

Composite Cathode for High Power Density SOFCs

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SECA Core Technology Program



Rationale

- Cathode polarization limits power densities at low operating temperature
- Reducing operating temperature is a key for SOFC commercialization
 - Enabling metallic interconnects
 - Minimizing balance of plant cost
- A successful low-T cathode would be a key element in successful SOFC commercialization

Technical Issues Addressed

- Cathode material needed to provides low polarization resistance below 700°C
- Results from LSCF-GDC suggest this is possible, but issues remain:
 - LSCF-YSZ reactions
 - Long-term stability of porous structure
 - Manufacturable cathode process needed
- More basic data needed

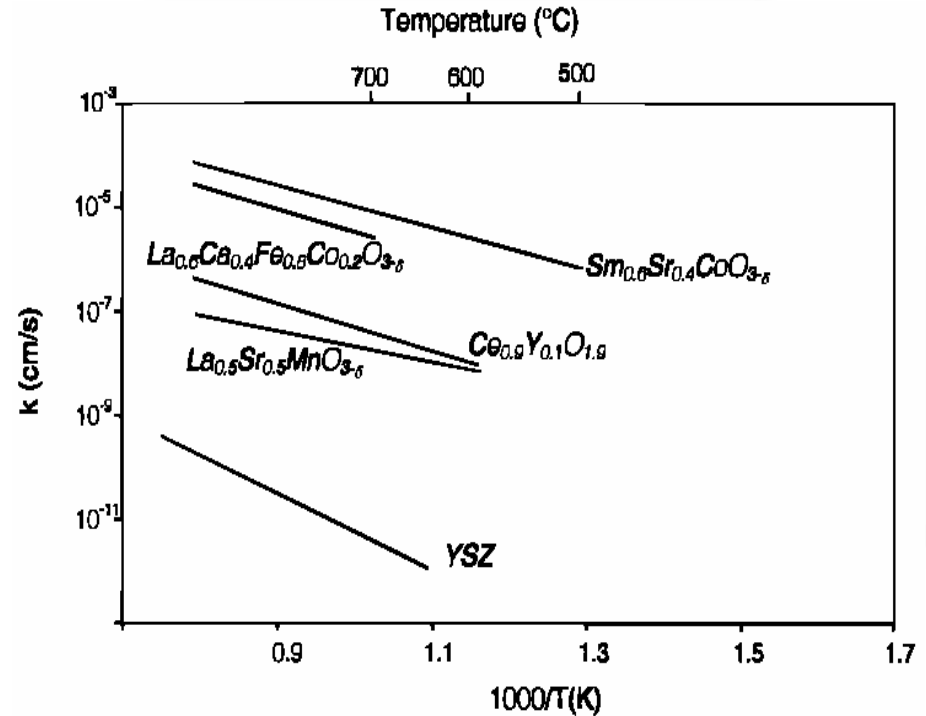
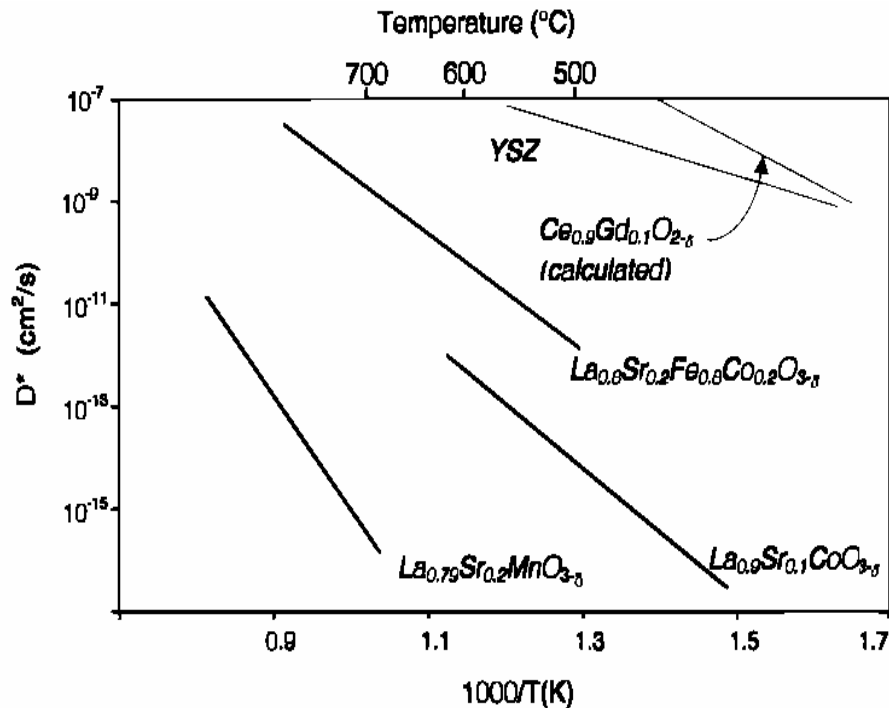
Mixed-Conducting Cathodes

- In LSCF, reaction zone is extended beyond three-phase boundaries
- $R_{\text{chem}} = (RT/2F^2)[\tau/(1-\varepsilon)aC_o^2D^*k]^{1/2}$
 - τ = tortuosity = 1.5
 - ε = fractional porosity = 0.3
 - a = surface area/volume = 20,000 cm⁻¹
 - C_o = oxygen concentration = 0.09 mol cm⁻³
 - D^* = oxygen bulk diffusion coefficient
 - k = surface exchange coefficient

Steele, et al. Solid St. Ionics 135 (2000) 445

- Cathodes should have large D^* , k , and a , along with good electronic conductivity

Electrode Data



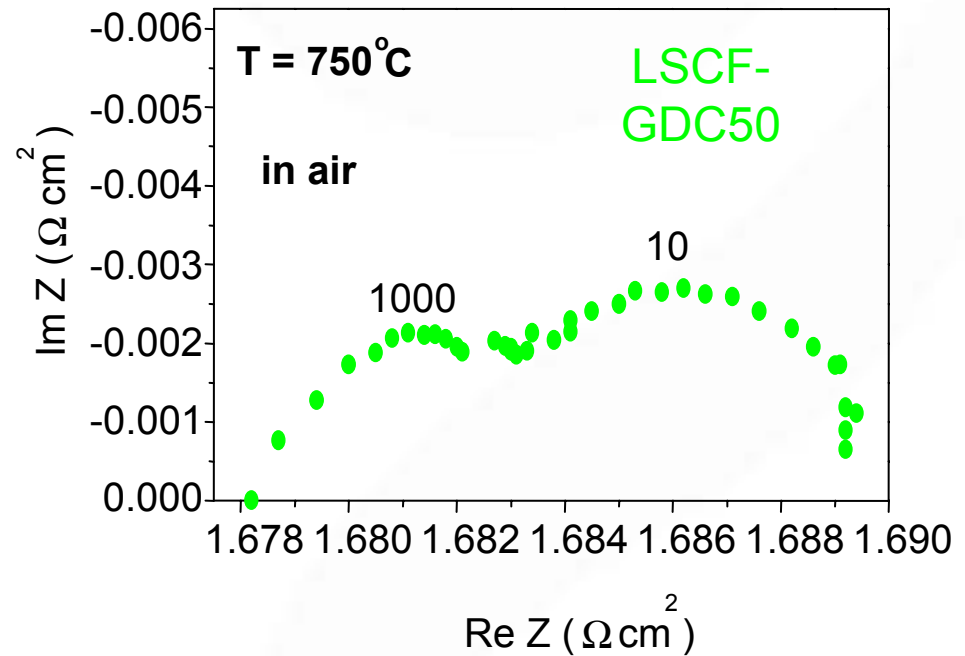
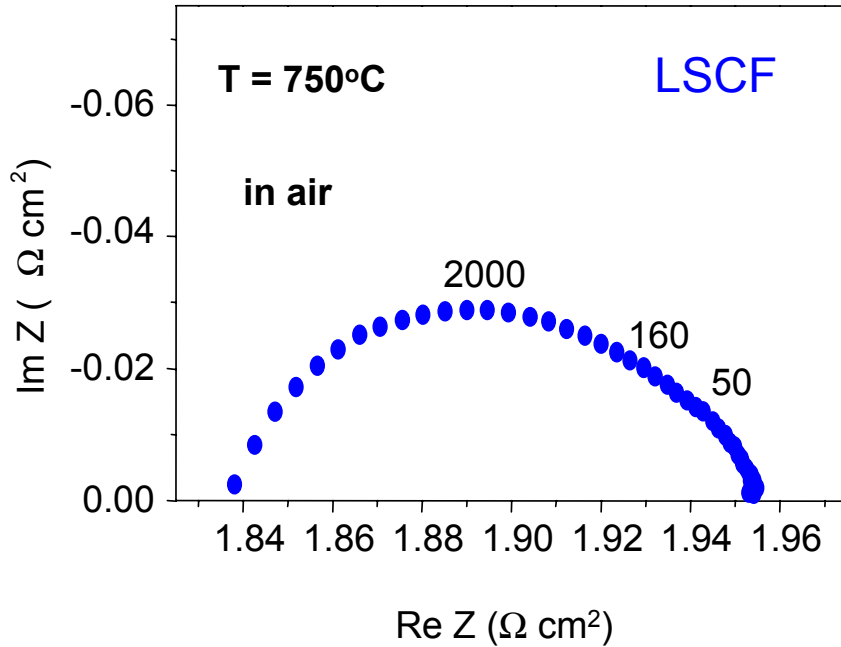
- Co-based cathodes most desirable e-conductors, but D^* and k not large enough below 700°C
- Not as good oxygen diffusivity as Ceria

Doshi et al., J. Electrochem. Soc. 146 (1999) 1273.

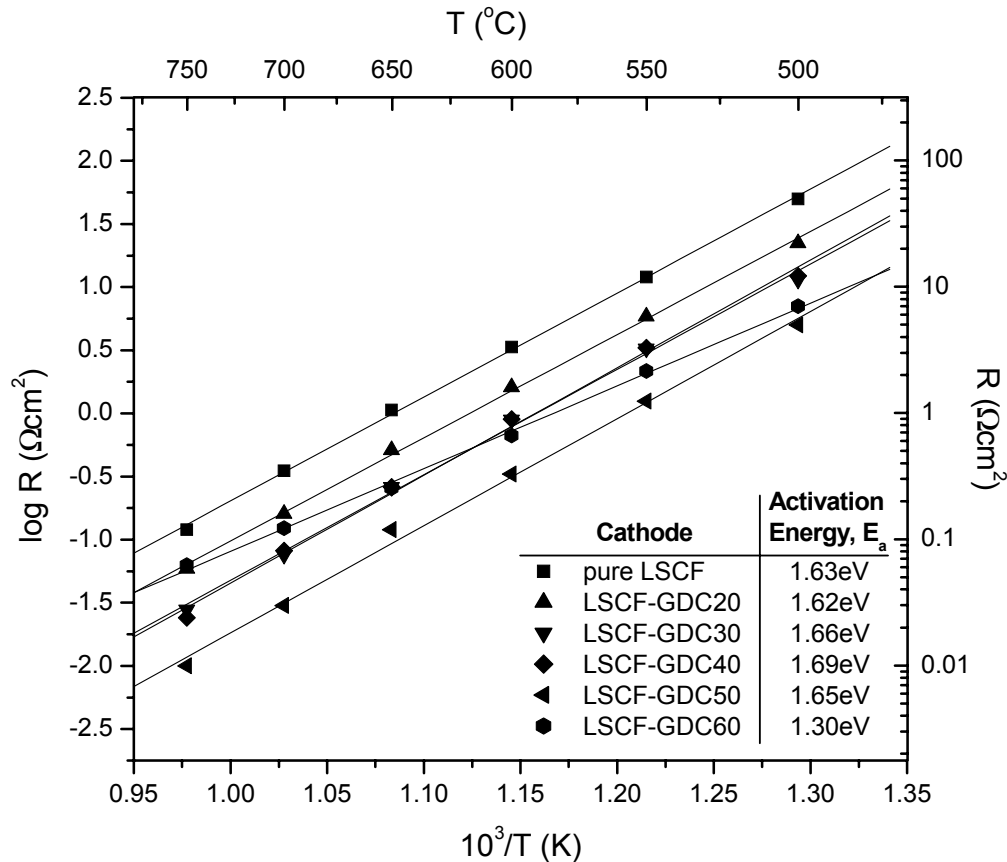
LSCF-GDC Composites

- Composite combines:
 - High k of LSCF
 - High D^* of GDC
- No reactions/interdiffusion between LSCF and GDC
- GDC can be used to separate LSCF and YSZ, avoiding reactions

Impedance Spectra: LSCF-GDC



LSCF-GDC on YSZ



- Spin coating
- Lowest polarization resistance at 50% GDC
 - $0.3 \Omega\text{cm}^2$ at 600°C
 - $0.03 \Omega\text{cm}^2$ at 700°C
 - 100 times better than LSM
 - 10 times better than LSCF

Murray and Barnett, Solid St. Ion. 148, (2002) 27



R&D Objectives

- Determine electrochemical reaction kinetics
 - Surface exchange rate, oxygen diffusivity
 - Structural effects: surface reactions versus 3-phase boundaries
- Determine effectiveness of GDC interlayer to prevent LSCF-YSZ reactions
 - GDC interlayer
- Determine long-term stability of porous LSCF-GDC

R&D Approach

- Mechanisms: impedance spectroscopy and modeling with idealized LSCF on GDC
 - Surface oxygen exchange, oxygen diffusivity
- LSCF-YSZ reactions:
 - XRD, microscopy, long-term tests
- Microstructure effects:
 - Initial work: develop screen printing process
 - LSCF versus LSCF-GDC
 - GDC interlayers
 - SEM/EDX, impedance spectroscopy, cell tests
- Stability: accelerated testing and modeling with cell testing

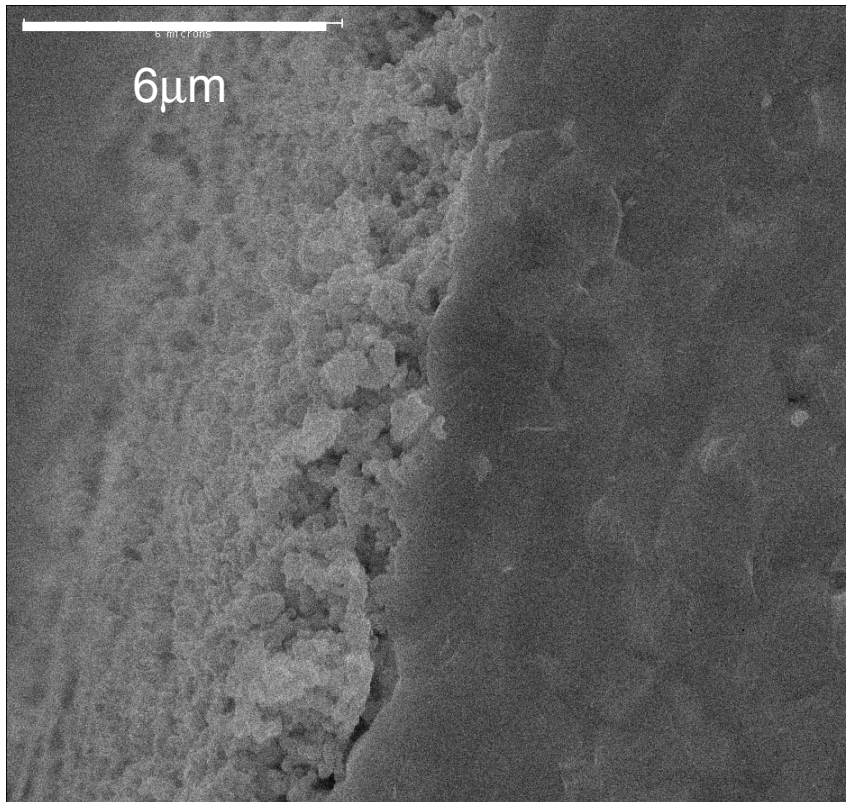
Results to Date

- LSCF layers by spray coating
- Screen printed LSCF-GDC electrodes
- Structure characterization
- Impedance spectroscopy

“Idealized” Electrodes

- Attrition milled powder
- $\text{La}_{0.6} \text{Sr}_{0.4} \text{Co}_{0.2} \text{Fe}_{0.8} \text{O}_{3-\delta}$
- Sprayed colloidal suspension with low solid loading
- Symmetrical cathodes on YSZ single crystals
- Spray coating layers thickness ranging 300nm to 30 microns.
 - Initial results showed porous layers
 - More work needed to achieve dense layers

Cross-Sectional SEM Images



- Layers not dense
- Apply ALS model to obtain basic data
- Estimate porosity, surface area from images
- In upcoming work, will utilize higher sintering temperature to obtain dense layers.

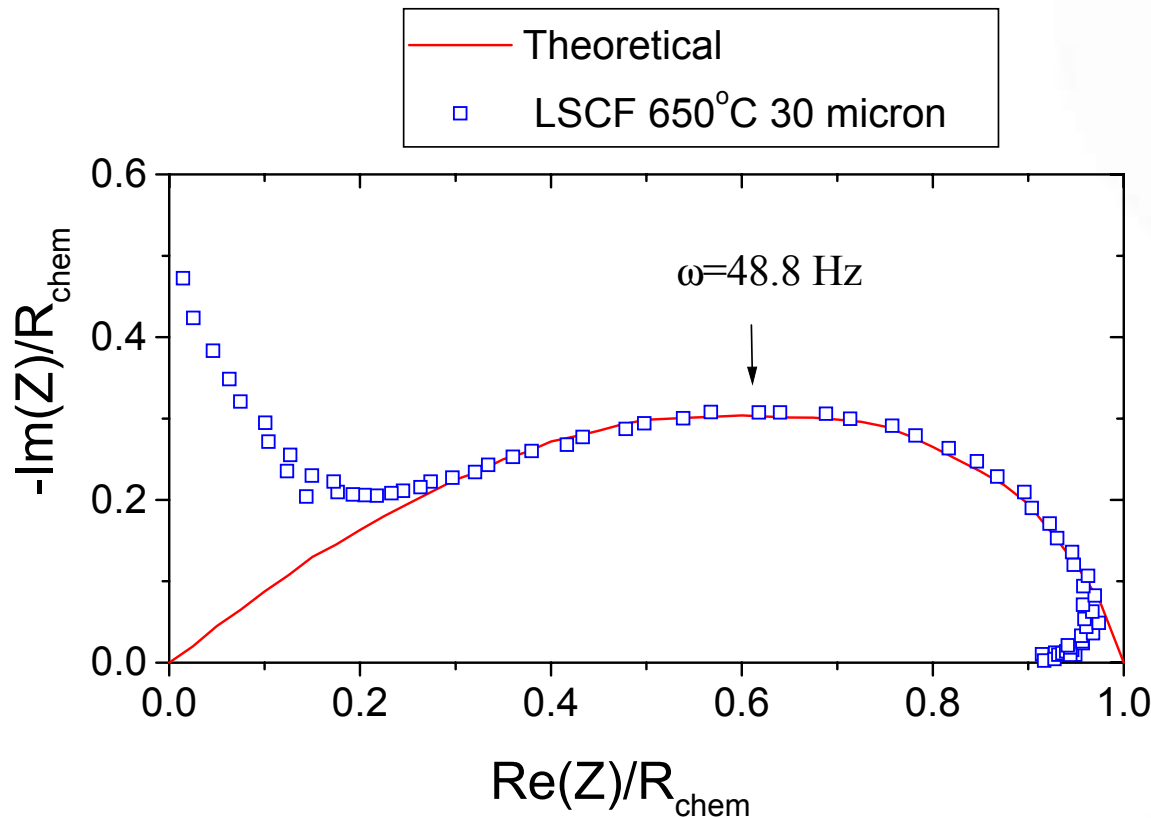
Analysis Using ALS Model

- $Z_{\text{chem}} = R_{\text{chem}}(1 + j\omega t_{\text{chem}})^{-1/2}$
- $R_{\text{chem}} = (RT/2F^2)[\tau/(1-\varepsilon)aC_o^2D^*k]^{1/2}$
- $t_{\text{chem}} = (1-\varepsilon)/Aak$
 - τ = tortuosity = 1.5
 - ε = fractional porosity = 0.3
 - a = surface area/volume = 20,000 cm⁻¹
 - C_o = oxygen sites concentration = 0.001 mol cm⁻³
 - D^* = oxygen bulk diffusion coefficient
 - k = surface exchange coefficient
 - A = 1/4 ~1/8

Adler et al. J Electrochem. Soc. 143, (1996) 3554

Steele, et al. Solid St. Ion. 135 (2000) 445

Fits To Impedance Arcs



- Thick LSCF Films (30 micron)
- Relatively Good agreement with ALS model
- $D^* \sim 1 \cdot 10^{-8}$ and $k \sim 1 \cdot 10^{-5}$ assuming $\varepsilon \sim 0.3$ and $a \sim 2 \cdot 10^5$
- High Frequency arc interferes with left hand side of arc

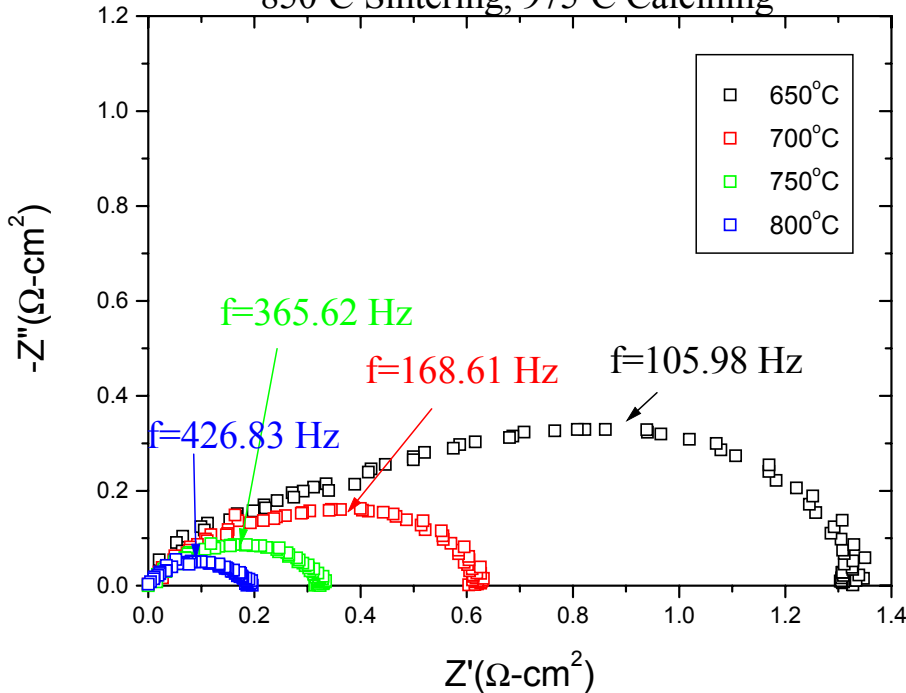
Screen Printing

- Powder processing
 - Mix as-received powders
 - Attrition mill mixed powders
 - Calcine at various temperatures
- Mix with vehicle in three-roll mill
- Print
- Sinter at various temperatures

Impedance Spectroscopy

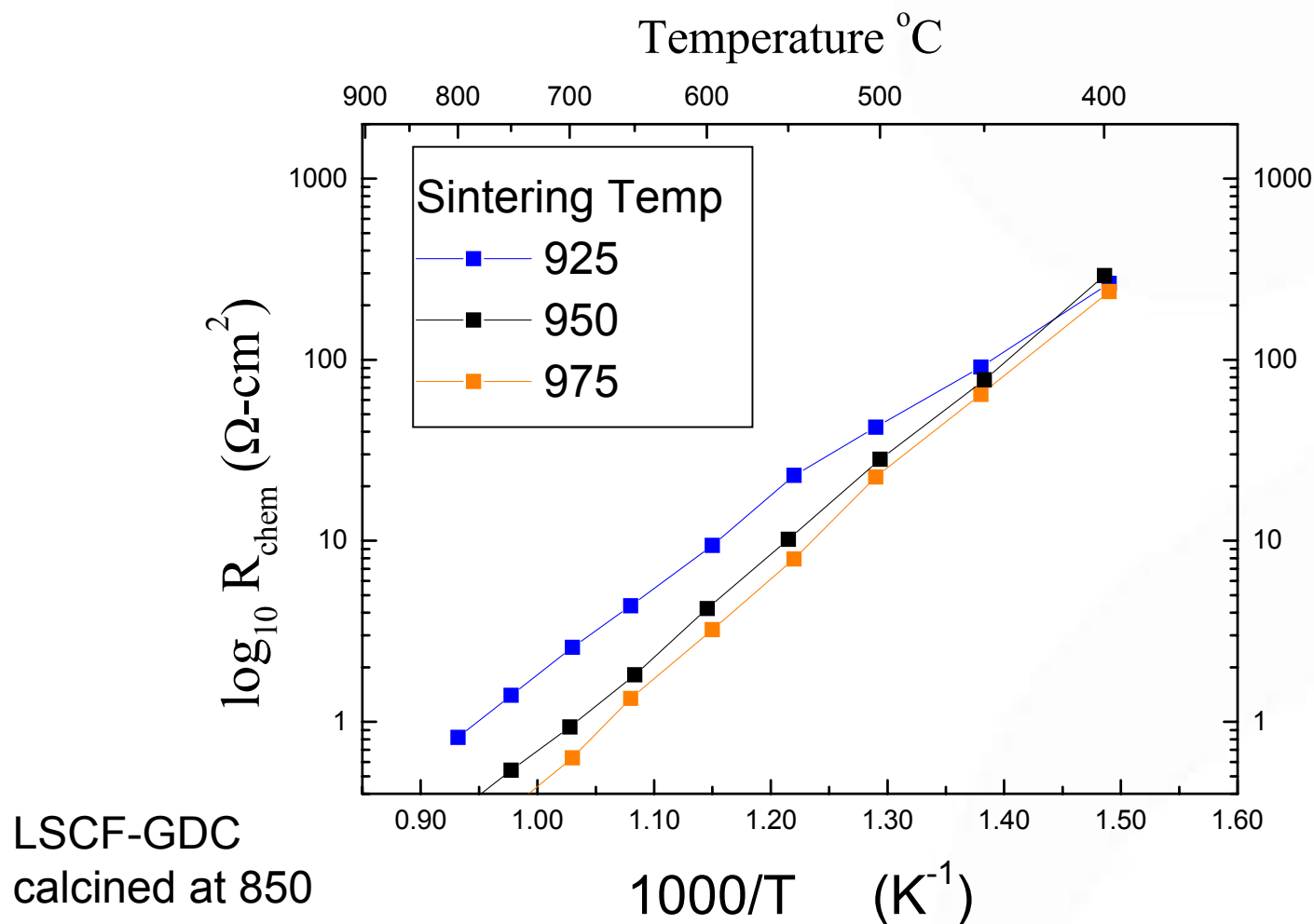
LSCF-GDC

850°C Sintering, 975°C Calcining

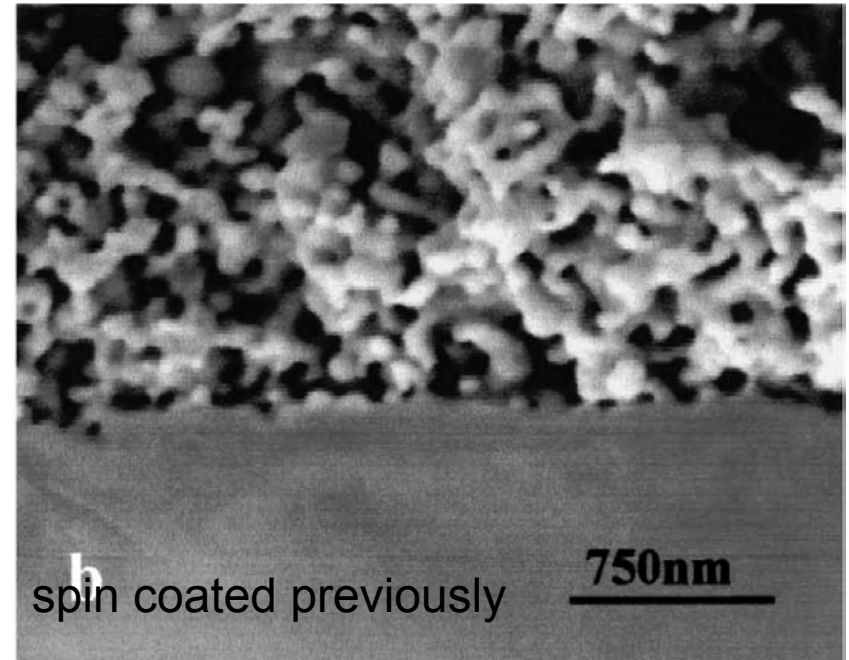
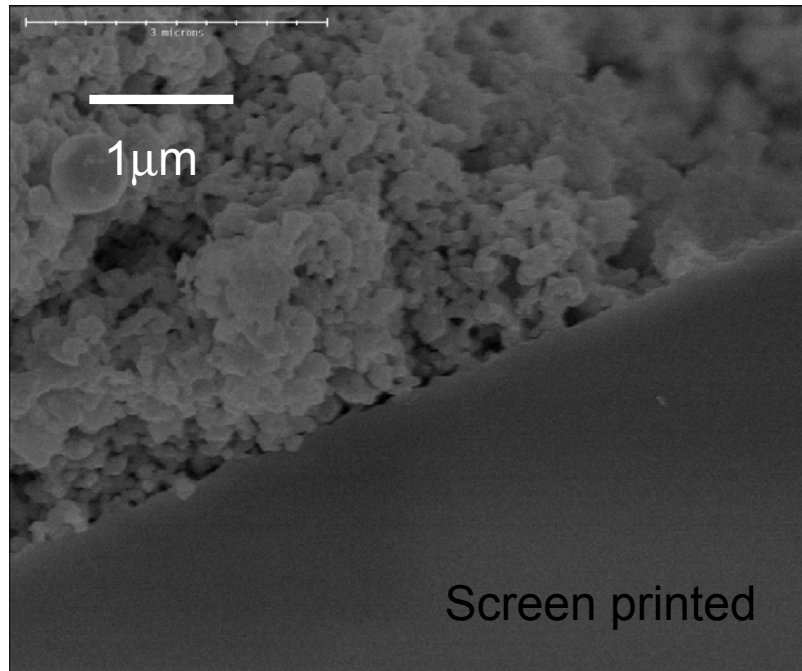


- “Gehrischer”-type arc at lower T, symmetric at higher T
- Strong T dependence agrees with prior work
- Best results thus far
 - Polarization resistance higher than prior reports
 - More work needed

Impedance Spectroscopy: Effect of Sintering Temperature

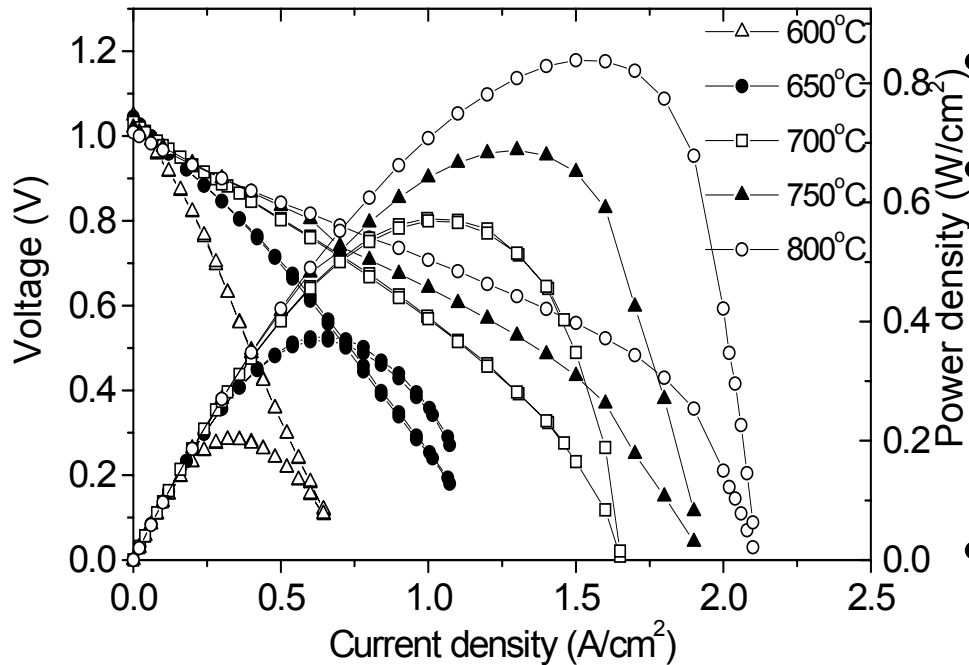


Cross-Sectional SEM Images



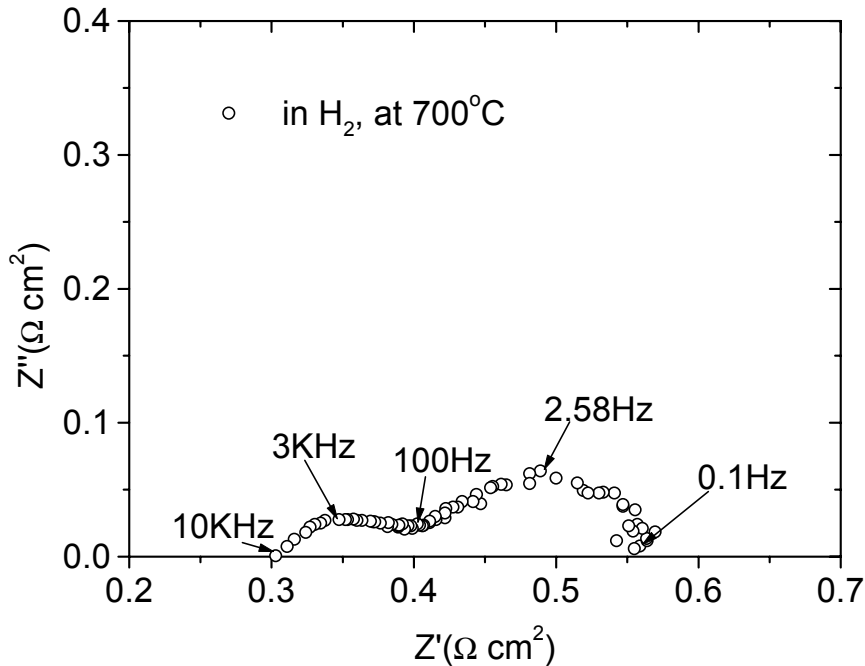
- Calcined at 850°C Screen Printed and sintered at 950°C
- Non- homogeneous, Interfaces are not well connected (higher temp sintering resulted lower impedance.)
- 750°C calcined sample showed more agglomeration, indicating that milling and powder processing appears to have dominant effects.

Cell Testing



- LSCF-GDC cathode
- Anode-supported cell
- Relatively good power density at $<700^{\circ}\text{C}$
 - 0.2 W/cm^2 at 600°C
 - 0.35 W/cm^2 at 650°C
- Limiting current at high T due to anode

Impedance During Cell Test

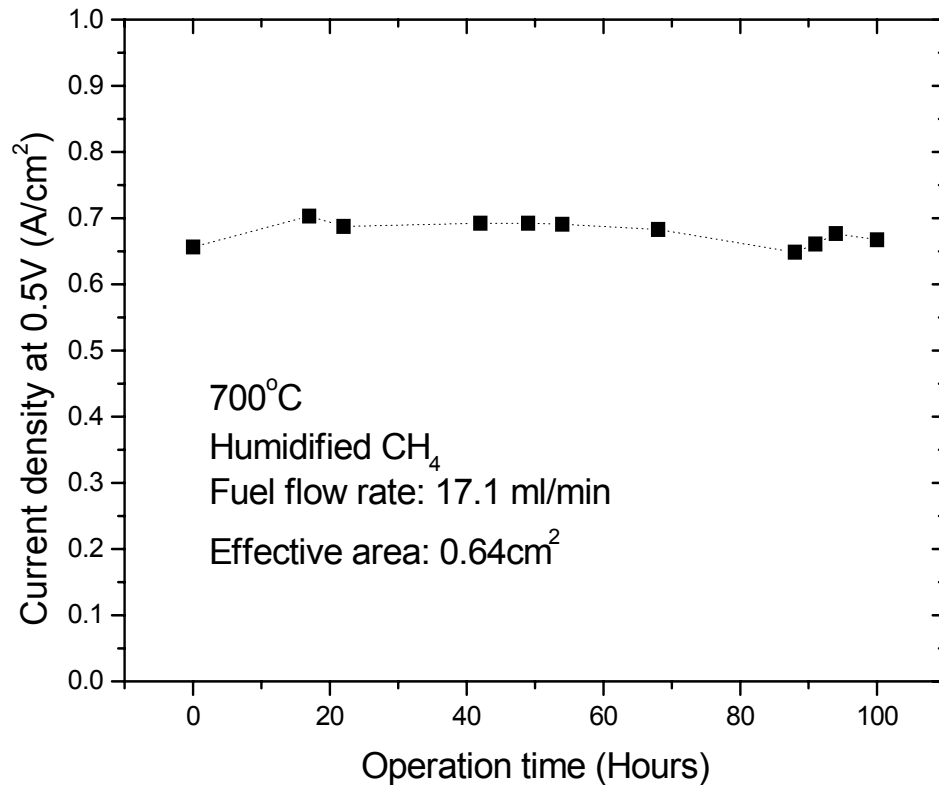


- LSCF-GDC cathode arc at low frequency
 - $\sim 0.2 \Omega \text{ cm}^2$ at 700°C
 - Larger than prior report: $0.03 \Omega \text{ cm}^2$ at 700°C

Murray and Barnett, Solid St. Ion. 148, (2002) 27

- Screen printed cathode structure needs to be improved

Cell Stability



- LSCF-GDC cathode stable over 100 h
- Accelerated testing planned

Applicability to SOFC Commercialization

- LSCF-GDC have potential to maintain high SOFC power density below 700°C
 - Reduced problems with metallic interconnect
 - Less sensitivity of LSCF to Cr poisoning than LSM – Tokyo Gas study (2000)
 - Reduced balance of plant cost
- Screen printing process being developed is readily scalable, low-cost
 - Currently used by some Industrial Teams
 - Easy to replace LSM-YSZ in anode-supported cells

Activities for the next 6-12 Months

- Improve processing conditions to obtain dense LSCF
 - Obtain high quality oxygen surface exchange and diffusivity data
- Optimization of processing conditions of screen printed LSCF-GDC
- Effect of cathode structure on polarization resistance
 - LSCF versus LSCF-GDC
 - GDC interlayers
 - Particle size effects
 - SEM/EDX, impedance spectroscopy, cell tests
- Long-term stability:
 - Look for LSCF-YSZ reactions, structural changes
 - Accelerated testing combined with modeling