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:ZrO₂ 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 CeO₂ Characterized
  - The electrical conductivity of both doped and undoped CeO₂ show grain size dependence.
  - Ionic conductivity of nanocrystalline Gd doped CeO₂ less than that of the microcrystalline.
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- Films of 16% Sc:ZrO$_2$ Characterized
  - The ionic conductivity is about one order of magnitude higher than YSZ.
  - Electronic Conductivity becomes significant for oxygen activity less than 10$^{-14}$ 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$_2$ suspensions for deposition onto LSM substrate
    - Control of cathode surface porosity to sizes <0.1 micron
    - 3-5 micron thick CeO$_2$ layers planarize LSM substrate to surface roughness <0.1 micron.
    - Developed a graded LSM substrate
- Developed a process by which 1-5µm 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 cm² our existing clean room must be improved)
  - Doubled size.
  - More filters and air flow.
  - This was completed March 1, 2001.
Research Planned for FY 2001-2002

- Continue Optimization of the Cathode Substrate. Evaluate:
  - The influence of porous CeO$_2$ layer on SOFC performance.
  - The influence of the addition of LSCF into CeO$_2$ layer on SOFC performance.
  - The influence of the conductivity of the CeO$_2$ layer on SOFC performance.

- Make Single Cell Fuel Cell Measurements
  - Cell performance as a function of electrolyte thickness and temperature.
    - YSZ electrolyte
    - CeO$_2$ electrolyte
  - Cell performance as a function of electrode composition.
    - Anode
    - Cathode
• Continue Studies Related to Placing Thin Electrolyte Films onto Porous Substrates
  o Polymer precursor onto a graded substrate.
  o Transfer of dense films to a porous substrate.
  o 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
- H₂O
- Nitric acid
- Ethylene glycol
- Citric acid

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

Baking
- Hot plate: ±1 °C uniformity
- 320°C - 2 min

Crystallization
- 400-1000°C

Rheological Characterization

Repeat

Electrical Characterization

Microstructural Characterization
YSZ thin film annealed at 400°C for 2 hrs. dg= 6nm
Optical Density of YSZ thin Films on Si Substrates

% theoretical density

Grain size (nm)

400°C  600°C  700°C  800°C
Grain size versus time for unsupported YSZ thin films at different annealing temperatures.
$\text{ZrO}_2$: x\%Y - thin film on alumina

- square - temp. up
- triangle - temp down

$\text{Log } \sigma \, [\text{S/cm}]$

- 8%
- 4%
- 1%

bulk - 16\%Y
Films of Undoped and Gd Doped CeO$_2$ Characterized

- The electrical conductivity of both doped and undoped CeO$_2$ show grain size dependence

- Ionic conductivity of nanocrystalline Gd doped CeO$_2$ less than that of the microcrystalline

- Electronic conductivity enhanced as grain size decreases below 50 nm
Electronic & Ionic Conductivity of CeO$_2$:20Gd

**Electronic conductivity**

CeO$_2$:20Gd
Thin film on sapphire substrate
$P$_{O$_2$}=1 atm

$E_a=2.5\pm0.1$ eV

$T_e=2.2\times10^3$ K

$d_g=11$ nm
$d_g=15$ nm
$d_g=20$ nm
$d_g=36$ nm

**Ionic conductivity**

CeO$_2$:20Gd
Thin film on sapphire substrate
$P$_{O$_2$}=1 atm

$\sigma_i(T) = \sigma_{0i} \exp\left(\frac{E_i}{RT}\right) \exp\left(-\frac{E_i}{kT}\right)$

$\sigma_{0i}=5.0 \times 10^3$ S/cm K

$E_i=0.8$ eV
$E_i=1.3$ eV
$E_i=1.0$ eV

$\sigma_i$ (microcrystalline) $> \sigma_i$ (nanocrystalline)

$g$ (d$_g=36$ $\rightarrow$ 9 nm)

grain boundary conductivity

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