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

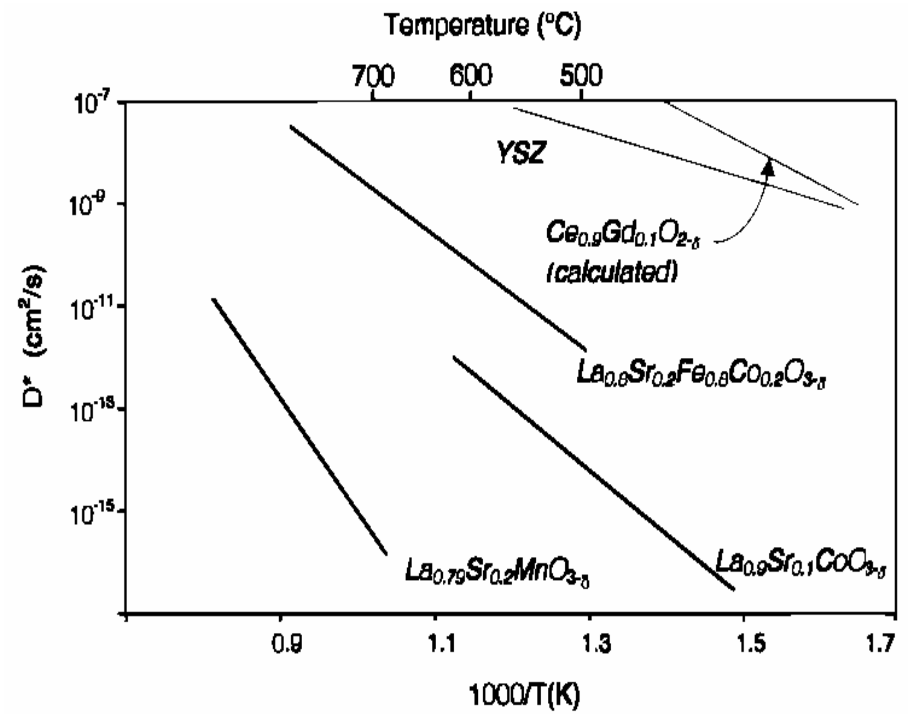
- Cathode material needed to provides low polarization resistance below 700°C
- Results from LSCF-GDC suggest this is possible, but issues remain:
  - LSCF-YSZ reactions
  - Long-term stability of porous structure
  - Manufacturable cathode process needed
- More basic data needed

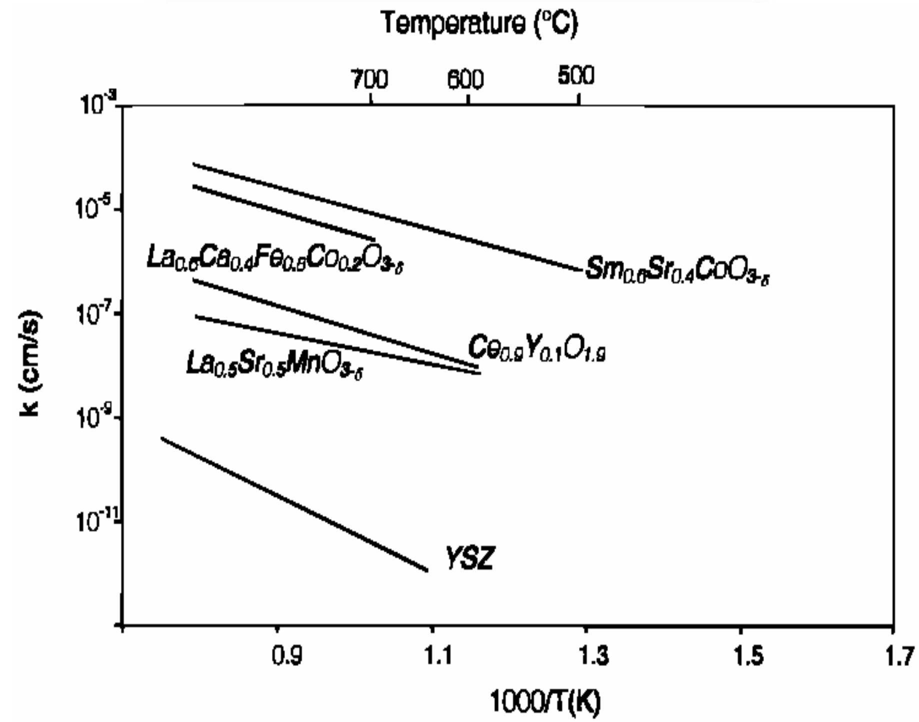
Mixed-Conducting Cathodes

- In LSCF, reaction zone is extended beyond three-phase boundaries
- $R_{chem} = (RT/2F^2)[\tau/(1-\varepsilon)aC_o^2D^*k]^{1/2}$
  - τ = tortuosity = 1.5
  - ε = fractional porosity = 0.3
  - a = surface area/volume = 20,000 cm^{-1}
  - C_0 = 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





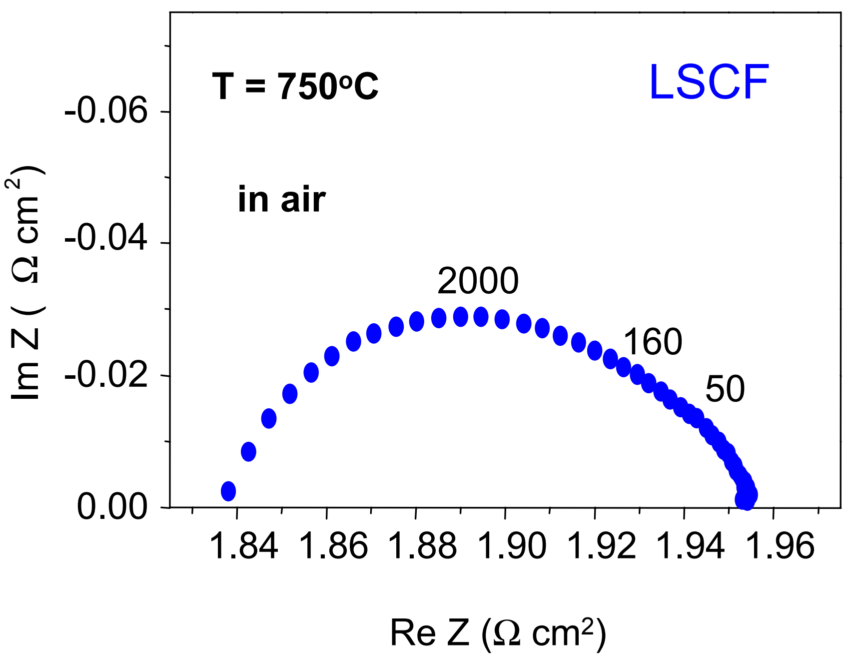
Doshi et al., J. Electrochem. Soc. 146 (1999) 1273.

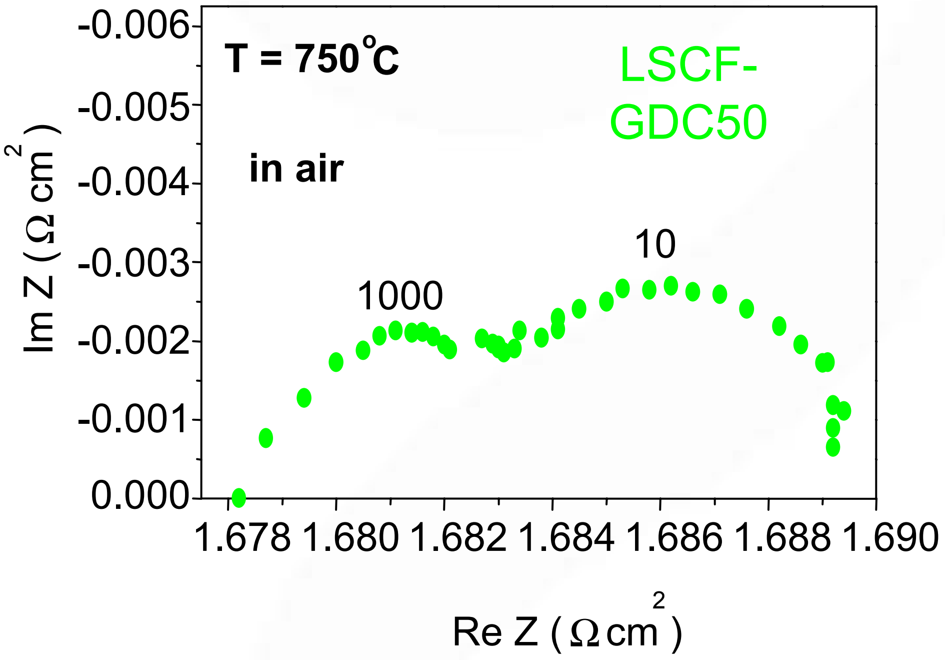
- Co-based cathodes most desirable e-conductors, but *D** and *k* not large enough below 700°C
- Not as good oxygen diffusivity as Ceria

LSCF-GDC Composites

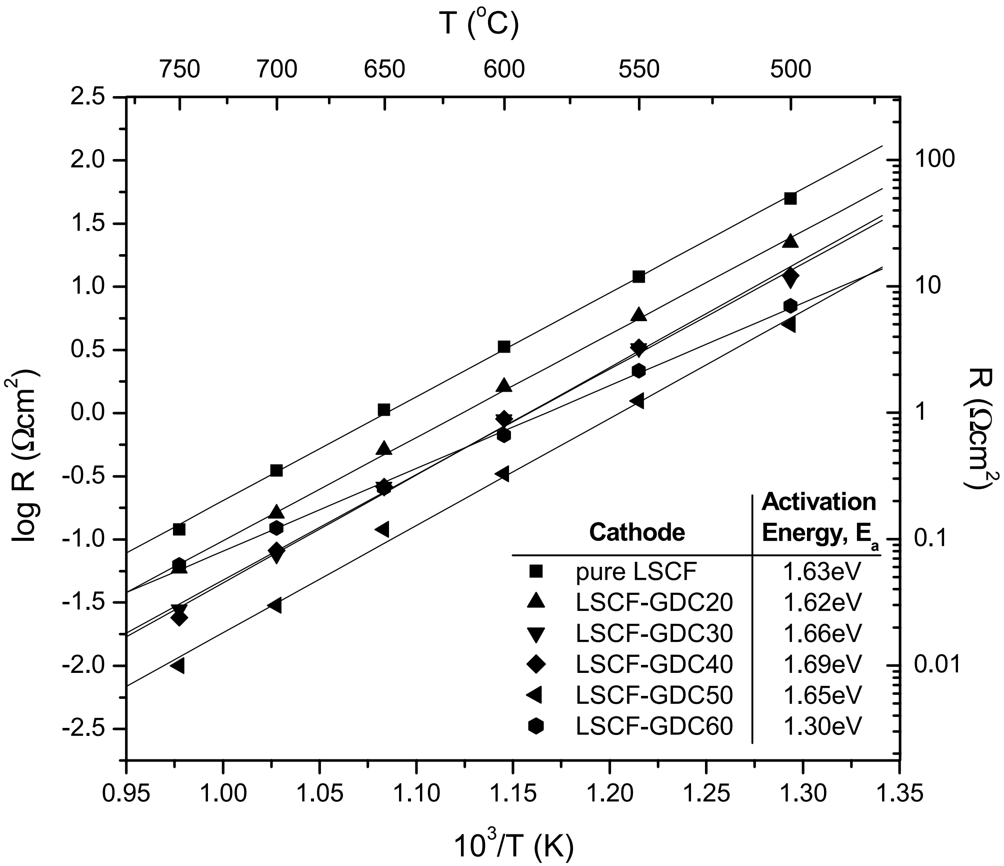
- Composite combines:
  - High k of LSCF
  - High D^* of GDC
- No reactions/interdiffusion between LSCF and GDC
- GDC can be used to separate LSCF and YSZ, avoiding reactions

Impedance Spectra: LSCF-GDC





LSCF-GDC on YSZ



- Spin coating
- Lowest polarization resistance at 50% GDC
  - 0.3 Ωcm^2 at 600 °C
  - 0.03 Ωcm^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

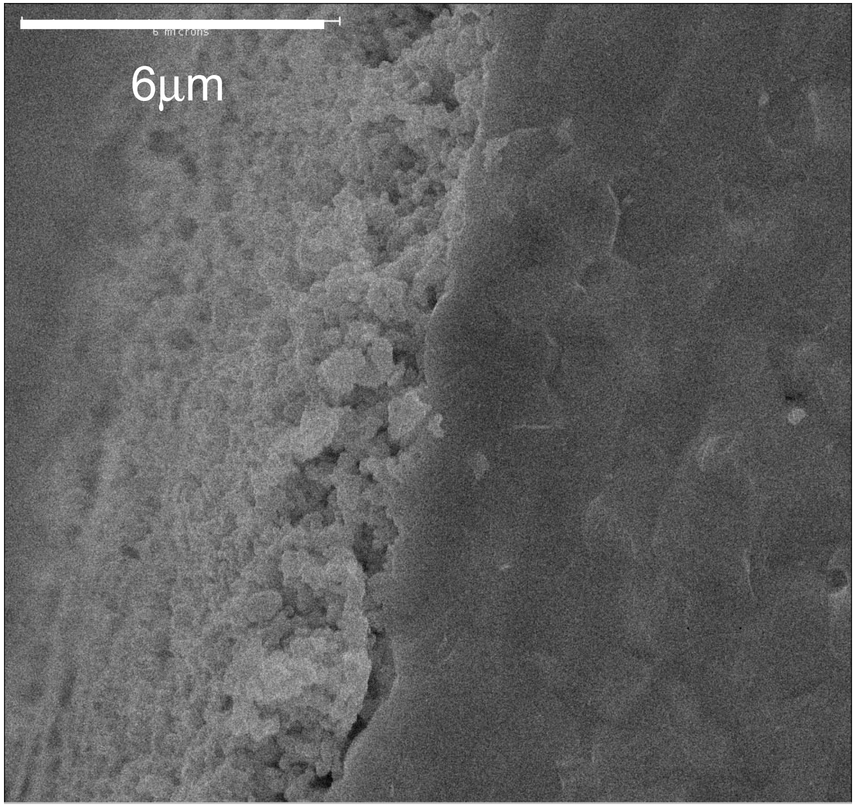
Results to Date

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

“Idealized” Electrodes

- Attrition milled powder
- $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
- 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.

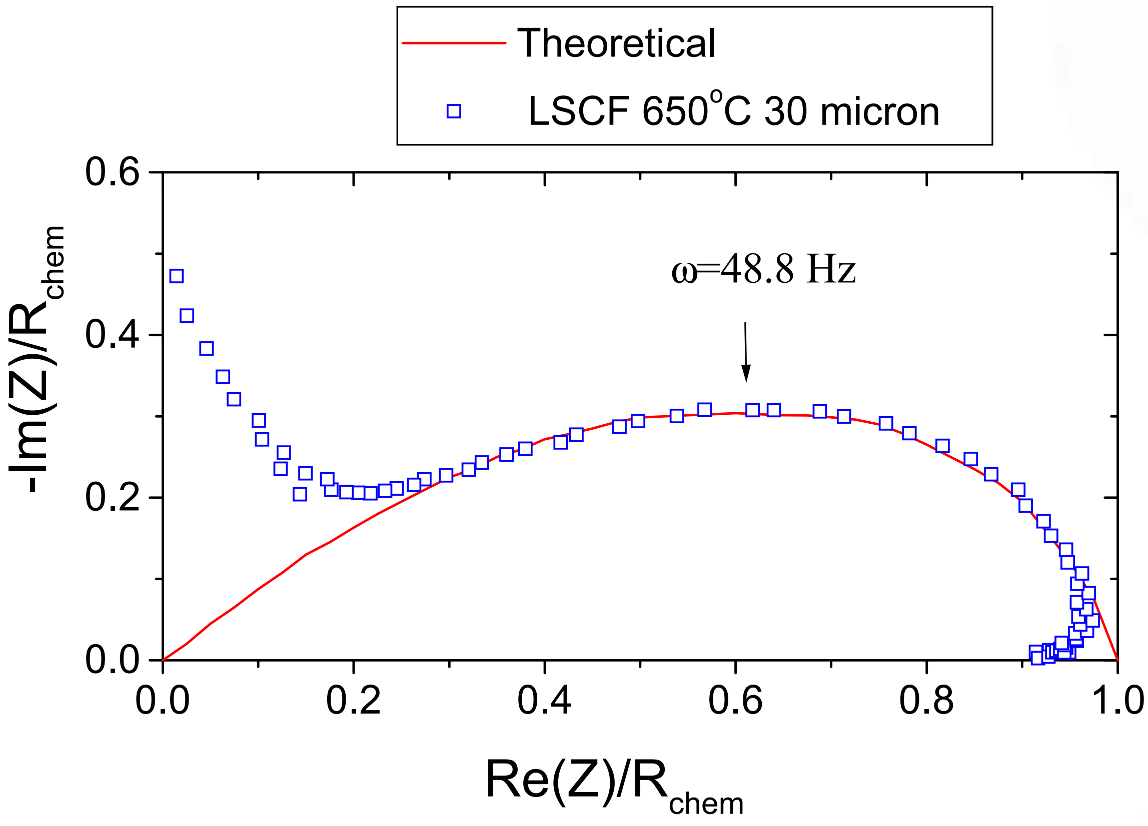
Analysis Using ALS Model

- $Z_{chem} = R_{chem}(1 + j\omega t_{chem})^{-1/2}$
- $R_{chem} = (RT/2F^2)[\tau/(1-\varepsilon)aC_o^2D^*k]^{1/2}$
- $t_{chem} = (1-\varepsilon)/Aak$
  - τ = tortuosity = 1.5
  - ε = fractional porosity = 0.3
  - a = surface area/volume = 20,000 cm^{-1}
  - C_0 = 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



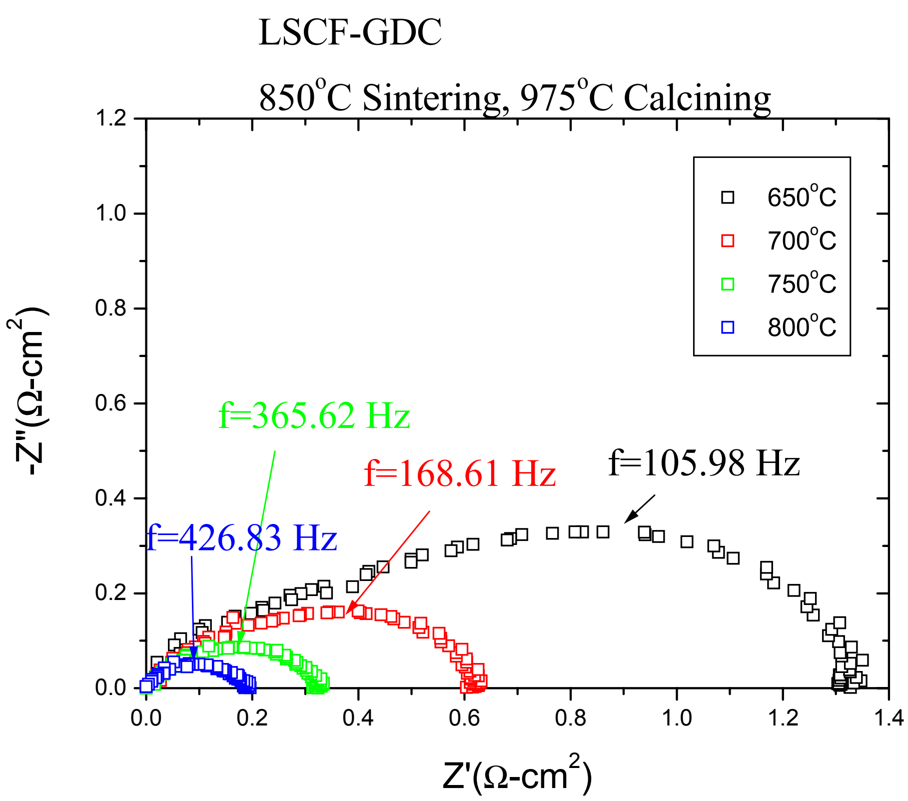
- Thick LSCF Films (30 micron)
- Relatively Good agreement with ALS model
- *$D^* \sim 1*10^{-8}$ and $k \sim 1*10^{-5}$ assuming $\varepsilon \sim 0.3$ and $a \sim 2x10^5$*
- High Frequency arc interferes with left hand side of arc

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

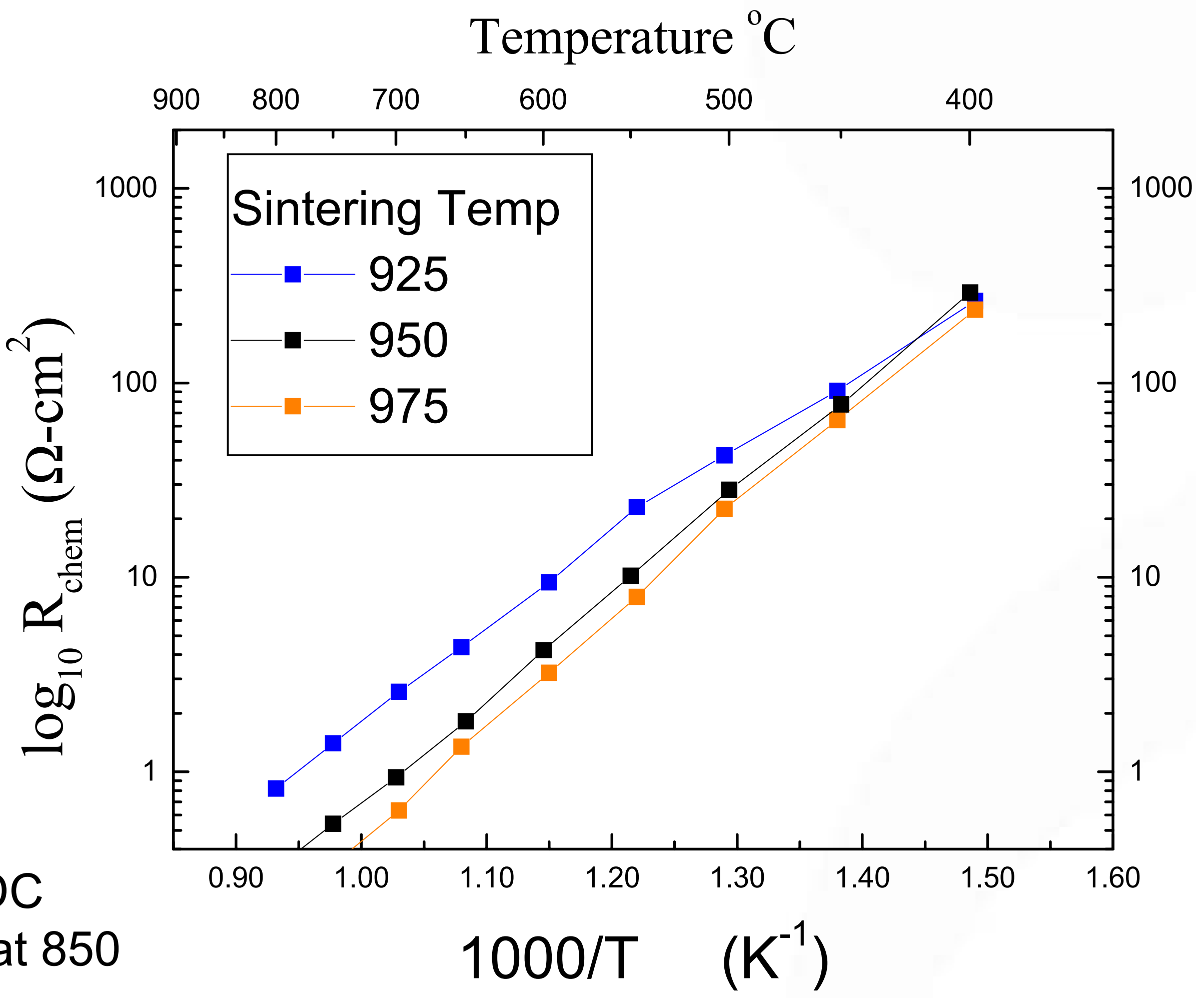
FCT

Impedance Spectroscopy



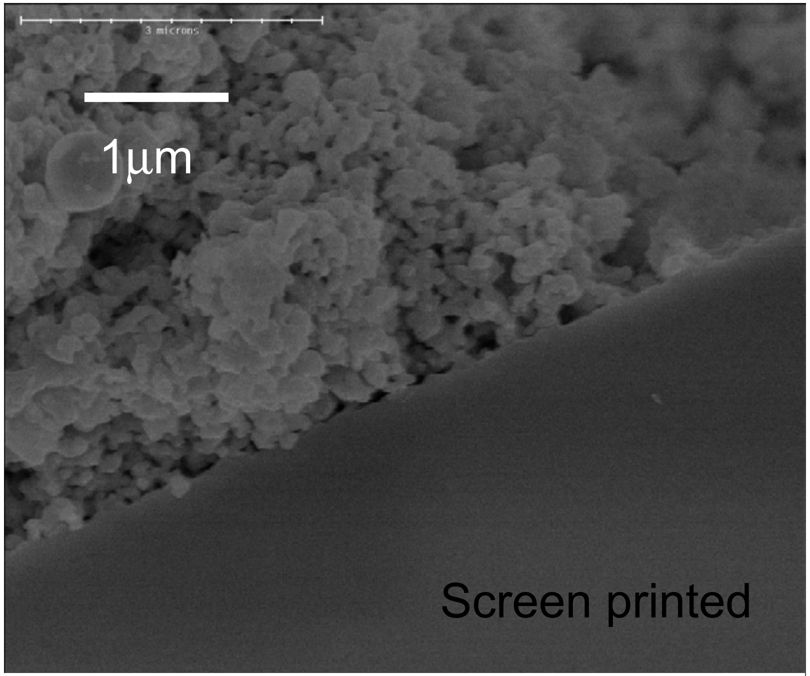
- "Gehrischer"-type arc at lower T, symmetric at higher T
- Strong T dependence agrees with prior work
- Best results thus far
  - Polarization resistance higher than prior reports
  - More work needed

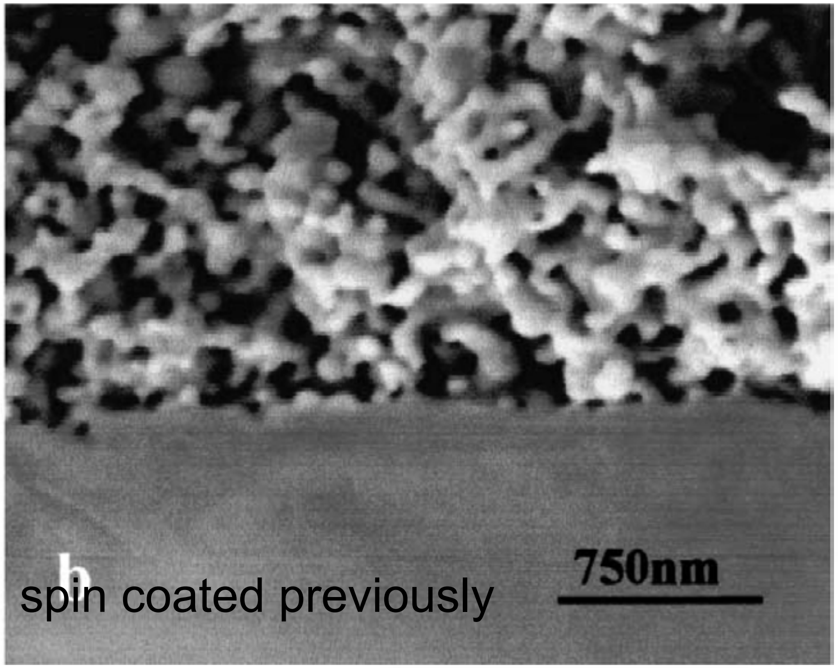
Impedance Spectroscopy: Effect of Sintering Temperature



LSCF-GDC
calcined at 850

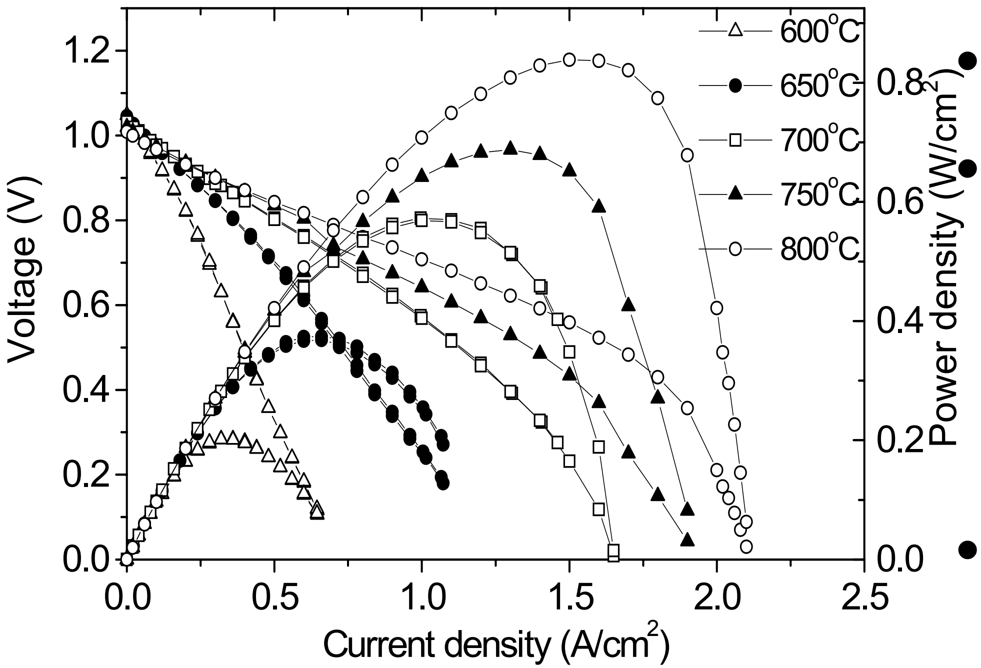
Cross-Sectional SEM Images





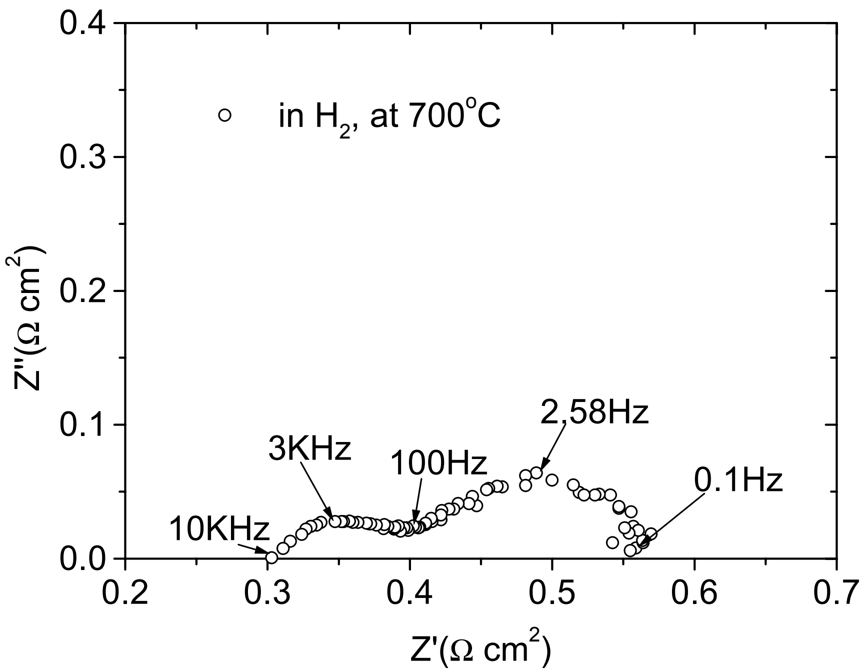
- Calcined at 850°C Screen Printed and sintered at 950°C
- Non- homogeneous, Interfaces are not well connected
  (higher temp sintering resulted lower impedance.)
- 750°C calcined sample showed more agglomeration, indicating that milling and powder processing appears to have dominant effects.

Cell Testing



- LSCF-GDC cathode
- Anode-supported cell
- Relatively good power density at <700 °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

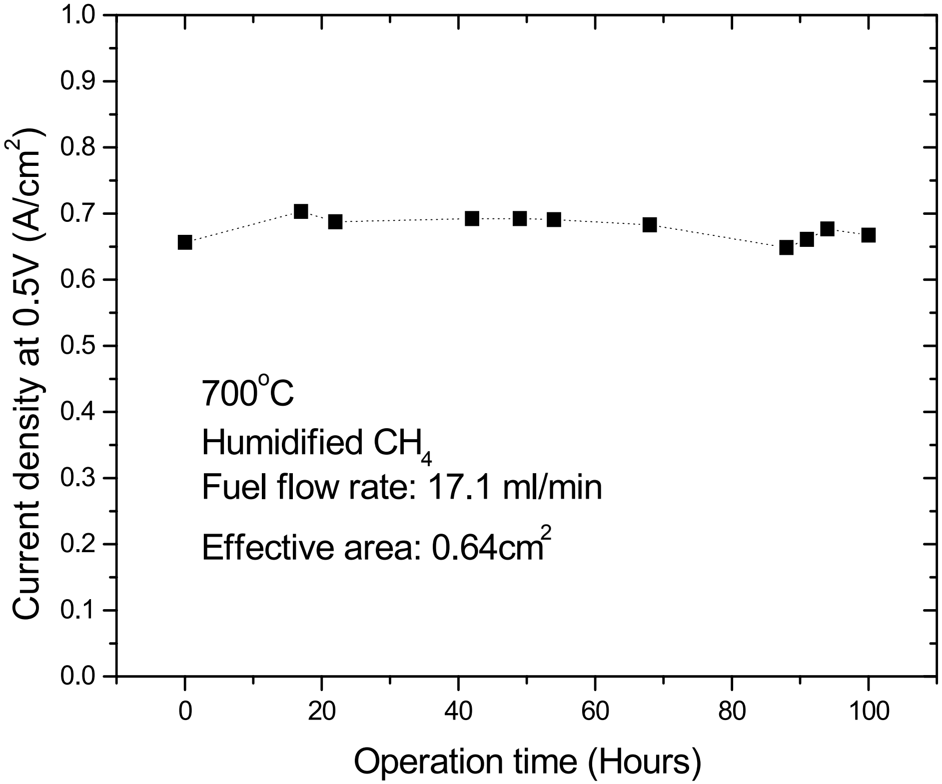


- LSCF-GDC cathode arc at low frequency
  - ~0.2 Ωcm^2 at 700°C
  - Larger than prior report: 0.03 Ωcm^2 at 700°C

  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