Novel and Improved Electrode Structures Through Infiltration

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Presented at 8th Annual SECA Workshop and Peer Review
Core Technology Program – Electrodes: Performance and Degradation
August 7th – 9th 2007
LBNL SECA Core Program

In FY07 the LBNL core effort was focused on the following areas:

1) Infiltration of perovskites and other appropriate catalysts into composite cathodes to form an interconnected network of nanoparticulate coating;

2) Infiltration of ceria and other appropriate materials into Ni-YSZ anodes to improve sulfur tolerance;

3) Determination of baseline performance and long term stability of infiltrated and non-infiltrated electrodes;

4) Design and fabrication of 2-cell stack for national labs and industrial teams as a standard platform for testing electrodes, interconnects, contact paste, and seals in a manner that allows reliable comparison across research teams;

5) Continued optimization of interconnect coating technology and elucidation of the mechanism of chromium migration through protective coatings.
Metal Stability & Interactions

- Oxidation behavior
- Oxide spallation
- Area specific resistance
- Chromium migration

LBNL stack components

- Air electrode (La_{0.8}Sr_{0.2}MnO_{3-x})
- Stainless steel interconnect
- Transpiration

- Vapor chromium transport
- Bulk & grain boundary Cr transport
- Surface migration
Risk of scale spalling increases above ~3-5µm. (use 3 µm to be safe!)

Time (hours) vs Chromia Scale Thickness (microns)

- ~$10^{-14}$ g$^2$/cm$^4$/sec for transportation 5,000 – 10,000 hrs
- ~$10^{-15}$ g$^2$/cm$^4$/sec for stationary 50,000 – 100,000 hrs
High Temperature Oxidation of Metal Components
Long-term Stability of Coatings for Preventing Cr Loss

- Oxidation: 1073 K, $P_{H2O} = 2.0 \times 10^3$ Pa, $3.33 \times 10^{-6}$ m$^3$s$^{-1}$ (200ml/min)
- Cr test: 1073 K, 86.4 ks (24 hrs), $P_{H2O} = 1.0 \times 10^4$ Pa, $3.33 \times 10^{-6}$ m$^3$s$^{-1}$ (200ml/min)
Condition for minimum spallation of (~1%) scales on 430ss after isothermal oxidation and fast cooling to RT

The lower the operating temperature the thicker the scale can be

Cr$_2$O$_3$ not only grows slower but also can be thicker before failure

RE slow scale growth and increase adhesion/thickness

Reducing atmosphere treatment also increase adhesion

Sweet spot between 650–750 C

Scale thickness decrease because of higher thermal stresses and/or more defect formation at high oxidation temperatures
Conditions to reach ~1% Spallation in static air after isothermal oxidation and fast cooling to RT

Time to Minimum Spallation

Oxidation time to spallation (hr)

Temperature (C)

- as-received surface
- H2-treated & Y coated

Did not fail

Coated 430?
What have we done to solve the Cr problem?

**Cr Evaporation**
- Coat steel to prevent Cr diffusion to electrodes
- Density of coating seems more important than coating material

**Cr Deposition**
- Pairwise MOx-Cr interactions suggest Cr tolerant catalysts
- Enhance Cr tolerance of commercially available electrodes by infiltration
Rxn Couples

LSM + Cr₂O₃

LNF + Cr₂O₃
LNF Does Not React With Cr\textsubscript{2}O\textsubscript{3}

Pellets of LNF-Cr\textsubscript{2}O\textsubscript{3} and LSM-Cr\textsubscript{2}O\textsubscript{3} powder mixtures reacted for 150h at 700°C and 900-950°C.

**LSM-Cr\textsubscript{2}O\textsubscript{3}**
- 700°C minor reaction
- 950°C complete reaction

**LNF-Cr\textsubscript{2}O\textsubscript{3}**
- 700°C NO reaction
- 900°C NO reaction
LBNL Infiltration Core Program

– Improve existing structures (and novel electrode design)
  • Improve cathode performance at low temperature
  • Improve tolerance to Cr
  • Sulfur tolerant anodes

– Novel Electrode Design
  • Infiltration technology allows flexibility in SOFC design and processing
  • Enables mSOFCs
Infiltration Structures & Challenges

**Electrolyte supported**: porous electrodes - straightforward

**Anode supported**: cathode is straightforward, anode may be too dense in unreduced state

**Metal supported**: engineered for infiltration - entire electrode structure is infiltrated
Infiltration Step

Nitrate-Surfactant Concentrated Precursor

Surfactant dispersed Electrode Precursors

Porous electrolyte matrix

Composite Commercial electrodes (YSZ-LSM)

e-electronic conductor

ionic conductor

O²- ionic conductor

O₂ oxygen

Sc₀.₁Zr₀.₉O₂

Mn³⁺ Mn³⁺

La²⁺ La²⁺

Sr²⁻ Sr²⁻
Sulfur Tolerant Ni-YSZ

0% degradation over 180 hrs

973 K, 0.4 Acm⁻²

H₂ + 40 ppm H₂S, 500 hours

Cell Voltage / V

Time / hours

Infiltrated cell
Non-infiltrated cell
LBNL Collaboration with Electro Sciences Lab to Improve Performance of ESL SOFC product

Performance @ 0.7' 

Performance @ Peak Power

Working on standard cell for 700°C operation - available to industrial teams, Universities, and National Labs - US supplier
Commercial Symmetric Electrolyte Supported LSCF Cell from INDEC
LSCF-YDC/TZ3Y/YDC-LSCF
HC Starck LSCF/LSCF Cell

Electrolyte supported cell: electrode Impedance before and after infiltration 700 °C

=>45% improvement in cell resistance

Ceria infiltration

Electrolyte supported cell: electrode Impedance before and after infiltration 700 °C
Core Technology Program
Technology Transfer

- Infiltration workshop
- Transfer technology to companies to U.S. companies and labs
- Guidance to manufacturers of cell stack components (ESL) to enhance U.S. competitiveness
Infiltration Workshop: February 16th, 2007

- Argonne National Laboratory
- Pacific Northwest National Lab
- Georgia Tech
- Instructional DVD from Workshop available
LBNL 2-cell Standard Stack Core Effort

Based on 2.5 cm x 2.5 cm SOFC plates for 2” bore furnace
Original design by Hideto Kurokawa
Scaled-up Standard Stack:
LBNL lead with Lane Wilson & Wayne Surdoval

5 cm x 5 cm SOFC plate design to fit into 3” bore furnace ($1500)
Quotation 4418

McAllister Technical Services
West 280 Prairie Avenue
Coeur d'Alene, ID 83815
Ph: 208-773-9527
Fax: 208-773-3264
Email: solutions@mcallister.com
URL: www.mcallister.com

Date: 02-Feb-07
This estimate is good for 30 days from the
data shown above. Prices quoted are for
quantities shown.

To: Steven J. Visco
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Berkeley, CA 94720
Ph: 510.486.5921
Fax: 510.486.4481
avisco@llnl.gov

Terms Offered: Net-30
Delivery: 12 Wks., ARO
(based on current workload)
F.O.S.: Factory, Coeur d'Alene, Idaho

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Thank you for the opportunity to quote on this project!

Sales Tax: N/A
Shipping: at cost

Name: Robert McAllister, President
McAllister Build of 2-cell 5 x 5 cm SOFC Plate Stack

- Standardized test platform
- Allows testing of electrodes, seals, contact pastes, in a uniform manner
- Allows comparison of results between labs, universities, and industry
- Fits in inexpensive furnaces
- Is not intended as a precursor to commercial device
- ~ $800/ea. after initial build
LBNL Work on mSOFCs

- Build structure from low cost materials
- Obtain performance similar to anode supported cells
- Show long term stability (rapid progress)
- Work with cell manufacturers (licensing & sponsored research)
Rapid Thermal Cycling – Braze-Sealed Cell

Anode supported tubular cell cannot tolerate rapid thermal cycling. Cell failed, joint did not.

Metal-supported cell/brazed joint is robust to thermal cycling. Unexpected shutdowns, redox cycles.
650-700°C Performance

Moist hydrogen fuel, air
Infiltrated Electrodes Support High Power Density

Moist hydrogen fuel, pure oxygen (removes gas transport limitation)

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<th>Temperature</th>
<th>Max Power (mW/cm²)</th>
<th>Power at 0.7V (mW/cm²)</th>
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<tr>
<td>650°C</td>
<td>982</td>
<td>726</td>
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<tr>
<td>700°C</td>
<td>&gt;1300</td>
<td>993</td>
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<tr>
<td>750°C</td>
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Work with manufacturer to ensure manufacturability as continue cell development
High Volume Porous Metal Media

Coal: kW to MW?

5 x 5 cm mSOFC

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.
Transitioning Technology to Private Sector

- LBNL is in discussions with cell/stack manufacturers for licensing infiltration and mSOFC technology for both planar and tubular configurations.
- Wide range of IP being negotiated for SOFC, an coating for filtration (including spin-off applications for coal gasification).
- Commercial interest in infiltration and mSOFC technology is rising quickly.
Future Work

• Continued focus on infiltration technology as a means of improving cathode (and anode) performance at reduced cell temperatures
• Emphasis on baseline degradation studies on commercial cells as a metric of infiltration performance over time
• Continuing activities in technology transfer
• New stuff
Acknowledgements

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Thanks to Lane Wilson and Wayne Surdoval for their input to the LBNL program

Good luck to Lane at BES