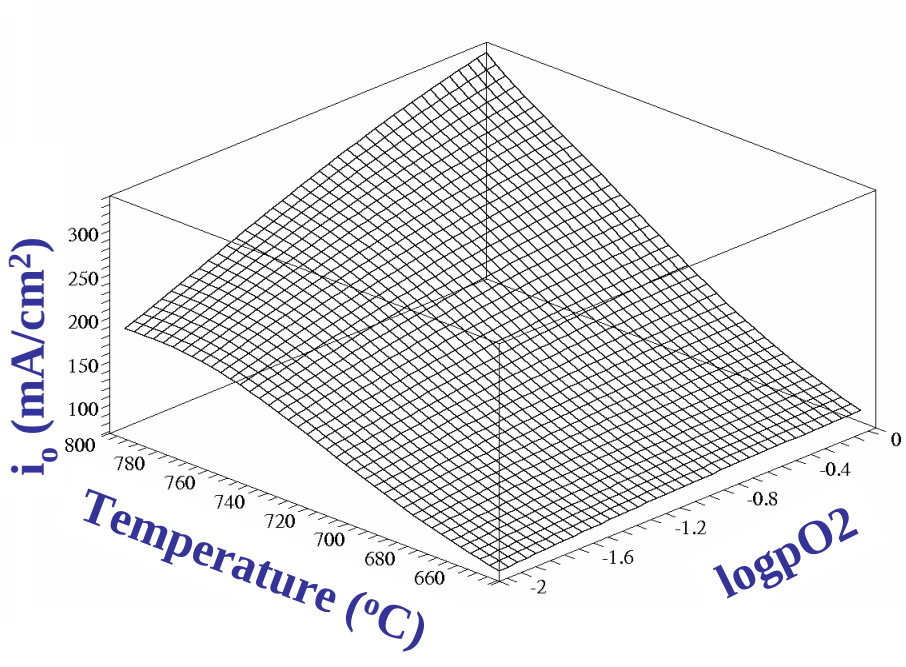
Calculated Effective Exchange Current Densities for LSM/YSZ and Pt/YSZ Composite Cathodes as Function of Temperature and Oxygen Partial Pressure

LSM/YSZ



Pt/YSZ

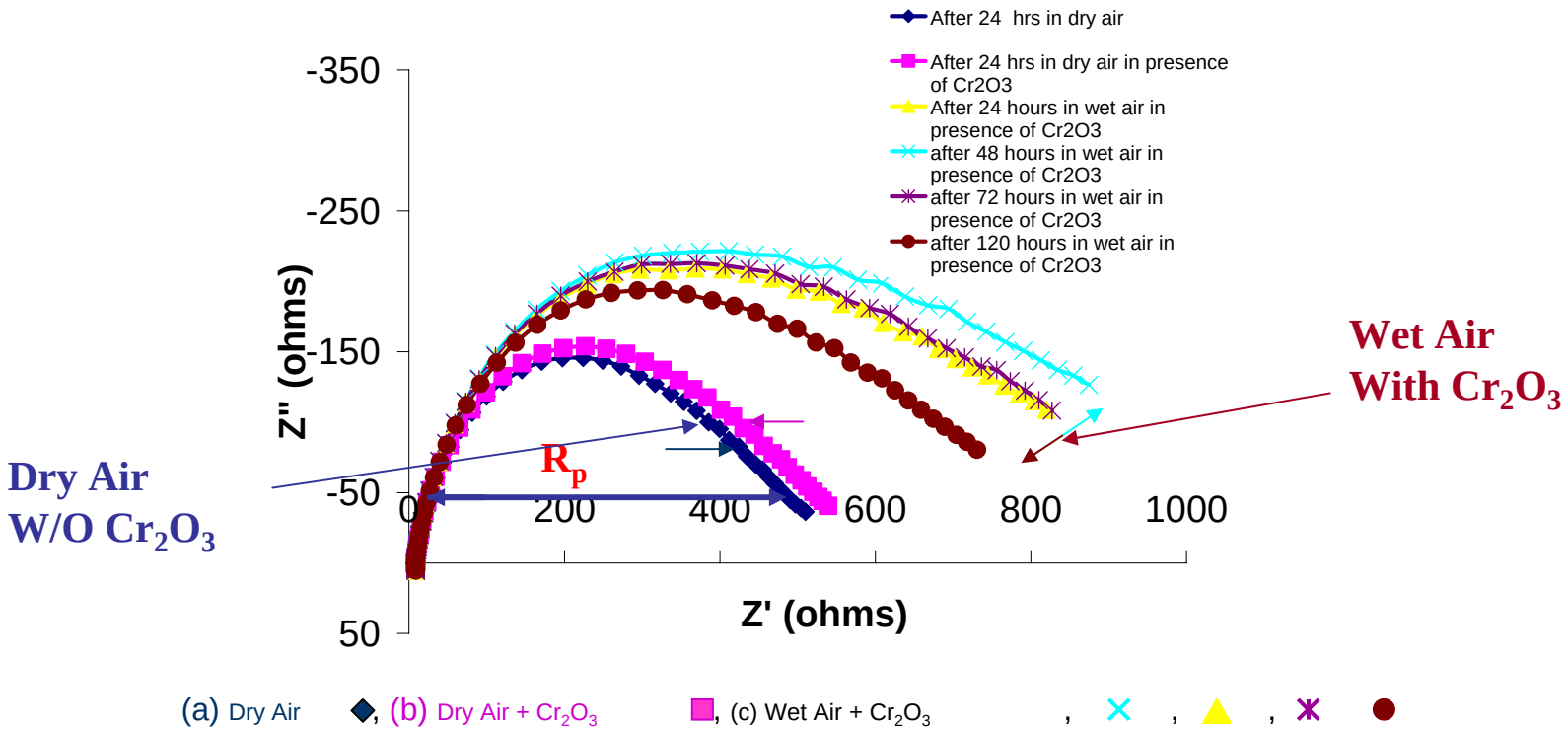


d = 2 microns

$V_v = 0.25$

$l_{TPB} = 10{,}000\ cm^{-1}$

Patterned LSM Electrodes for the Investigation of Chromium Poisoning: Preliminary Results



Polarization resistance increased from ~500 Ohms to ~1000 Ohms after exposure to Cr_2O_3 in flowing wet air at 800°C for 48 hours.

Single Phase Mixed Ionic Electronic Conducting (MIEC) Cathodes

- Ionic and electronic transport occurs through a single phase material. LSC, LSF, LSCF, etc.
- General features of the model are similar to those of composite cathodes, although the experimentally measured parameters are different.
- Composite cathodes: Ionic conductivity of the ionic conductor, grain size, charge transfer resistivity, porosity, and three phase boundary length.
- Single phase MIEC cathodes: Oxygen diffusion coefficient, surface exchange coefficient, porosity, and specific pore surface area.

$$R_p \approx \sqrt{\frac{\rho_{eff}\, d\rho_{ct}}{(1-V_v)\ell_{TPB}}}$$

Two Phase Composite MIEC Cathode

$$R_{chem} \approx \frac{RT}{2F^2}\sqrt{\frac{\tau}{(1-V_v)S_v C_o^2 D k_{exc}}}$$

Single Phase MIEC Cathode

Relevant Chemical Parameters for Single-Phase MIEC Cathodes

Diffusion Coefficient of Oxygen D

and

Surface Exchange Parameter k_{exc}

<u>Parameters Easily Measured Experimentally</u>

Chemical Diffusion Coefficient of Oxygen $\tilde{D}$ cm^2/s

and

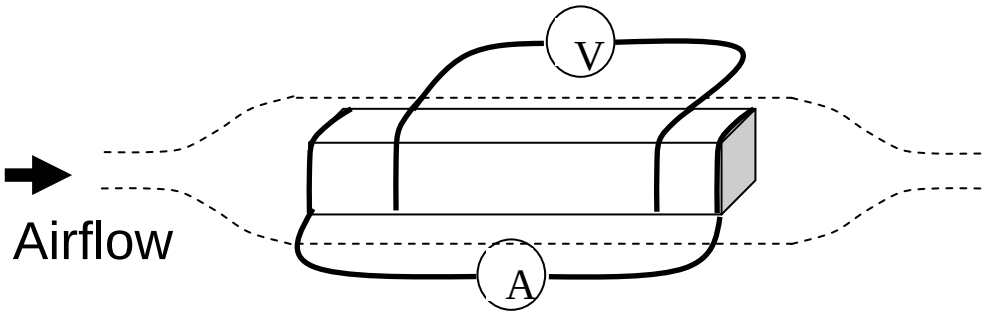
Chemical Surface Exchange Parameter k_{chem} cm/s

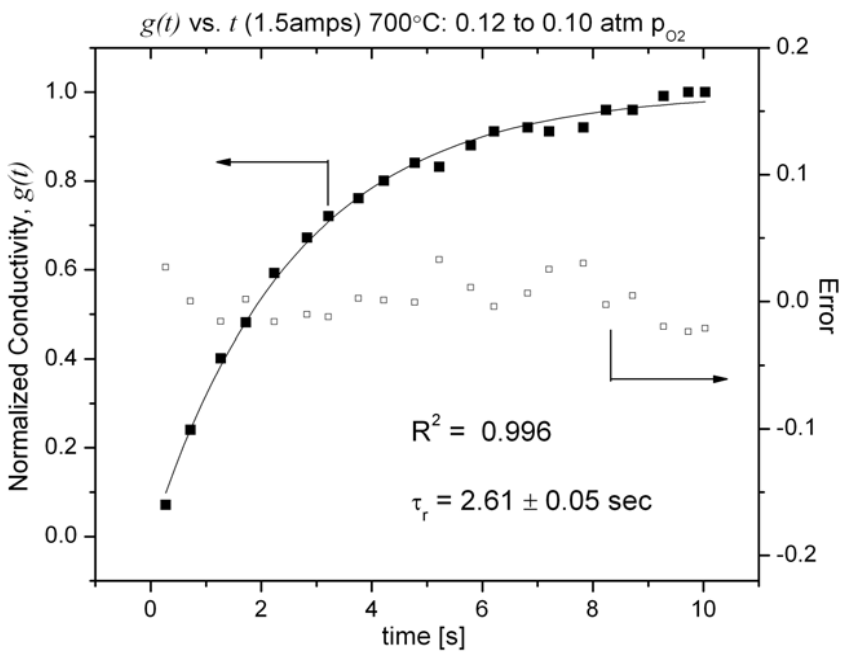
Technique used: Conductivity Relaxation (time response of conductivity change to an abrupt change in oxygen partial pressure)

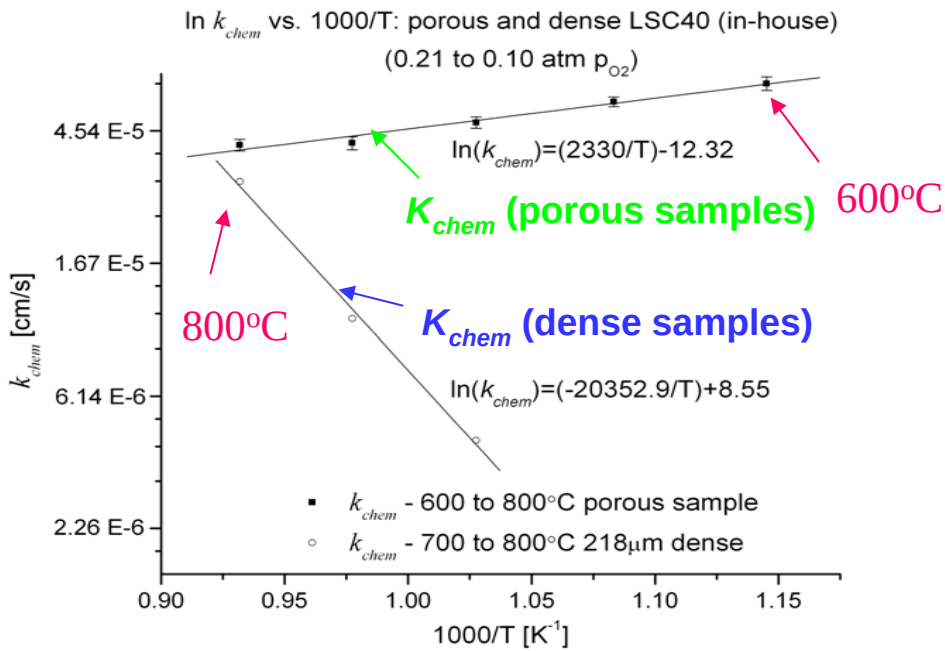
Usual Approach: To use a dense bar-shaped sample.

Our Approach: To use a porous bar-shaped sample.

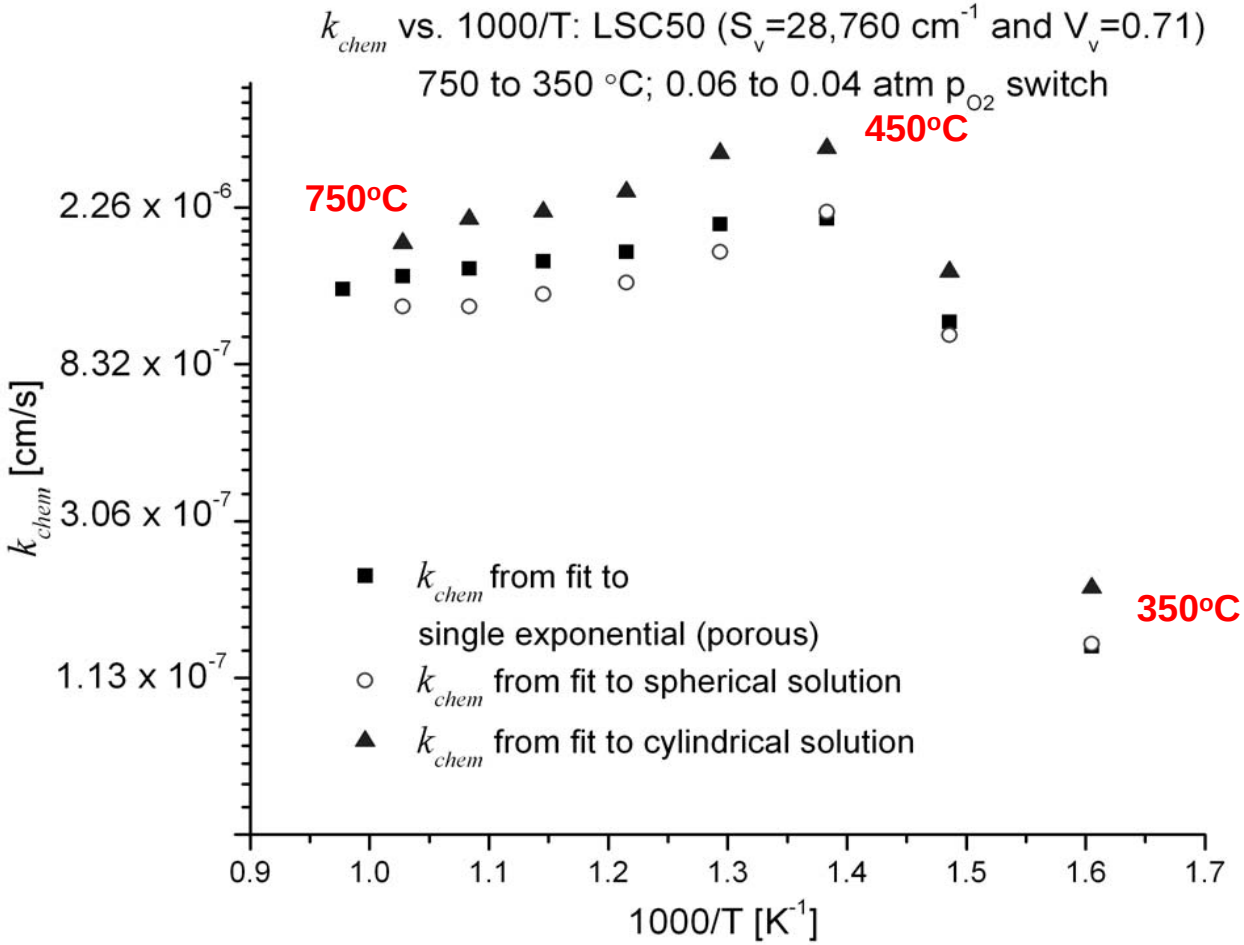
Characterization of MIEC Cathodes: Measurement of Surface Exchange Coefficient by Conductivity Relaxation using Porous Bodies







Measurement of Surface Exchange Coefficient on Porous Bodies: LSC Between 350 and 750°C



Above 450°C, k_{chem} decreases with increasing temperature.
Below 450°C, k_{chem} decreases with decreasing temperature.

Potential implications for SOFC cathodes: Identify materials with high k_{chem} at lower temperatures.

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Summary: Important Factors for Lowering Electrode Polarization

- Anode Concentration Polarization: High porosity (~50%), low tortuosity, small thickness (~0.4 to ~0.5 mm).
- Cathode Concentration Polarization: High porosity (~50%), low tortuosity, small thickness (~50 to 100 microns).
- Cathode and Anode Activation Polarization - microstructural: Small particle size (nanosize), large neck size.
- Cathode Activation Polarization – chemical: High ionic conductivity, low charge transfer resistivity, large TPB (>5,000 cm^{-1}), higher oxygen surface coverage at as low an oxygen partial pressure as possible. With MIEC materials: High diffusion coefficient, high surface exchange coefficient.