

**Overview of  
DOE Contract No.: DE-AC-26-99FT40710  
at University of Missouri-Rolla**

**Low Temperature Cathode Supported Electrolytes**

**Harlan U. Anderson (presenter)**

**Igor Kosacki**

**Vladimir Petrovsky**

**Wayne Huebner**

**Presented at  
SECA Core Technology Program  
Review Meeting at**

**Hyatt-Regency at Pittsburgh International Airport  
Pittsburgh, PA**

**November 16, 2001**

## **ACHIEVEMENTS – FY 1999-2000**

- Films of 16% Y:ZrO<sub>2</sub> Characterized
  - Ionic conductivity of <50 nm grain one micron thick films measured to room temperature (*conductivity of the grains dominates*).
  - Grain size <50 nm for annealing temperatures <800°C.
  - Produced >95% theoretical dense YSZ at 600°C.
- Films of Undoped and Gd Doped CeO<sub>2</sub> Characterized
  - The electrical conductivity of both doped and undoped CeO<sub>2</sub> show grain size dependence.
  - Ionic conductivity of nanocrystalline Gd doped CeO<sub>2</sub> less than that of the microcrystalline.

## **ACHIEVEMENTS – FY 2000-2001**

- Films of 16% Sc:ZrO<sub>2</sub> Characterized
  - The ionic conductivity is about one order of magnitude higher than YSZ.
  - Electronic Conductivity becomes significant for oxygen activity less than 10<sup>-14</sup> atm.
- Developed Cathode Substrate for Deposition of 0.5 to 2 Micron Thick YSZ Films for Use as Electrolyte in SOFCs
  - Fabricated porous LSM substrates
  - Synthesized nanoscale CeO<sub>2</sub> suspensions for deposition onto LSM substrate
    - Control of cathode surface porosity to sizes <0.1 micron
    - 3-5 micron thick CeO<sub>2</sub> layers planarize LSM substrate to surface roughness <0.1 micron.
    - Developed a graded LSM substrate

- Developed a process by which 1-5 $\mu$ m thick electrolyte layers can be produced on dense and porous substrate without shrinkage.
- Improved Clean Room (*in order to make electrolyte of areas larger than 0.2 cm<sup>2</sup> our existing clean room must be improved*)
  - o Doubled size.
  - o More filters and air flow.
  - o This was completed March 1, 2001.

## **Research Planned for FY 2001-2002**

- Continue Optimization of the Cathode Substrate.  
Evaluate:
  - The influence of porous  $\text{CeO}_2$  layer on SOFC performance.
  - The influence of the addition of LSCF into  $\text{CeO}_2$  layer on SOFC performance.
  - The influence of the conductivity of the  $\text{CeO}_2$  layer on SOFC performance.
- Make Single Cell Fuel Cell Measurements
  - Cell performance as a function of electrolyte thickness and temperature.
    - YSZ electrolyte
    - $\text{CeO}_2$  electrolyte
  - Cell performance as a function of electrode composition.
    - Anode
    - Cathode

- Continue Studies Related to Placing Thin Electrolyte Films onto Porous Substrates
  - Polymer precursor onto a graded substrate.
  - Transfer of dense films to a porous substrate.
  - Nanocrystalline/polymer precursor composites.



## Thin Film Processing

### Water Soluble Salts

- ♦ *Zr chloride*
- ♦ *La carbonate*
- ♦ *Co nitrate*
- ♦ *Ce nitrate*
- ♦ *Y nitrate*
- ♦ *Sr carbonate*
- ♦ *Fe nitrate*

### Precursor Preparation

- ♦ *H<sub>2</sub>O*
- ♦ *Nitric acid*
- ♦ *Ethylene glycol*
- ♦ *Citric acid*

*Rheological  
Characterization*

### Spin Coating

- ♦ *Brewer Science Spin-coater*
- ♦ *Class 100 clean room*
- ♦ *0-6000 rpm*

### Baking

- ♦ *Hot plate:  $\pm 1^{\circ}\text{C}$  uniformity*
- ♦ *320°C - 2 min*

*Repeat*

### Crystallization

- ♦ *400-1000°C*

*Electrical  
Characterization*

*Microstructural  
Characterization*

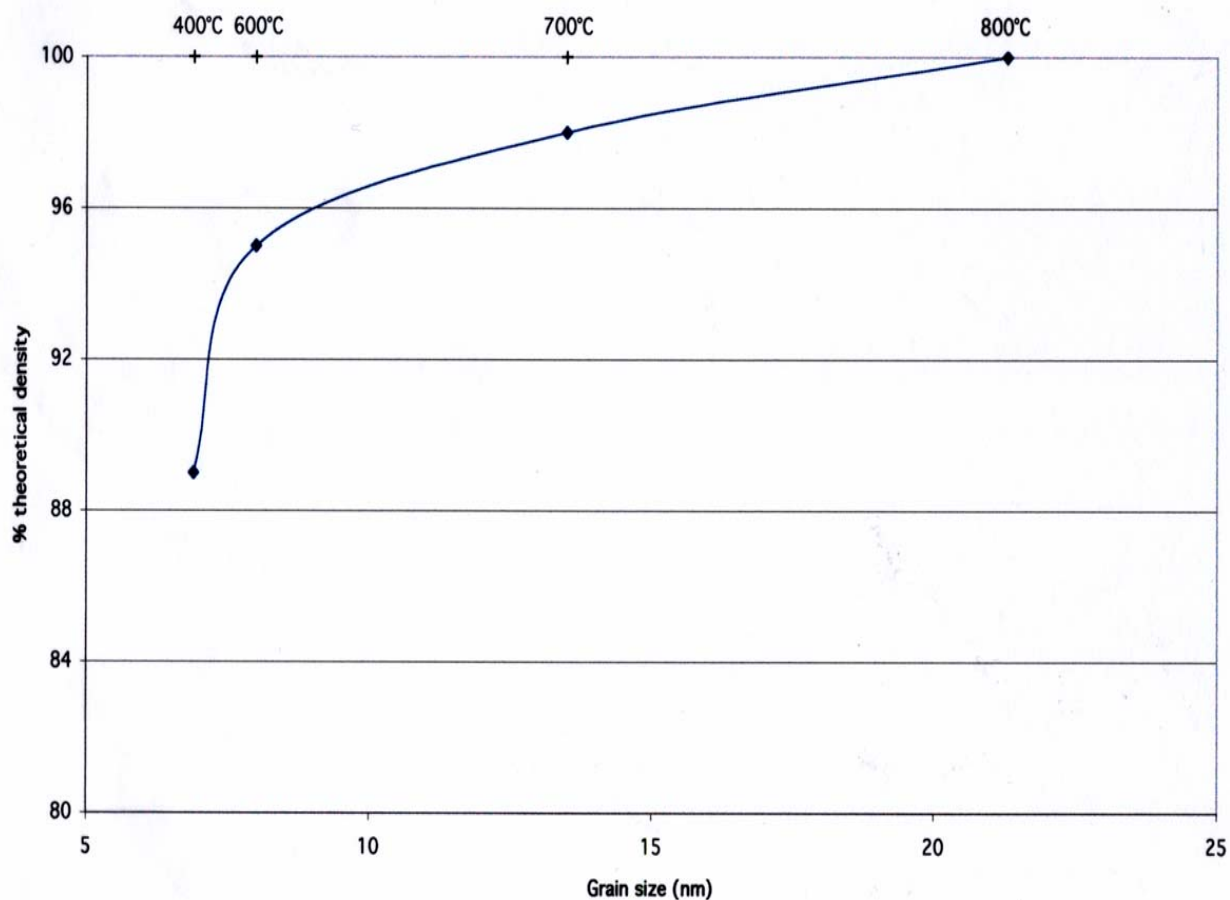


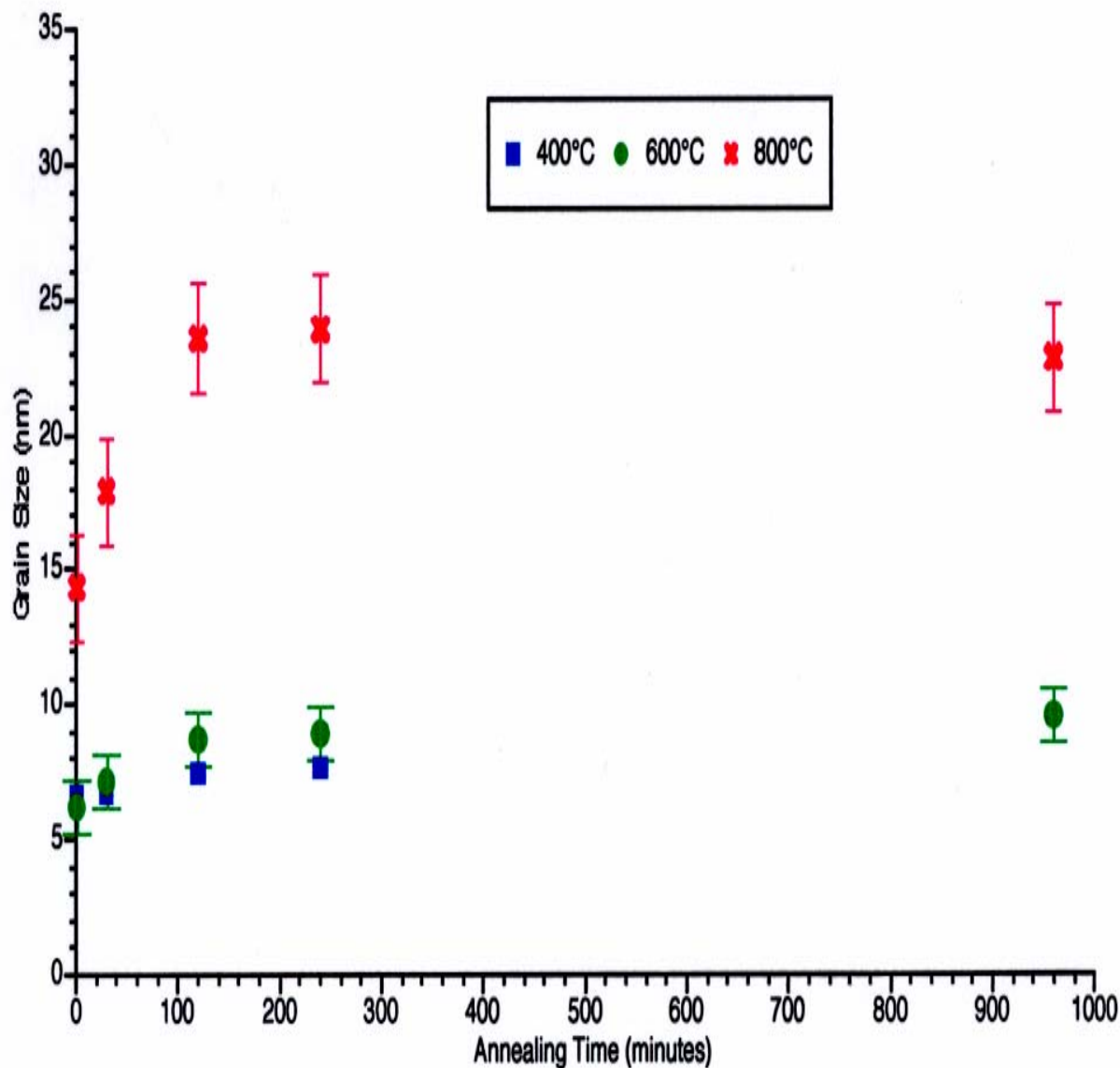


**YSZ thin film annealed at 400°C for 2 hrs.  $d_g = 6\text{nm}$**

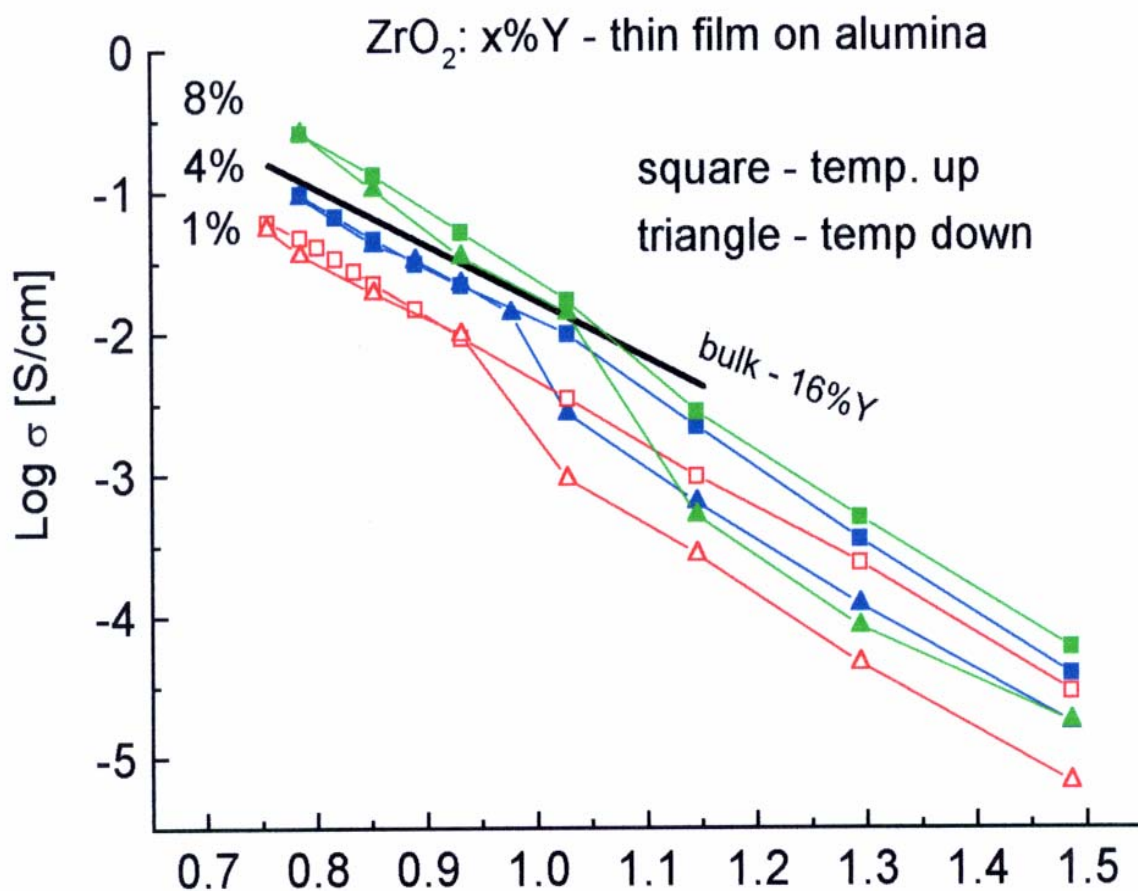


## Optical Density of YSZ thin Films on Si Substrates





Grain size versus time for unsupported YSZ thin films at different annealing temperatures.

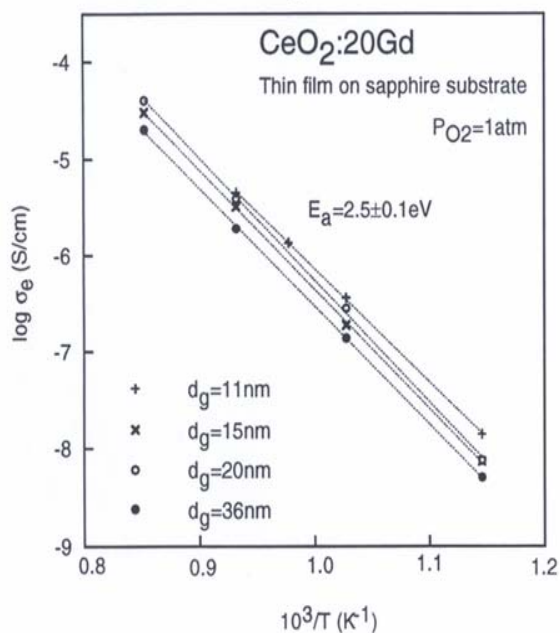


- **Films of Undoped and Gd Doped  $\text{CeO}_2$  Characterized**
  - **The electrical conductivity of both doped and undoped  $\text{CeO}_2$  show grain size dependence**
  - **Ionic conductivity of nanocrystalline Gd doped  $\text{CeO}_2$  less than that of the microcrystalline**
  - **Electronic conductivity enhanced as grain size decreases below 50 nm**

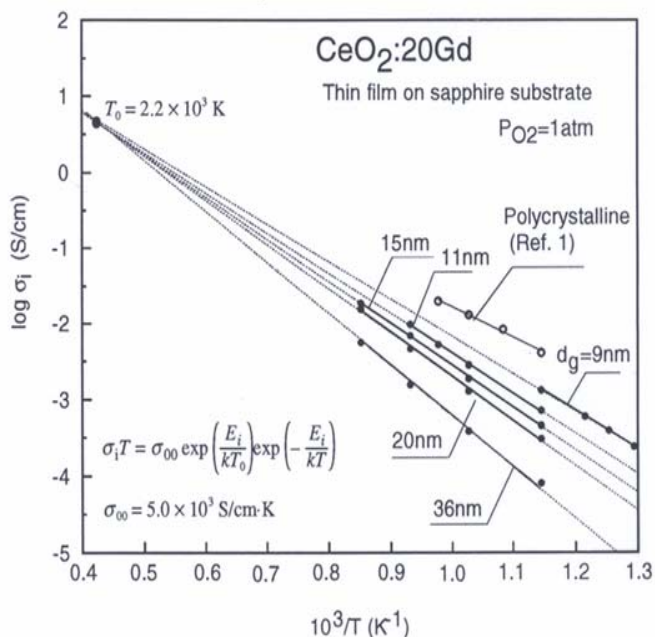


## Electronic & Ionic Conductivity of CeO<sub>2</sub>:20Gd

Electronic conductivity



Ionic conductivity



$\sigma_i \text{ (microcrystalline)} > \sigma_i \text{ (nanocrystalline)}$

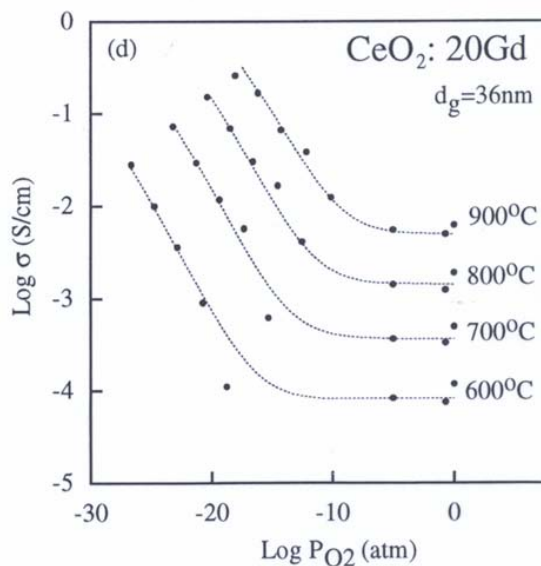
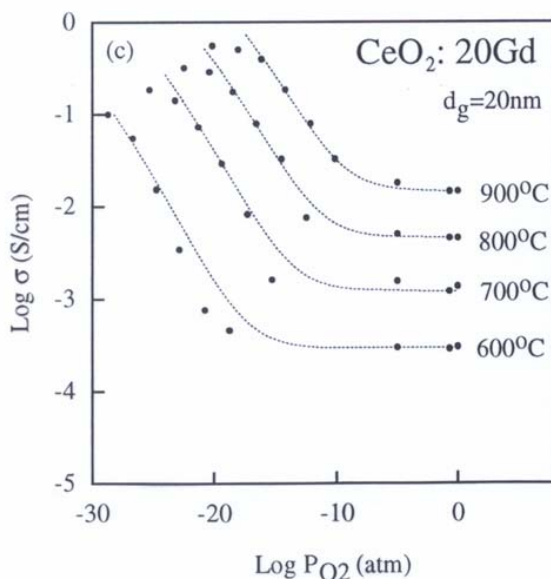
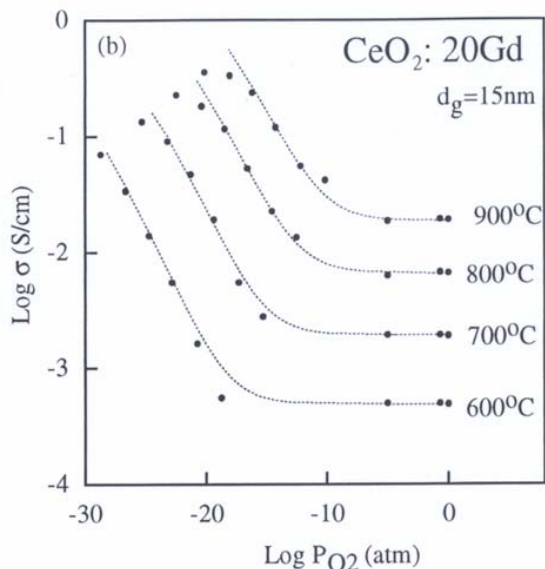
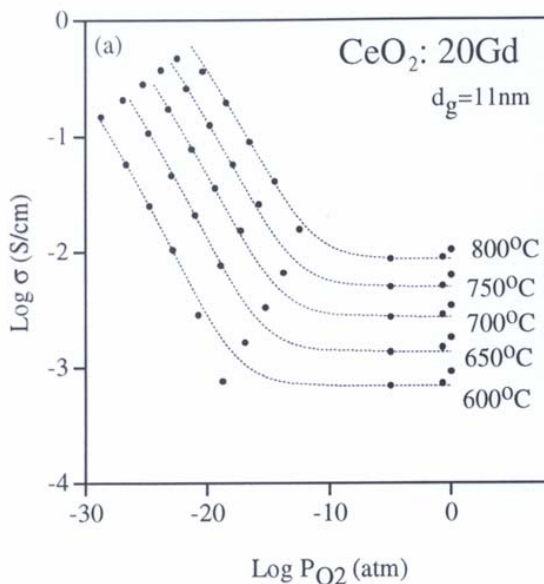
$E_i = 0.8\text{eV}$

$E_i = 1.3 \rightarrow 1.0 \text{ eV}$

$(d_g = 36 \rightarrow 9 \text{ nm})$

grain boundary conductivity

Ref.1 S. Lubke and H. D. Wiemhofer, Solid State Ionics, 117:229-243, (1999).



The electrical conductivity of  $\text{CeO}_2:20\text{Gd}$  thin films as a function of oxygen partial pressure and temperature. (a)  $d_g = 11\text{ nm}$  (b)  $15\text{ nm}$  (c)  $20\text{ nm}$  (d)  $36\text{ nm}$ .  
Film thickness = 300 - 400 nm.

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