Research on SOFC Electrodes

Anil V. Virkar, Yi Jiang, Tad J. Armstrong,
Feng Zhao, Nishant Tikekar, and Sachin Shinde
University of Utah

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Technical Issues Addressed

- Cathode polarization in anode-supported SOFC
- Anode polarization in anode-supported SOFC
- Kinetics of anode reduction
- Thermo-mechanical issues concerning anode-supported cells – thermal expansion coefficient of cathode

Technical Issues - Details

Cathode Polarization

- Effect of cathode atmosphere on polarization.
- Effect of cathode porosity on concentration polarization.
- Effect of cathode composition on polarization.

Anode Polarization

- Effect of anode gas composition on transport.

Kinetics of Anode Reduction

- Experimental studies on anode reduction kinetics.
- Simple analytical modeling of the anode reduction kinetics – effect of microstructure.

Thermo-Mechanical Issues

- Potential for delamination – electrolyte thickness
- Thermal expansion coefficient of the cathode

Results to Date

- Cathode Polarization

(a) Effect of oxidant diluents on cathode polarization. (N_2, Ar, CO_2).

(b) LSGM + LSM cathodes. Good prospect.

(c) Gas diffusion through porous cathodes. Effect of porosity investigated.

- Anode Polarization

(a) Effect of diluents on anode gas transport and polarization. (N_2, He, CO_2, H_2O).

- Anode Reduction Kinetics

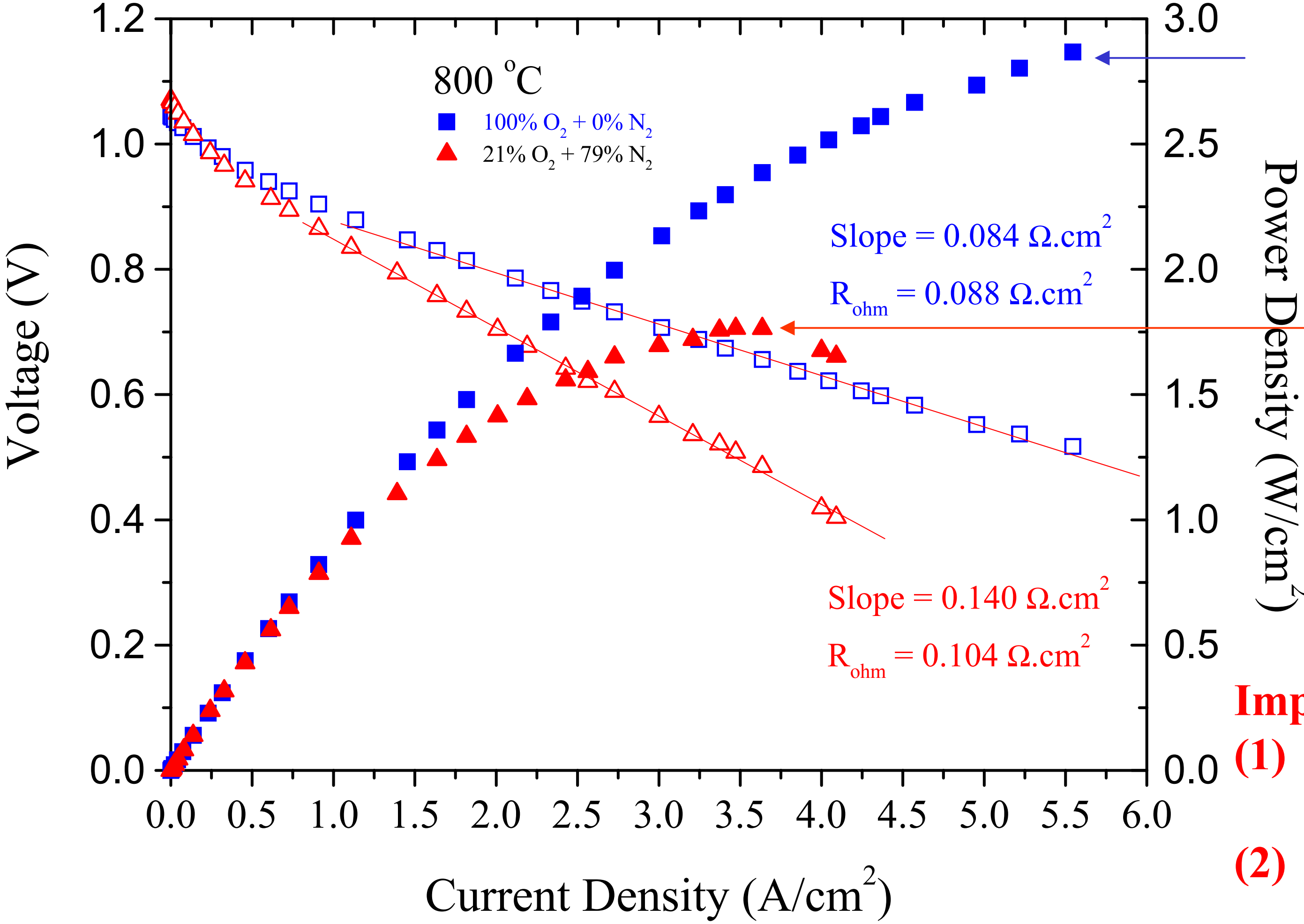
(a) Kinetic studies on NiO + YSZ reduction to Ni + YSZ. Interface-controlled.

- Thermo-Mechanical Issues

(a) Electrolyte thickness to prevent delamination. Thinner the better.

(b) Cathode matching with anode or electrolyte. Cathode matching with anode.

Effect of Cathode Gas Composition



MPD ~2.9 W/cm²
With H_2/O_2

MPD ~1.75 W/cm²
With H_2/Air

Cathode: LSC + SDC

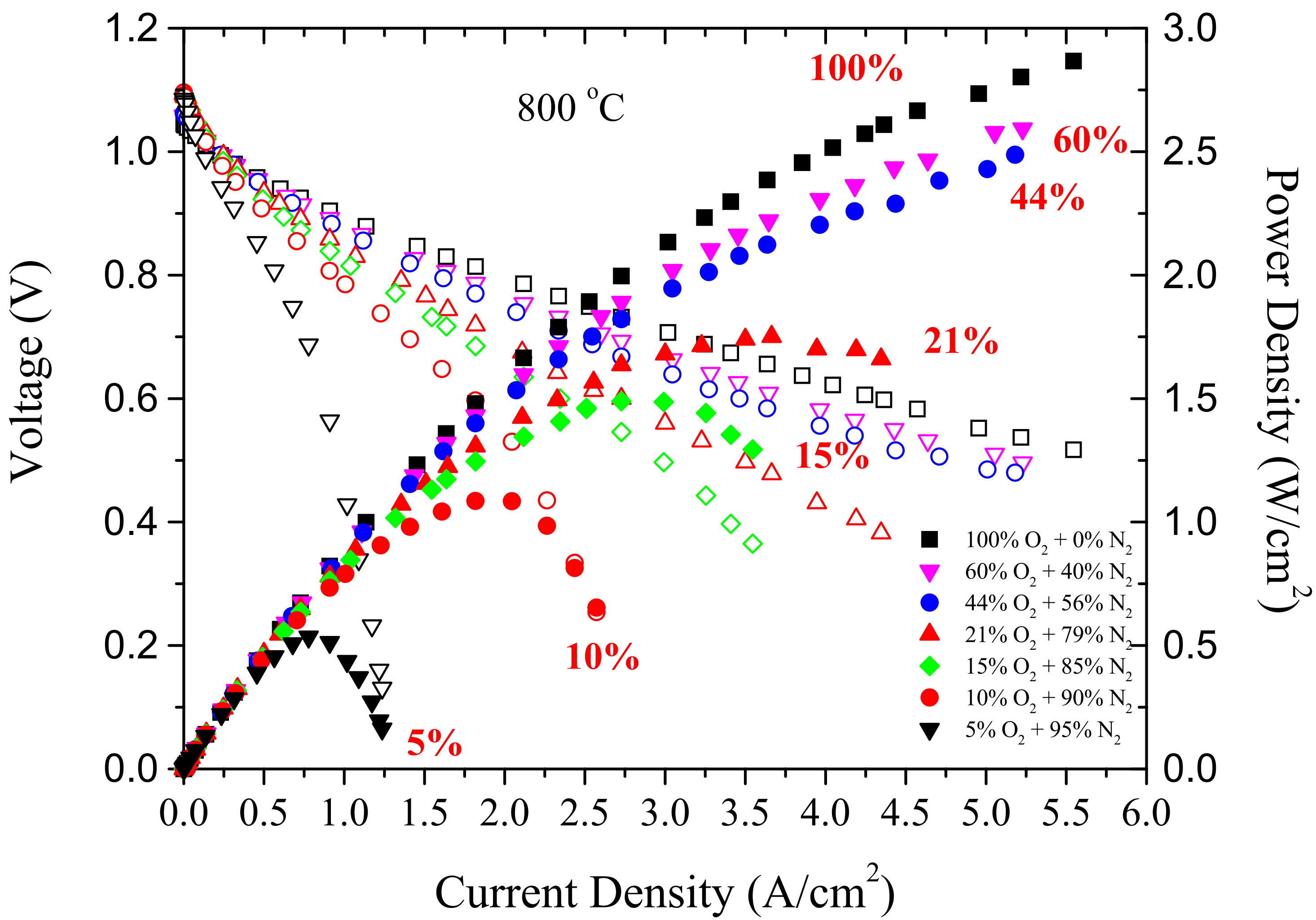
Important Observations

(1) In pure O_2, very low cathode polarization.

(2) Anode polarization is small.

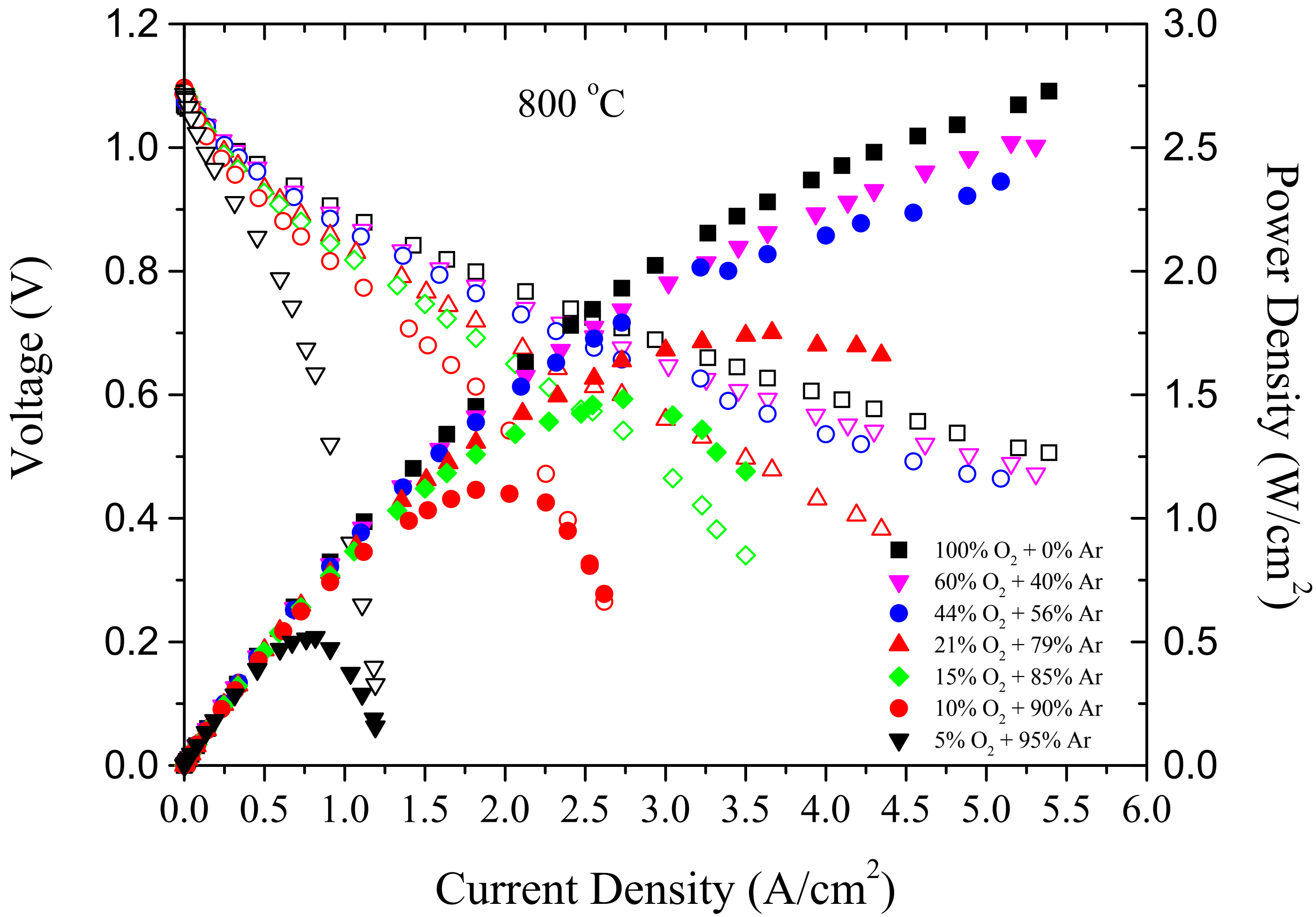
Effect of Oxidant Composition at 800^{o}C

Nitrogen as a Diluent



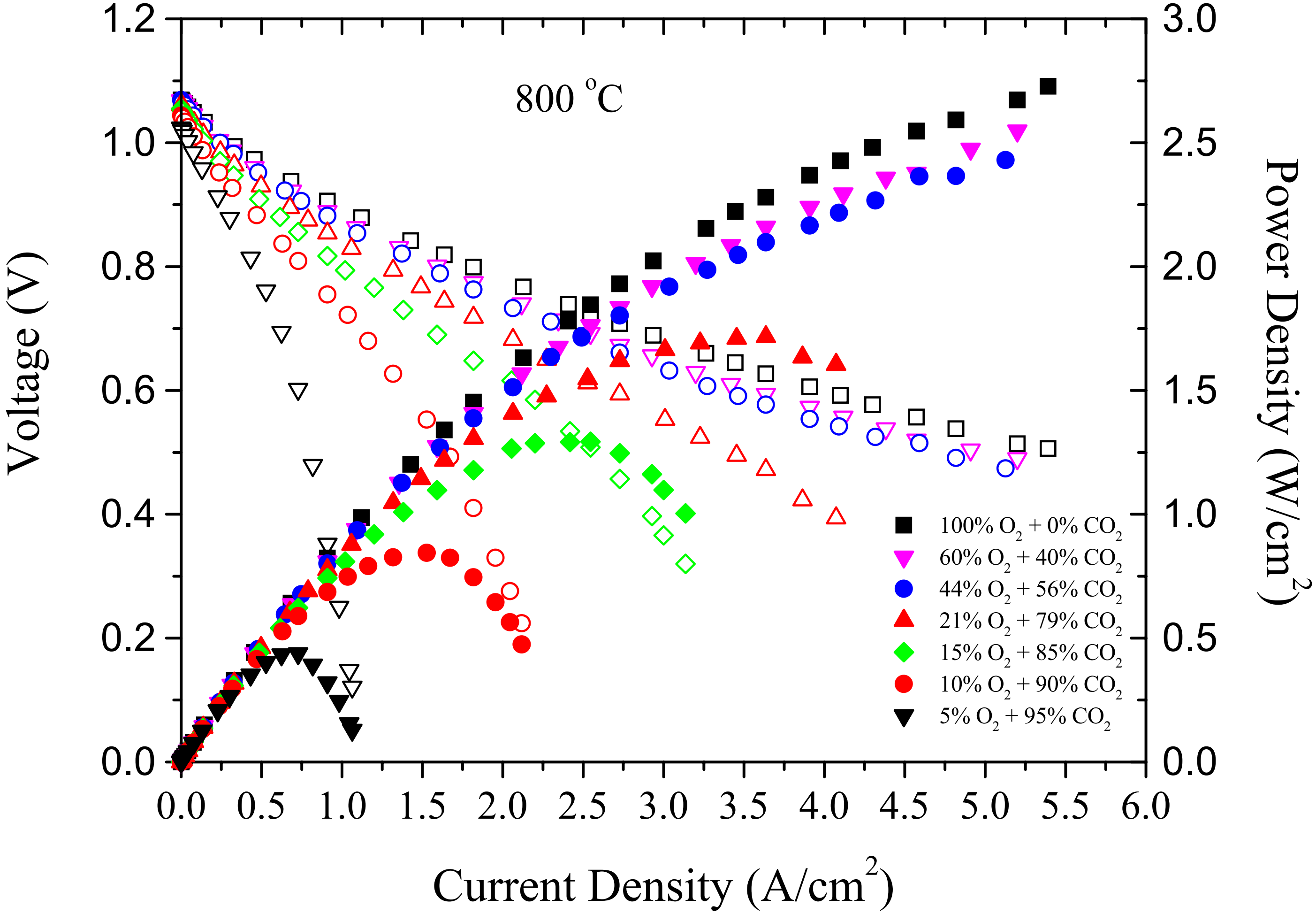
Effect of Oxidant Composition at 800°C

Argon as a Diluent



Effect of Oxidant Composition at 800°C

Carbon Dioxide as a Diluent



Cell ASR at Low Current Densities

Cathode Polarization ASR as a function of θ_{O_2}, fractional surface coverage

Cathode Ionic Resistivity

TPB Length

Cathode Polarization ASR

Cathode Grain Size

Charge Transfer ASR

Charge Transfer Resistivity

Adsorption Coefficients

$$R_p \approx \sqrt{\frac{d\rho_i R_{ct}}{(1-V_v)\theta_{O_2}}} = \sqrt{\rho_i \rho_{ct}}\sqrt{\frac{d}{l_{TPB}(1-V_v)}}\sqrt{\frac{1+b_{O_2}p_{O_2}+b_{N_2}p_{N_2}}{b_{O_2}p_{O_2}}}$$

Cathode Porosity

Fractional Surface Coverage

Intrinsic

Microstructural

Gas Adsorption

For low p_{O_2}, low b_{O_2}, and low b_{N_2}, the above reduces to

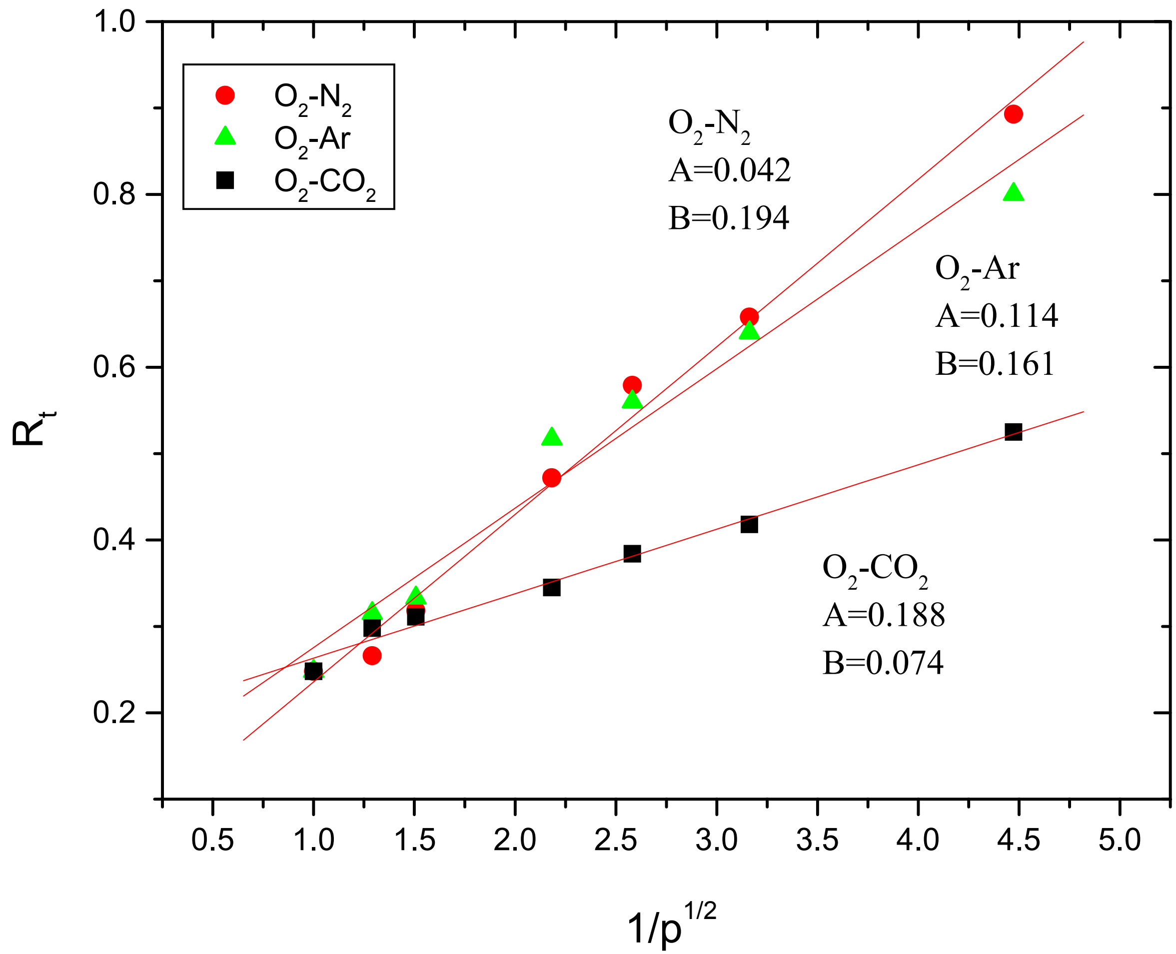
$$R_p \approx \sqrt{\frac{d\rho_i R_{ct}}{(1-V_v)\theta_{O_2}}} = \sqrt{\rho_i \rho_{ct}}\sqrt{\frac{d}{l_{TPB}(1-V_v)}}\sqrt{\frac{1}{b_{O_2}p_{O_2}}}$$

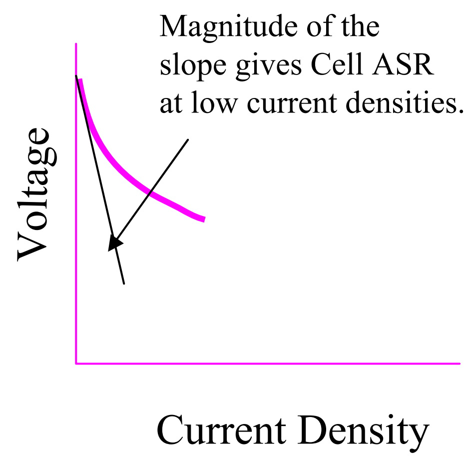
Thus, a plot of R_p vs. $\frac{1}{\sqrt{p_{O_2}}}$ should be a straight line.

Cell ASR at Low Current Densities

Total Cell ASR (low current density limit) as a Function of pO_2

$$R_{total} \approx R_{ohm} + R_p \approx R_{ohm} + \sqrt{\rho_i \rho_{ct}} \sqrt{\frac{d}{l_{TPB}(1-V_v)}} \sqrt{\frac{1}{b_{O_2} p_{O_2}}}$$





Cell ASR at Low Current Densities

Total Cell ASR (low current density limit): Curve fit

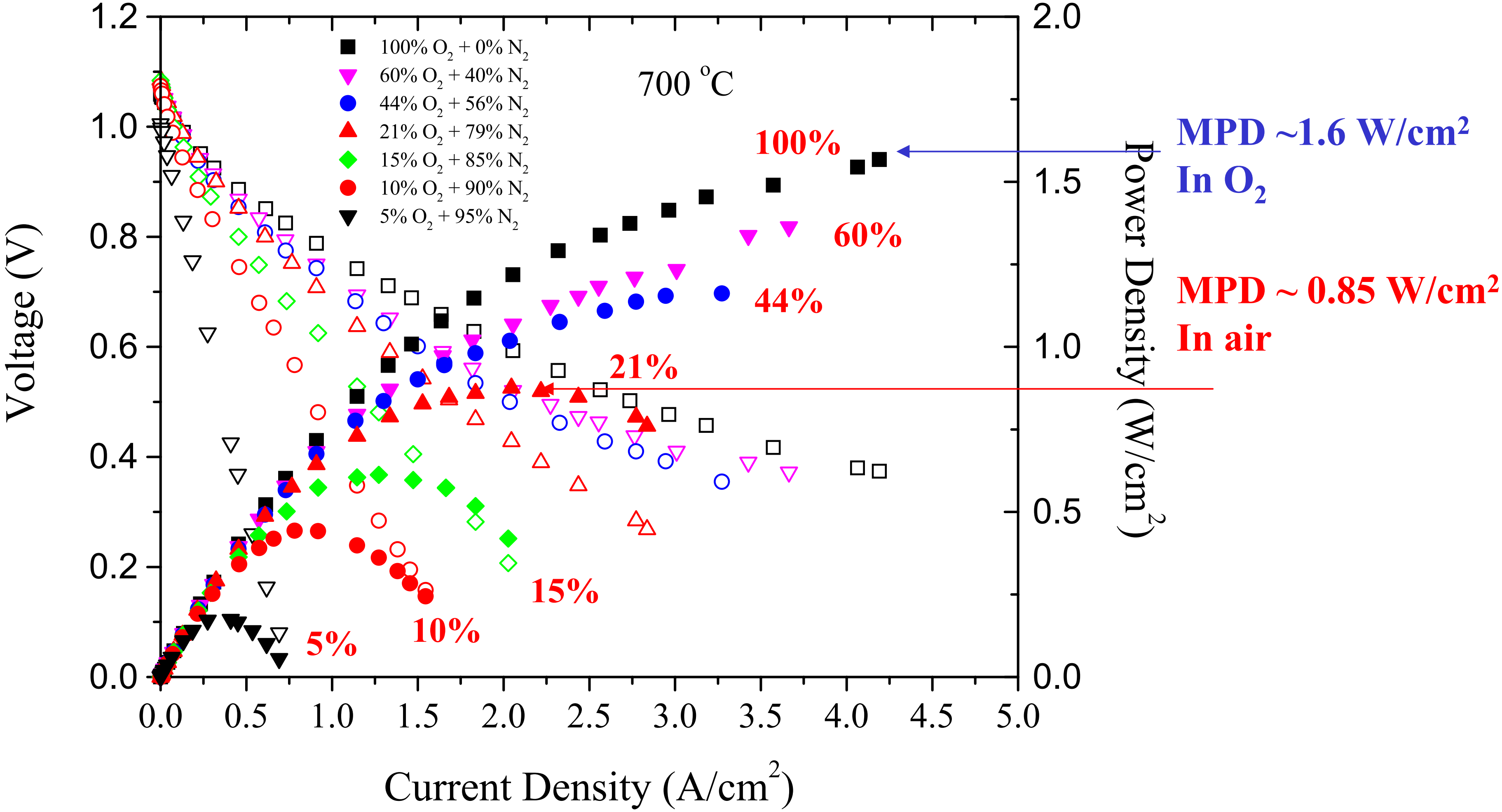
$$R_{total} \approx R_{ohm} + R_p \approx R_{ohm} + \sqrt{\rho_i \rho_{ct}} \sqrt{\frac{d}{l_{TPB}(1-V_v)}} \sqrt{\frac{1}{b_{O_2} p_{O_2}}}$$

Thus, the intercept should be R_{ohm}

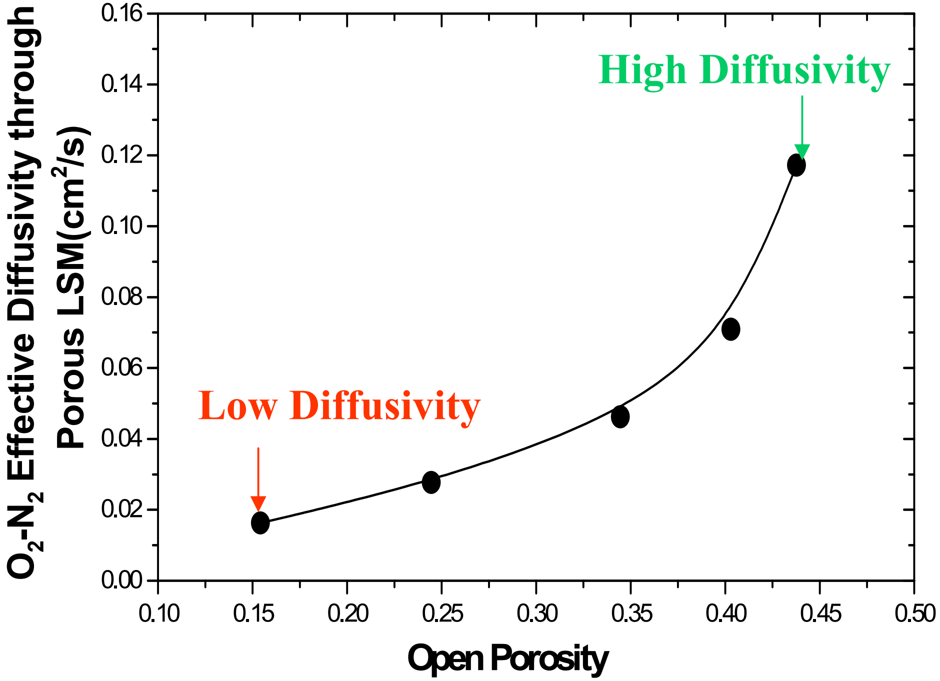
	O_2-N_2	O_2-Ar	O_2-CO_2
Slope	0.194	0.161	0.075
Intercept Rohm (Ωcm^2)	**0.042**	**0.114**	**0.188**

From current interruption, R_{ohm} ~**0.09** Ωcm^2.

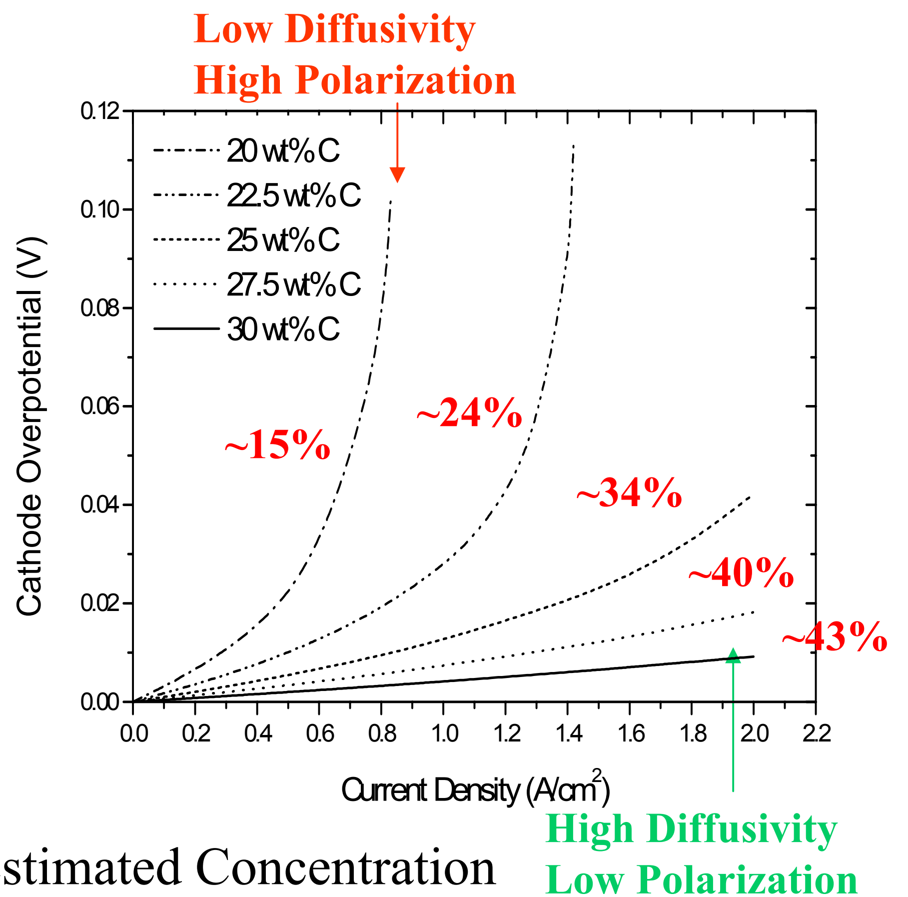
Effect of Oxidant Composition at 700°C



Effect of Cathode Porosity on Concentration Polarization

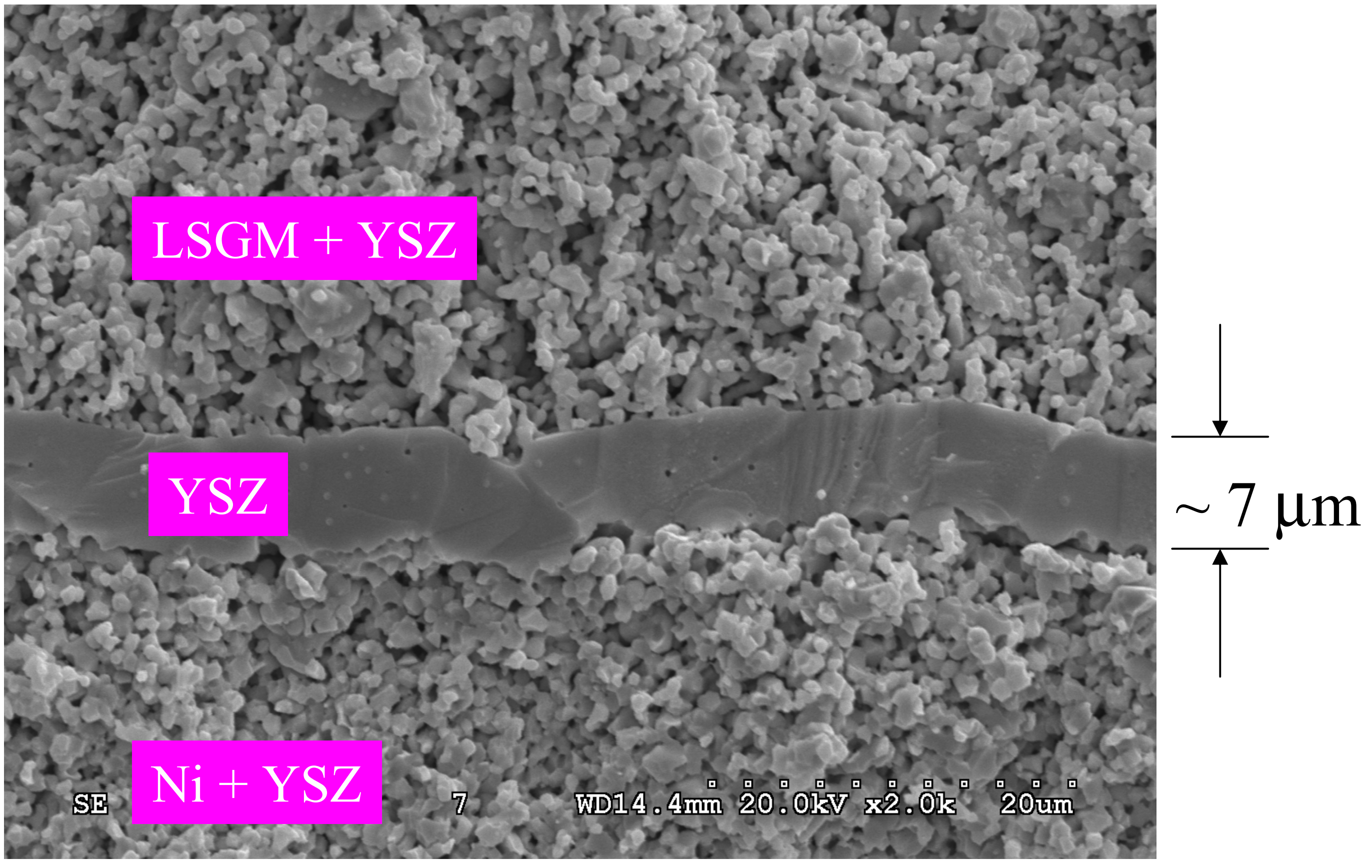


Experimentally Measured Effective Diffusivity as a Function of Porosity



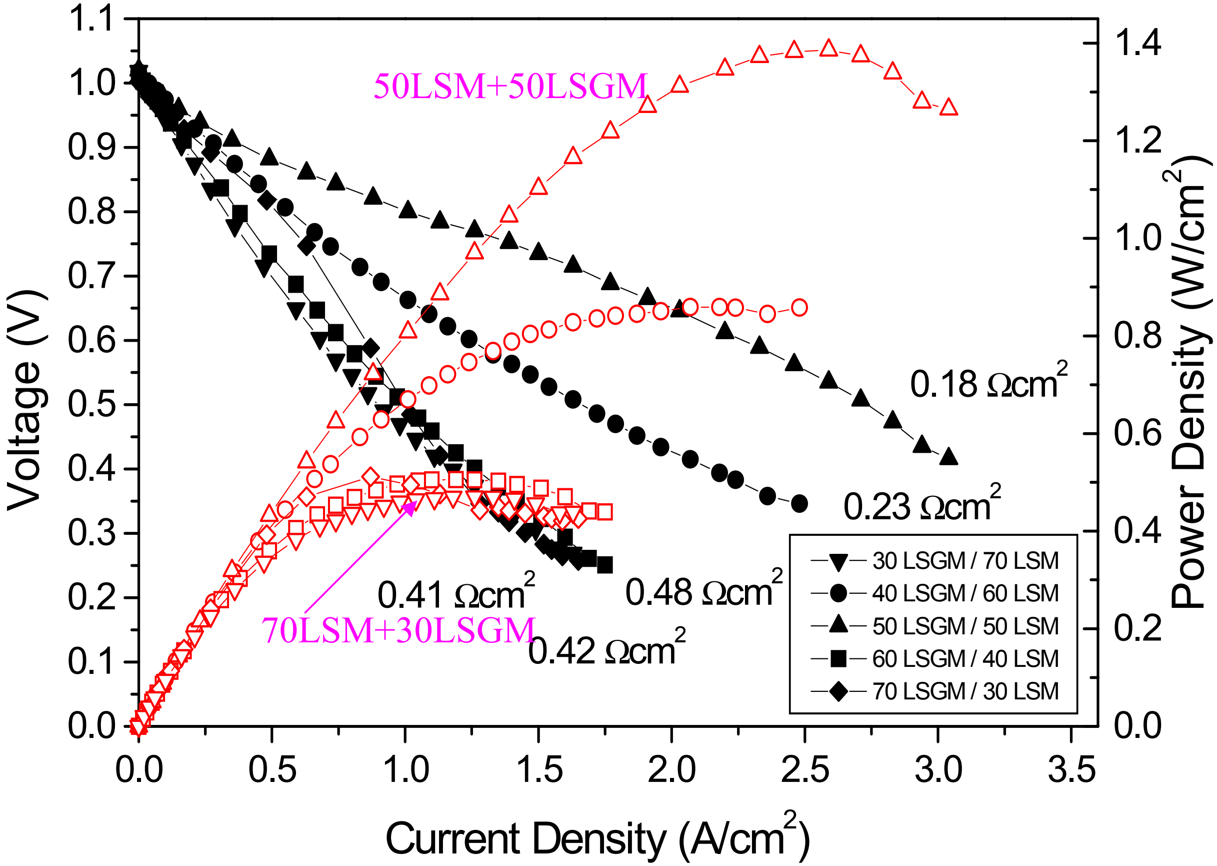
Estimated Concentration Polarization as a Function of Current Density for Cathodes of Different Porosities: Thickness = 200 Microns.

LSGM + LSM Cathodes for SOFC



LSGM + LSM Cathodes

Effect of Composition on Performance



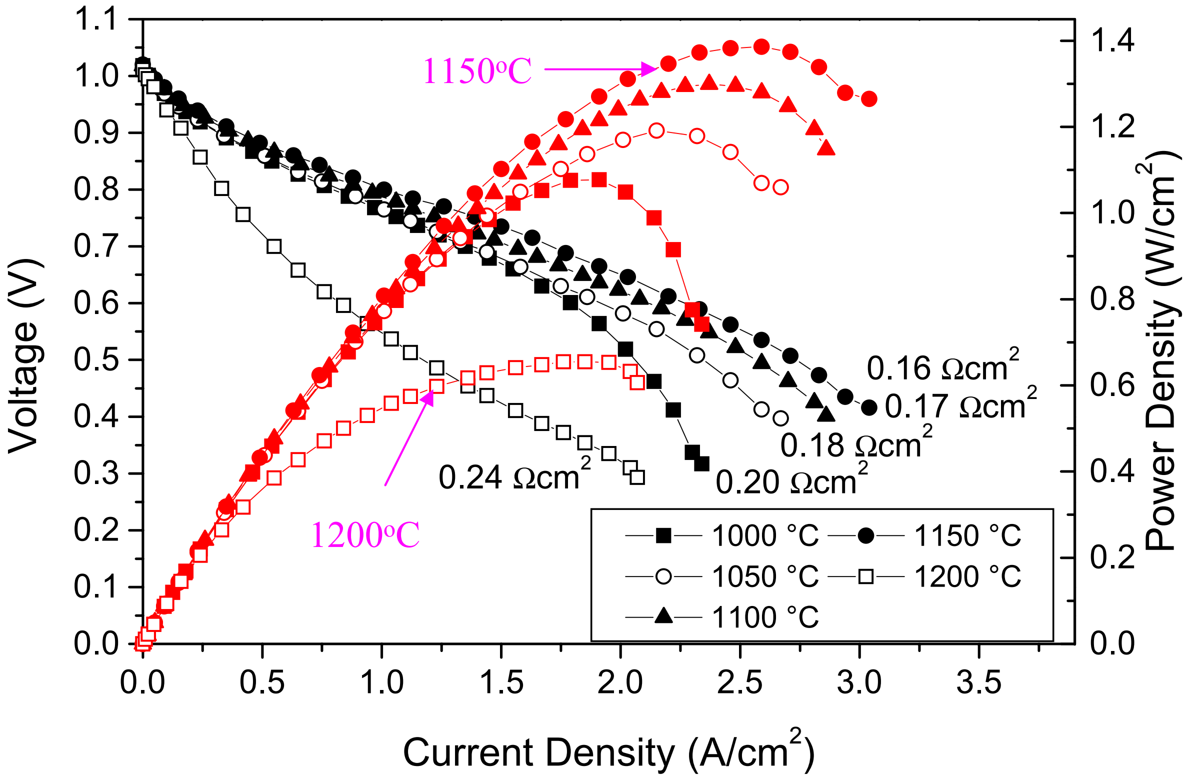
Important Observations

(1) Cathode composition has a profound effect on performance.

(2) Approximately 50/50 composition gives the best performance.

LSGM + LSM Cathodes

Effect of Firing Temperature on Performance



Important Observations

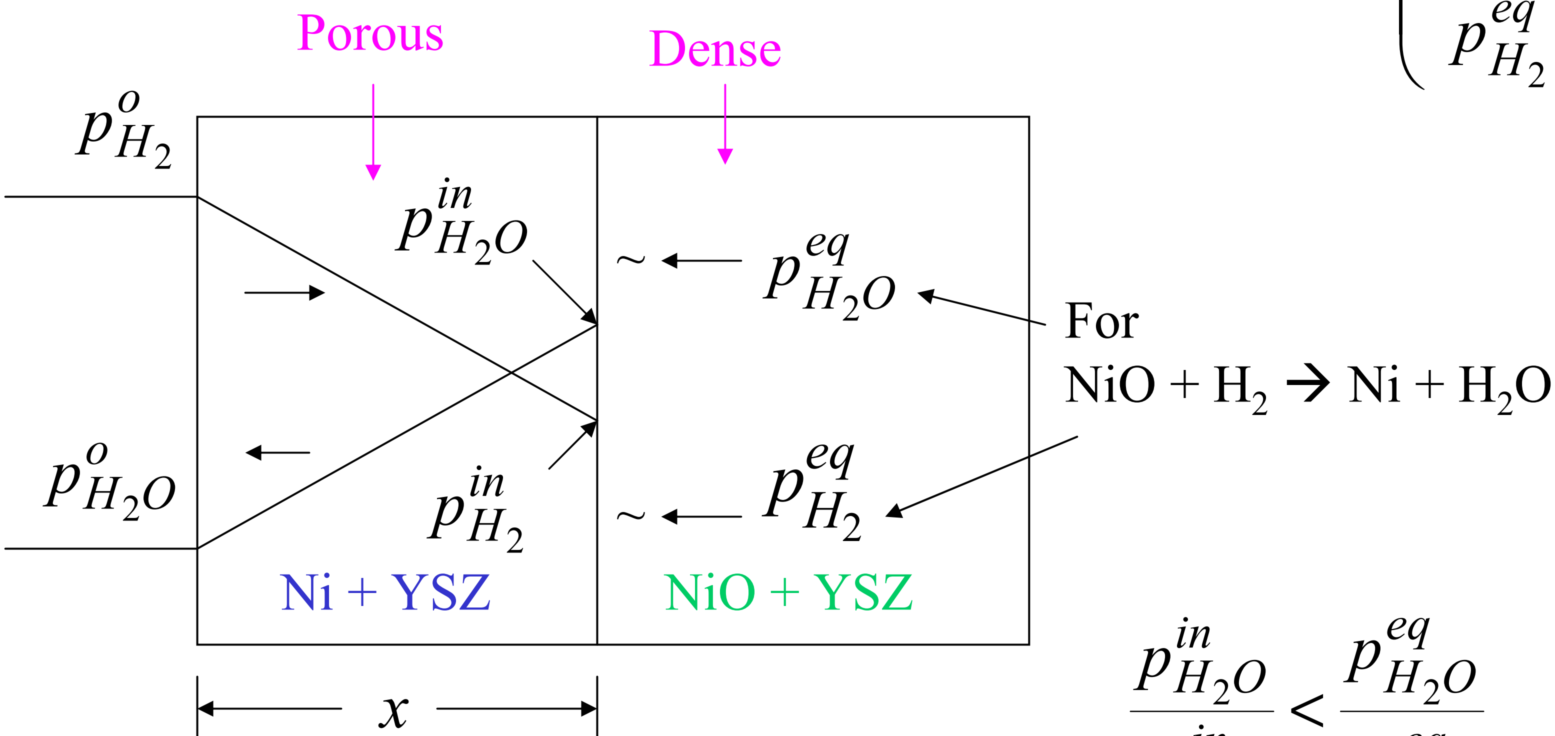
(1) Cathode firing temp. has a profound effect on performance.

(2) At 1200°C, LSGM and YSZ react to form deleterious $La_2Zr_2O_7$.

Kinetics of NiO + YSZ Reduction

Schematic

$$\Delta G^o = -RT \ln K = -RT \ln\left(\frac{p^{eq}_{H_2O}}{p^{eq}_{H_2}}\right)$$



$$\frac{p^{in}_{H_2O}}{p^{in}_{H_2}} < \frac{p^{eq}_{H_2O}}{p^{eq}_{H_2}}$$

Kinetics of NiO +YSZ Reduction

Nomenclature

$p_{H_2}^{o}$: Partial pressure of hydrogen in the reducing atmosphere

$p_{H_2}^{in}$: Partial pressure of hydrogen at the Ni +YSZ/NiO + YSZ interface

$p_{H_2}^{eq}$: Partial pressure of hydrogen corresponding to the reaction equilibrium $NiO + H_2 \rightarrow Ni + H_2O$

$p_{H_2O}^{o}$: Partial pressure of H_2O in the reducing atmosphere

$p_{H_2O}^{in}$: Partial pressure of H_2O at the Ni + YSZ/NiO + YSZ interface.

$p_{H_2O}^{eq}$: Partial pressure of H_2O corresponding to the reaction equilibrium $NiO + H_2 \rightarrow Ni + H_2O$.

Kinetics of NiO +YSZ Reduction

Nomenclature (contd.)

V_{NiO}^{M} : Molar volume of NiO.

$V_{f(NiO)}$: Volume fraction of NiO.

D_{eff} : Effective ternary diffusivity of H_2-H_2O-N_2 in porous Ni + YSZ.

R : Ideal gas constant.

T : Temperature.

k_s : Interface kinetic parameter for the reaction NiO (+ YSZ) + H_2 → Ni (+ YSZ) + H_2O.

t : Time of reduction.

x : Thickness reduced in time '*t*'.

Kinetics of NiO + YSZ Reduction

Kinetic Model

$$x^2 + \frac{D_{eff}}{RTk_s} x = \frac{2D_{eff}}{RT} \frac{V_{NiO}^{M}}{V_{f(NiO)}} \left[p_{H_2O}^{eq} - p_{H_2O}^{o} \right] t$$

Limiting cases: (a) Diffusion-controlled, (b) Interface-controlled.

(a) Diffusion-controlled: $x^2 >> \frac{2D_{eff}}{RTk_s} x$

$$x^2 \approx \frac{2D_{eff}}{RT} \frac{V_{NiO}^{M}}{V_{f(NiO)}} \left[p_{H_2O}^{eq} - p_{H_2O}^{o} \right] t \quad \text{or} \quad x^2 \approx K_d t$$

Parabolic

(b) Interface-controlled: $x^2 << \frac{2D_{eff}}{RTk_s} x$

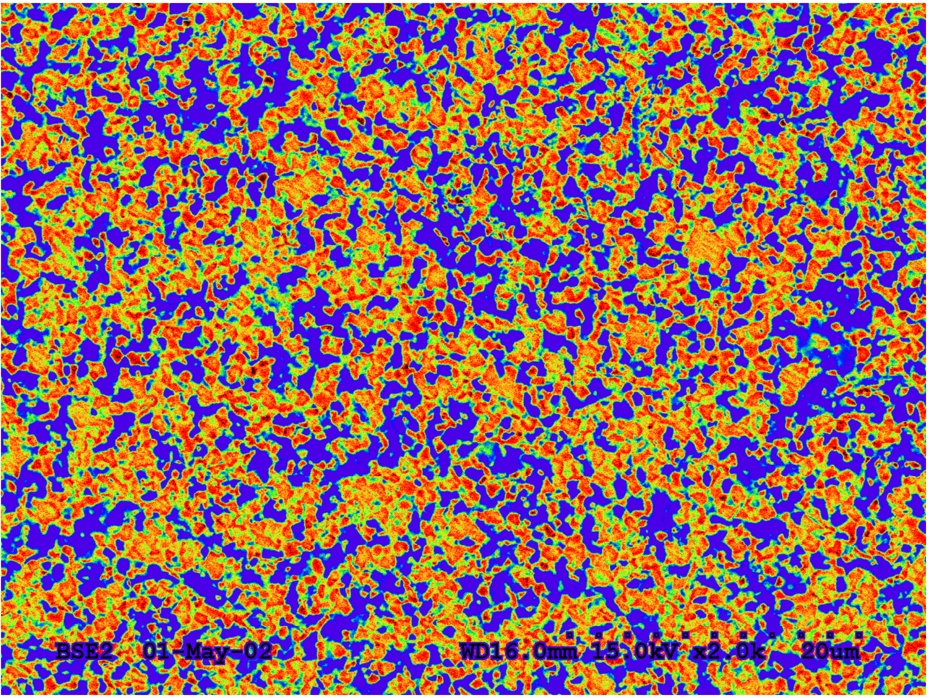
$$x \approx 2k_s \frac{V_{NiO}^{M}}{V_{f(NiO)}} \left[p_{H_2O}^{eq} - p_{H_2O}^{o} \right] t$$

Linear

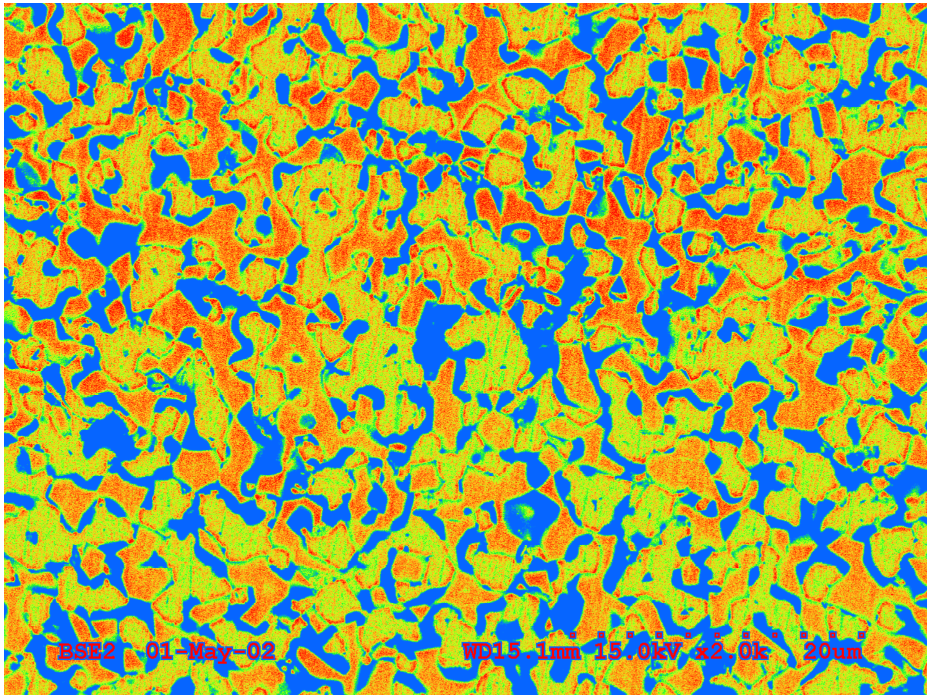
Or $x \approx K_s t$

Experimental Results

Microstructure of Reduced Samples



Sintered at 1400°C/2 hrs.
Reduced at 800°C

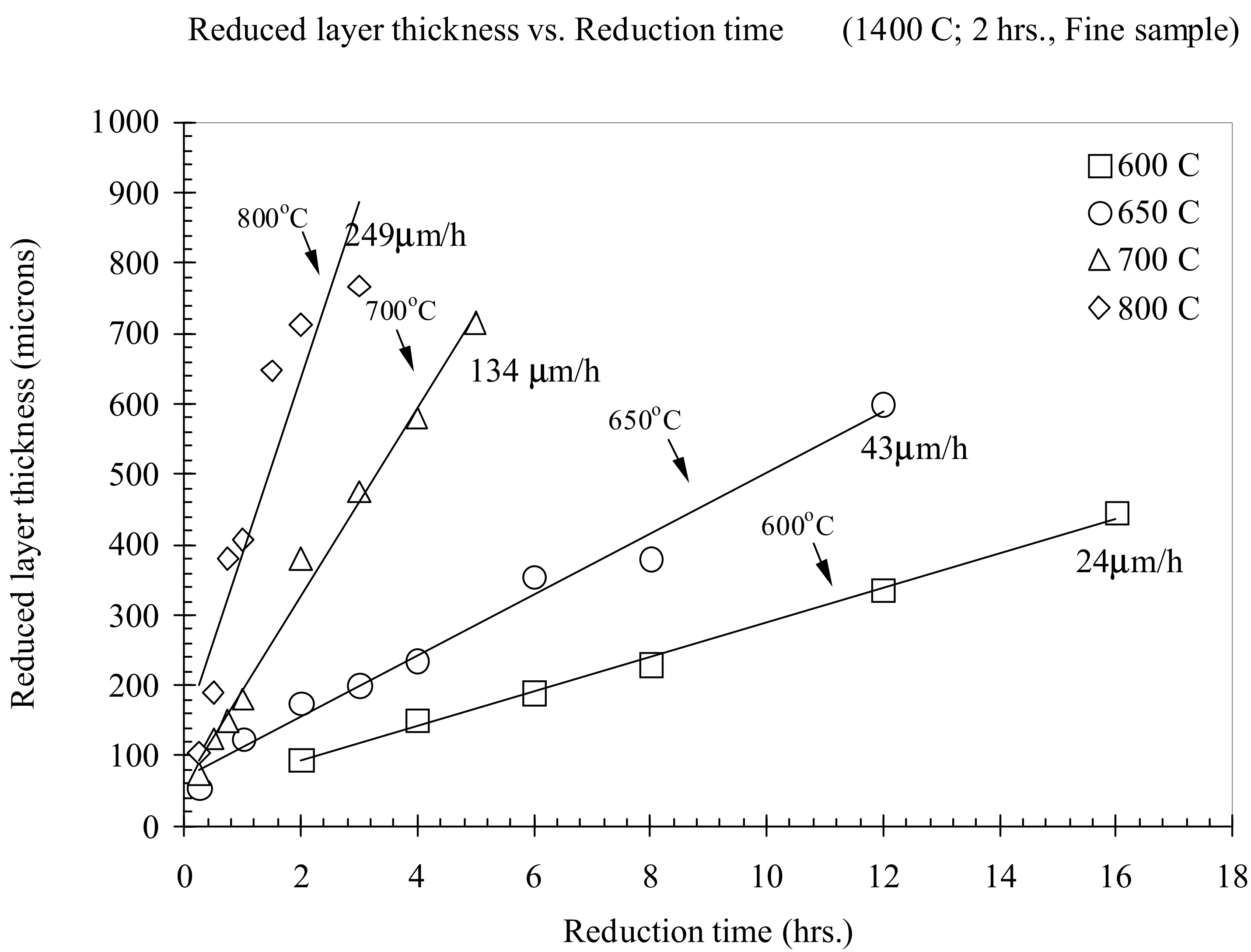


Sintered at 1600°C/10 hrs.
Reduced at 800°C

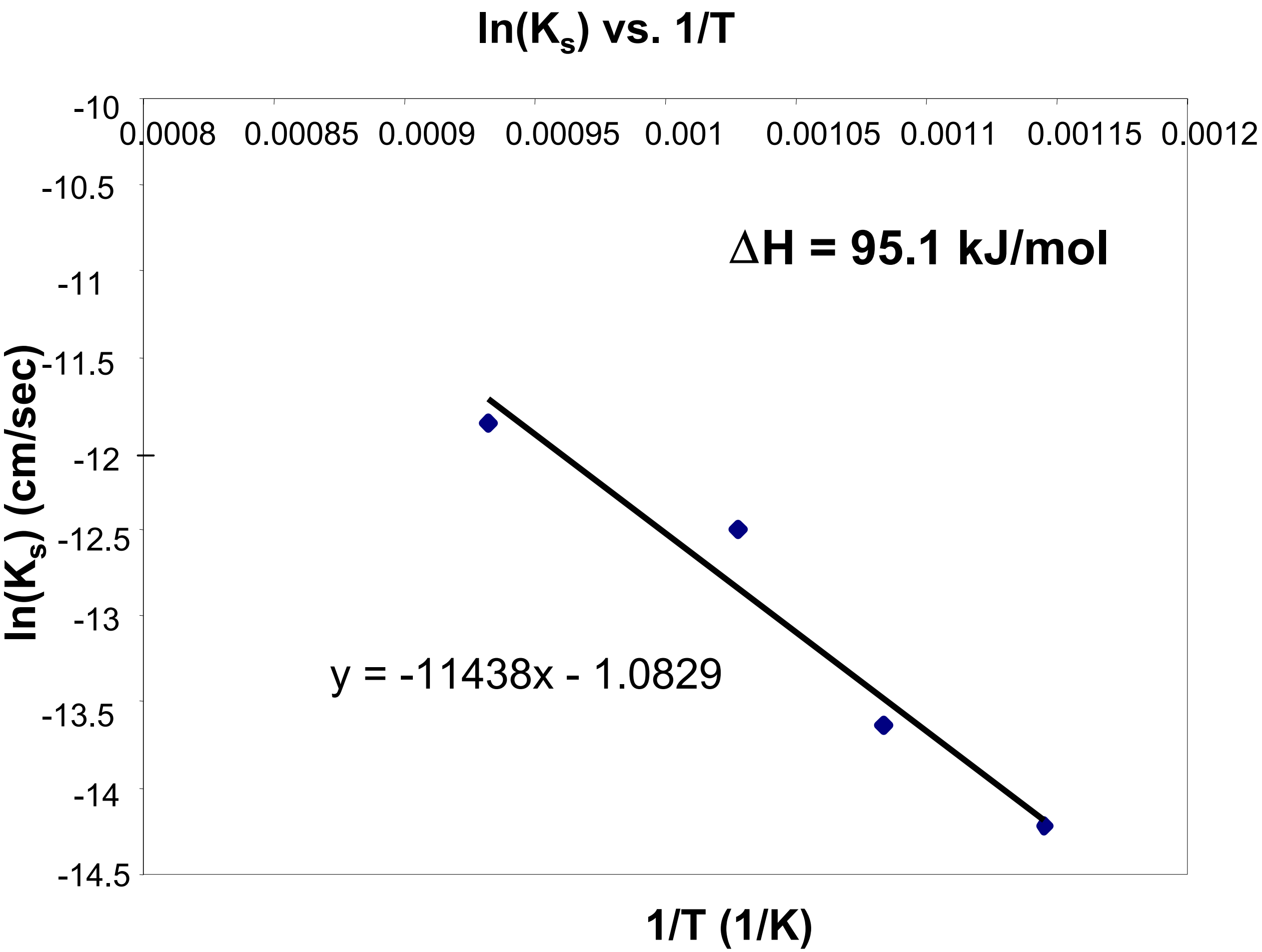
Orange: YSZ   **Green:** Ni   **Blue:** Pores

Experimental Results

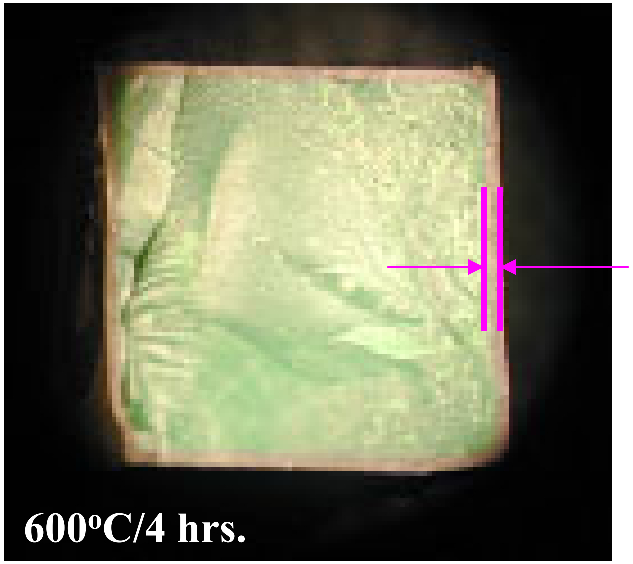
Reduction thickness vs. time as a function of temperature

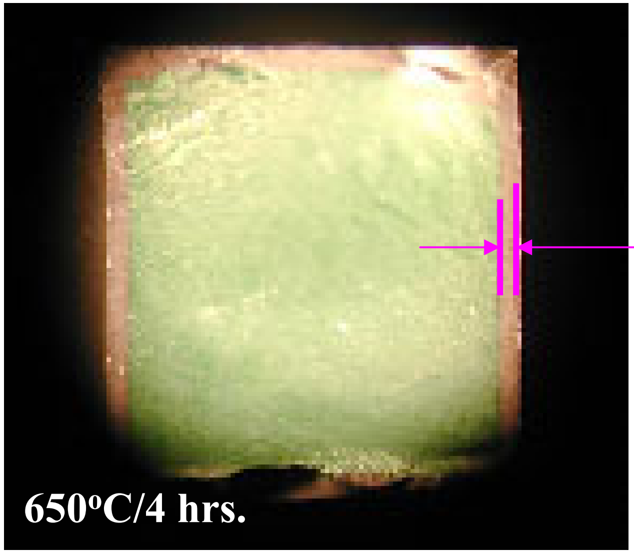


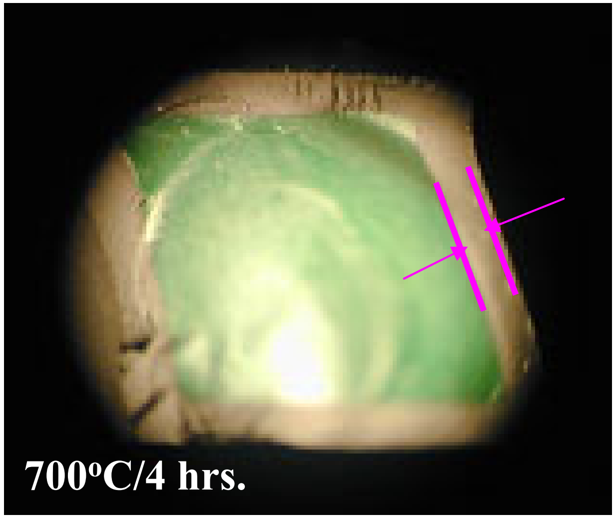
Rate Constant for Reduction as a Function of Temperature

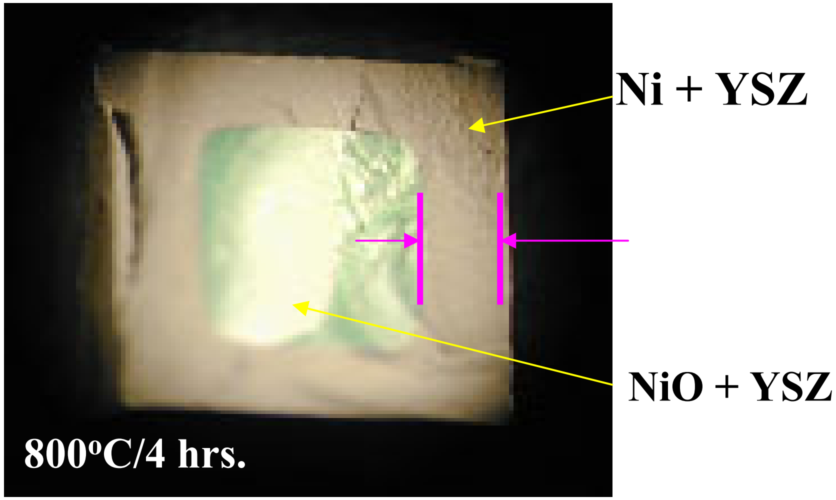


Photographs of Partially Reduced NiO + YSZ Samples



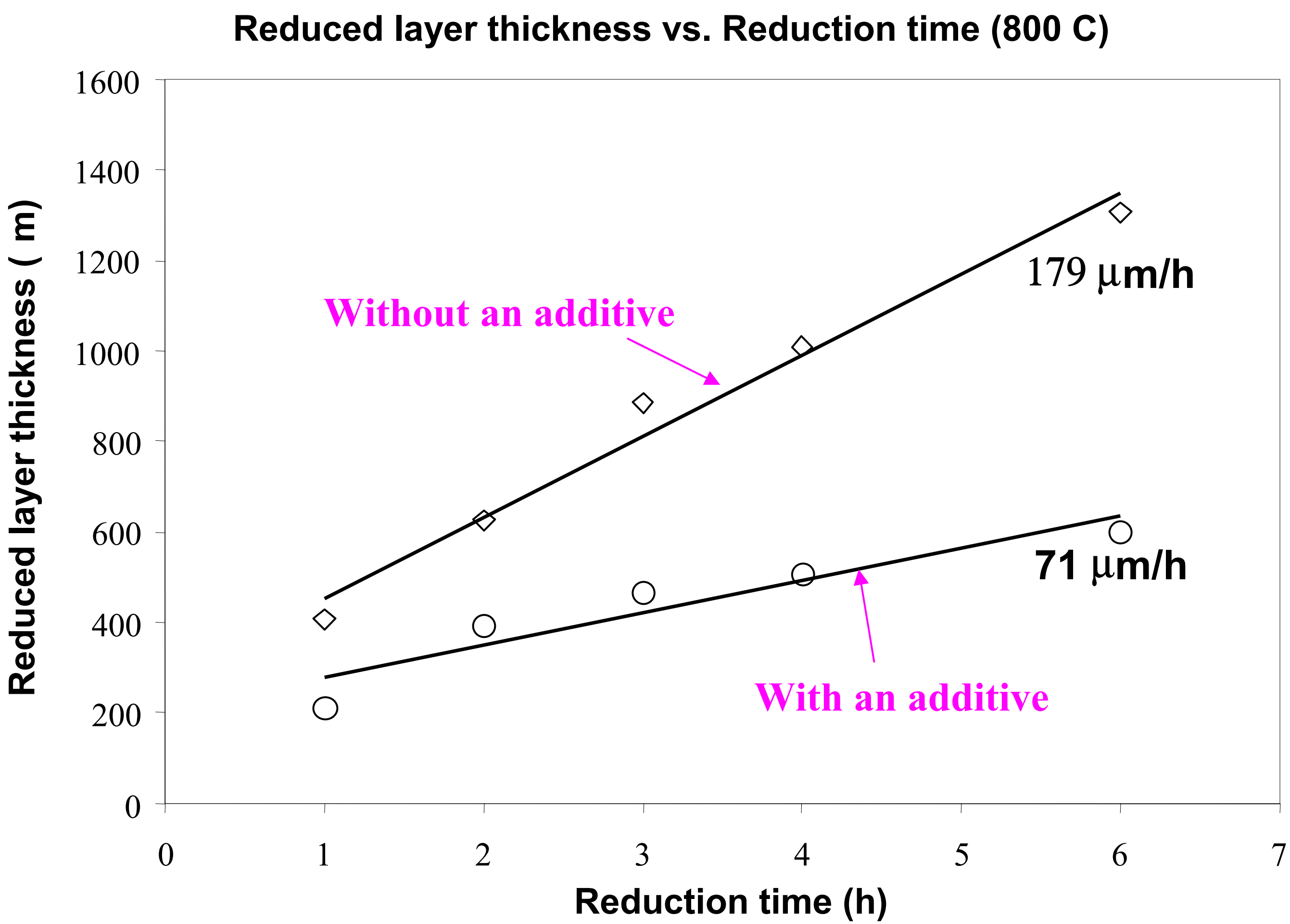






Reduced Thickness vs. Time at 800^{o}C

The effect of additives



NiO + YSZ Anode Reduction

Implications of the Results

- Kinetics of NiO + YSZ reduction is linear.
- This suggests that the kinetics of reduction is interface-controlled.
- The kinetics of NiO + YSZ reduction is thermally activated.
- Additives to NiO appear to have significant effect on reduction kinetics.

NiO + YSZ Anode Reduction and Re-Oxidation Kinetics

Anticipated work over the next 6-12 months

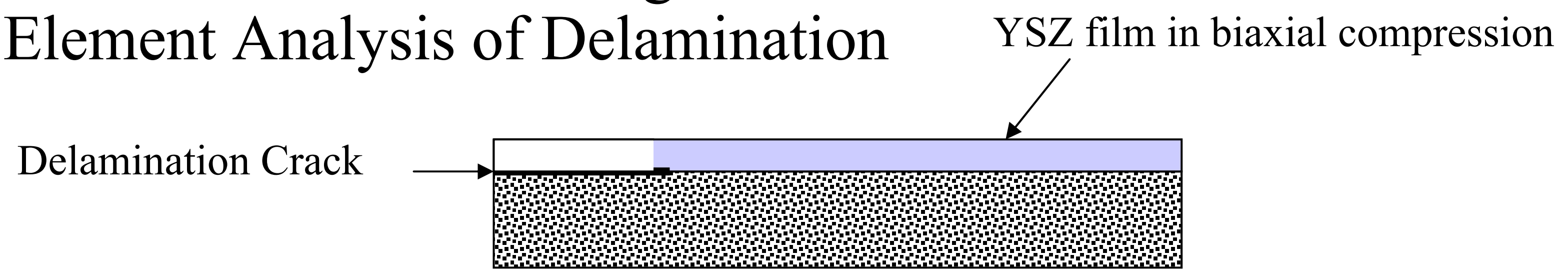
- To investigate the kinetics of anode re-oxidation.
  (a) Effect of temperature
  (b) Effect of composition (including additives)
  (c) Effect of microstructure

The overall objective is to develop redox-tolerant, Ni-based anodes.

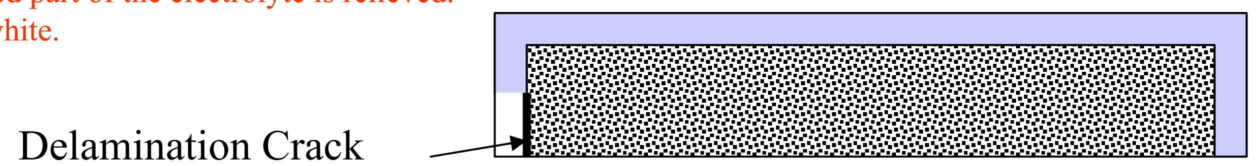
Finite Element Analysis of Anode-Supported Cells

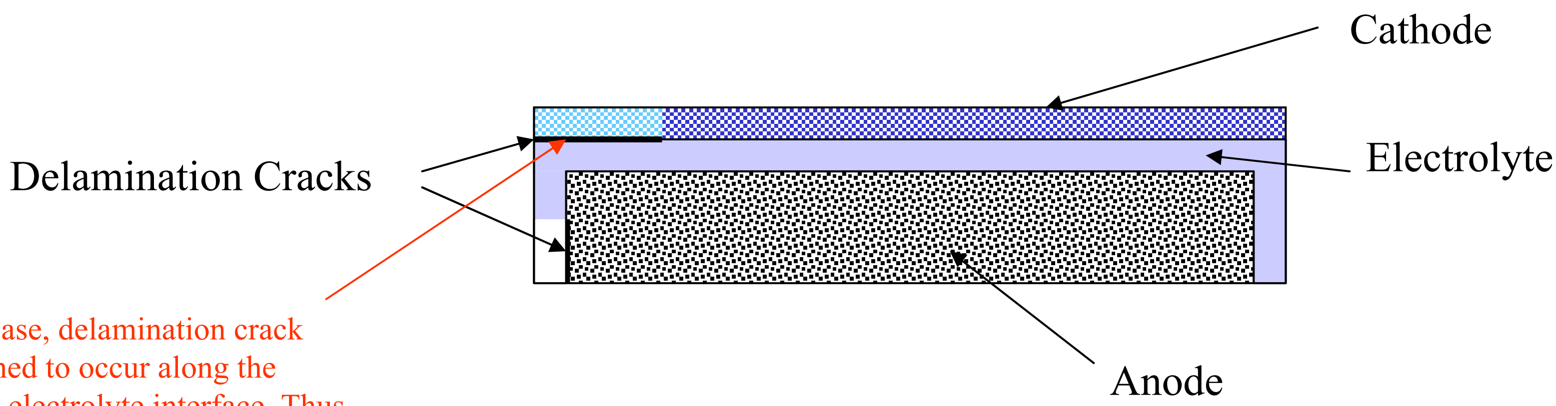
Issues Concerning Delamination

Finite Element Analysis of Delamination



Light violet color indicates the presence of a compressive stress in the electrolyte. If a crack forms, stress in the cracked part of the electrolyte is relieved. This is shown in white.





In this case, delamination crack is assumed to occur along the cathode-electrolyte interface. Thus, stress from the cracked part of the cathode is relieved – shown in light blue.

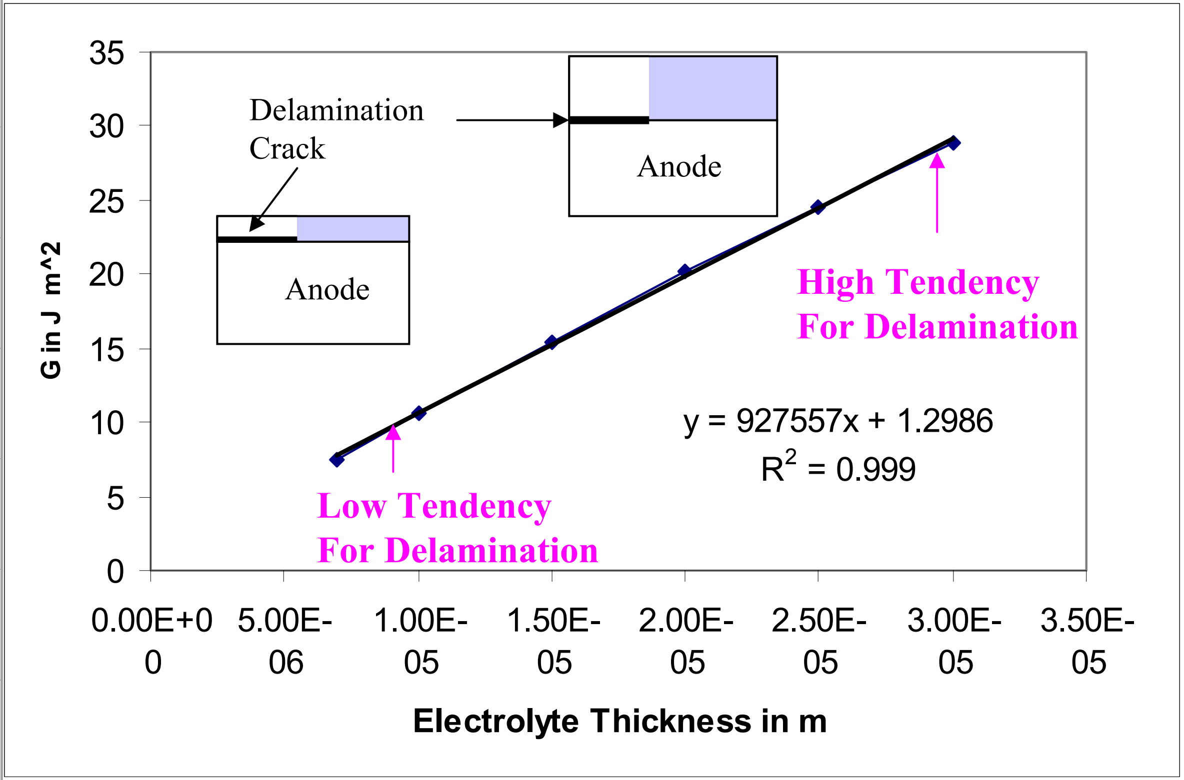
Thermo-Mechanical Issues

Elastic Energy Release Rate, G, for Delamination

The lower the G, the lower the propensity for delamination.
Thus, the thinner is the YSZ film, the better.

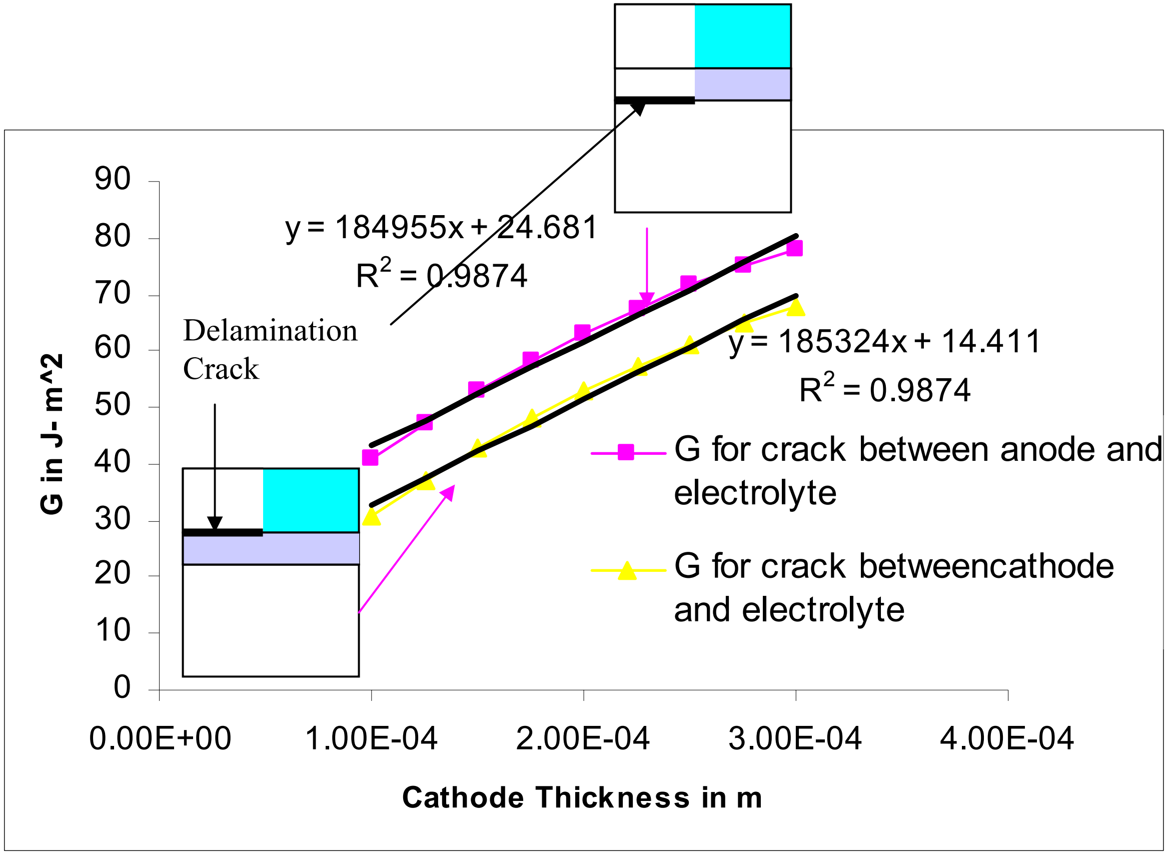
Electrolyte Thickness (µm)	G (J m^2)
7	7.5
10	10.56
15	15.46
20	20.12
25	24.6
30	28.8

Relative Thicknesses – not to scale



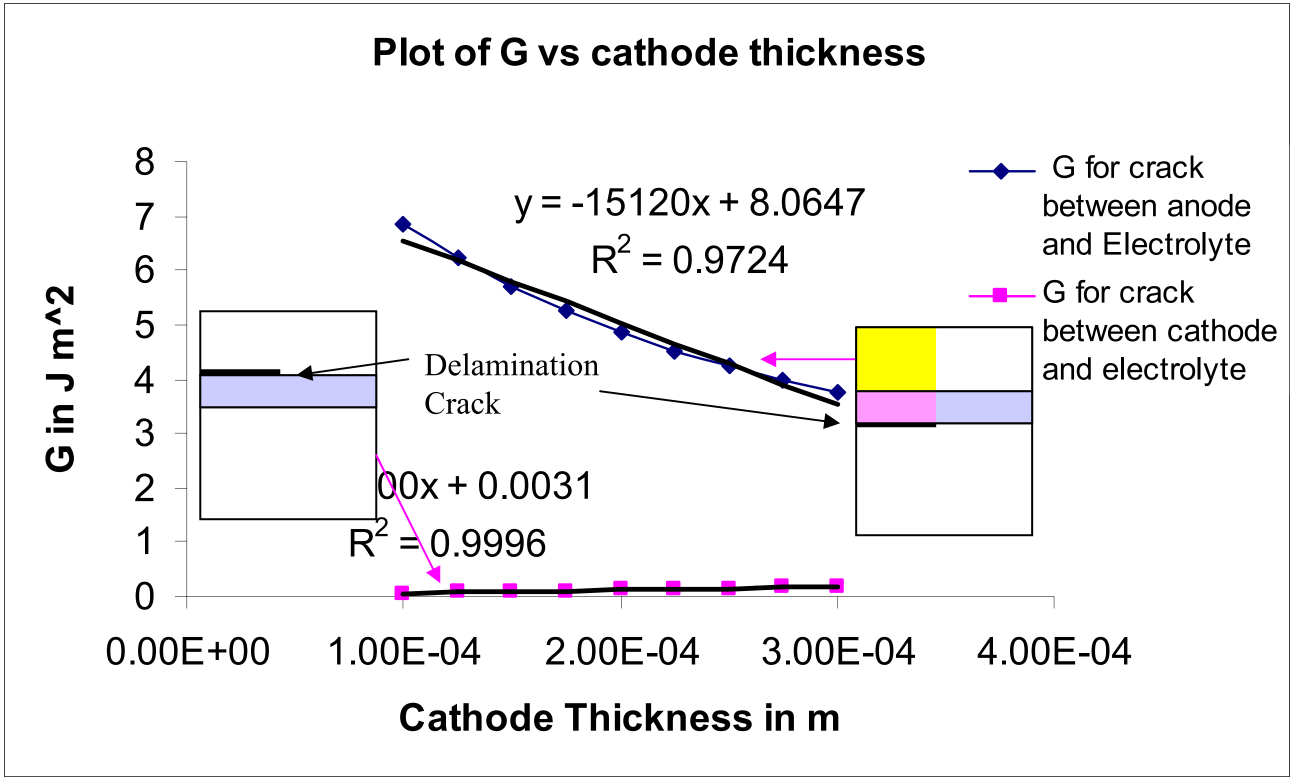
Thermo-Mechanical Issues

Propensity for Delamination: Cathode Matched with Electrolyte



Thermo-Mechanical Issues

Propensity for Delamination: Cathode Matched with Anode



Thermo-Mechanical Issues

Delamination: Comparison of Cathode Matching with Electrolyte and Cathode Matching with Anode

Cathode Thickness (μm)	G for Crack Between Anode and Electrolyte **(Cathode Matched with Anode) (J/m^2)**	G for Crack Between Cathode and Electrolyte **(Cathode Matched with Anode) (J/m^2)**	G for Crack Between Anode and Electrolyte **(Cathode Matched with Electrolyte) (J/m^2)**	G for Crack Between Cathode and Electrolyte **(Cathode Matched with Electrolyte) (J/m^2)**
10.0	6.85	0.062	40.97	30.73
12.5	6.22	0.078	47.29	37.06
15.0	5.69	0.094	53.09	42.88
17.5	5.24	0.108	58.39	48.20
20.0	4.86	0.124	63.21	53.02
22.5	4.53	0.138	67.56	57.38
25.0	4.24	0.154	71.48	61.3
27.5	3.98	0.168	74.97	64.80
30.0	3.76	0.182	78.08	67.91

Thermo-Mechanical Issues

Delamination: Comparison of Cathode Matching with Electrolyte or Anode: Implications

From the standpoint of propensity for delamination at either the electrolyte/anode interface or the electrolyte/cathode interface, it is preferable to match the thermal coefficient of the cathode with the anode rather than the cathode in the case of anode-supported cells. This is different from the case of cathode-supported cells.

Future Work

Next 6 to 12 months.

1) Cathode:
   (a) Composition and microstructure.
   (b) Effect of oxygen concentration.
2) Anode:
   (a) Re-oxidation kinetics.
3) Thermo-Mechanical.
   (a) FE analysis of cells with border holes.
   (b) FE analysis of cells of components with different material properties.
   (c) Experimental investigation of interface properties (critical elastic energy release rate, G_c, or toughness, K_c).