Interconnects

Steve Visco
Hideto Kurokawa, Mike Tucker,
Inna Belogolovsky, Grace Lau, Craig Jacobson,
Peggy Hou, Lutgard De Jonghe

Lawrence Berkeley National Laboratory
Berkeley, California USA

Presented at 7th Annual SECA Workshop and Peer Review
Core Technology Program - Interconnects
September 14th 2006
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

CrO$_2$(OH)$_2$

H$_2$O
Risk of scale spalling increases above ~3-5µm. (use 3 µm to be safe!)

~10^{-14} \text{ g}^2/\text{cm}^4/\text{sec} for transportation 5,000 – 10,000 hrs

~10^{-15} \text{ g}^2/\text{cm}^4/\text{sec} for stationary 50,000 – 100,000 hrs
Condition for minimum spallation of scales on 430ss after isothermal oxidation and fast cooling to RT. These are small and sporadic (1%?).

Scale thickness decrease because of higher thermal stresses and/or more defect formation at high oxidation temperatures.
High Temperature Oxidation of Metal Components

[Graph showing oxidation rate constant vs. temperature for different materials, including Alloy 446, Alloy 430, Ebrite, 22Cr-Nb-La alloy, Ebrite (Y), Ebrite (LSCrO), and 430 (MnCoO).]

- Oxidation Rate Constant (g/cm^2·s)
- Temperature (°C)
- Cr_2O_3 thickness after 10,000 hr (µm)

Key points:
- MnCoO_x powder
- Thin sol-gel LaCrO_3
Chromium Vaporization

- **Partial pressures of Cr gas species**

Cathode side: $P_{O_2} = 2 \times 10^4$ Pa, $P_{H_2O} = 2 \times 10^3$ Pa

- **Cr gas species**

<table>
<thead>
<tr>
<th>Species</th>
<th>Partial Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>CrOH</td>
</tr>
<tr>
<td>CrO</td>
<td>Cr(OH)$_2$</td>
</tr>
<tr>
<td>CrO$_2$</td>
<td>Cr(OH)$_3$</td>
</tr>
<tr>
<td>CrO$_3$</td>
<td>Cr(OH)$_4$</td>
</tr>
<tr>
<td>Cr(OH)$_5$</td>
<td>CrO$_2$(OH)</td>
</tr>
<tr>
<td>Cr(OH)$_6$</td>
<td>CrO$_2$(OH)$_2$</td>
</tr>
</tbody>
</table>

- **Alloy interconnect**

Results – uncoated and coated 430-SS

- 1073 K, 86.4 ks (24 hrs), $P_{H_2O} = 1.0 \times 10^4$ Pa, $3.33 \times 10^{-6}$ m$^3$s$^{-1}$ (200ml/s)
Experimental

Sample preparation

Pre-oxidation (for uncoated and coated 430SS)
1073 K, 172.8 ks, in Air
Cr vaporization test
873~1073 K (main test )
873~1273 K (preliminary test with Cr₂O₃ )
86.4~259.2 ks (1~3 days) in Air + 10% H₂O

Analysis method

ICPMS (Inductively coupled plasma mass spectrometry)
SEM (Secondary electron spectroscopy)
EDS (Energy dispersive spectroscopy)
Results – uncoated and coated 430 -SS

800°C, 86.4 ks (24 hrs), $P_{\text{H}_2\text{O}} = 1.0\times10^4$ Pa, $3.33\times10^{-6}$ m$^3$s$^{-1}$ (200ml/min)
Results – uncoated and coated 430-SS

\[ P_{\text{H}_2\text{O}} = 1.0 \times 10^4 \text{ Pa}, \ 3.33 \times 10^{-6} \text{ m}^3\text{s}^{-1} \ (200\text{ml/s}) \]

Cr Vaporization is decreased ~2 orders of magnitude
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)

Graph showing chromium transport rate over time.
Protected LSM Spray Coat on 434 Stainless Steel Mesh and Wool (sintered at 800°C for 1hr)

Before Treatment

After Spray and Sinter

Oxidation resistant, compliant current connects
Solid State Chromium Transport on Cathode Materials

Bulk or grain boundary diffusion at the edge of chromia block and interconnect.

Suppression of Cr Transport by coating with Ag? Pt? Sacrificial Material?
Solid State Diffusion Transport of Chromium on Cathode Materials Experimental Setup

Sinter in the furnace at 700°C, 750°C, 800°C respectively for 500 hr.
Benefits of Coatings

• Decrease oxidation rate >10 x
• Decrease Cr vaporization by 10-100 x
• Decreases spallation (thermal cycling)
  – RE improve adhesion
  – Outer layer prevents buckling
• Decreases contact resistance

But…

Cost effective?
Complete coverage?
In-situ repair if fails?
Long-term stability?
National Laboratory Stack Test Platform

- Interconnect to cathode contact
- Ag migration
- Seals
- Coatings
- 2.5 cm, 5 cm, and 10 cm sizes
National Laboratory Stack Test Platform
Vacuum leak test of ceramic cements for sealing

Test rig for vacuum leak test (plate: 430, tube: 316, welded with Nioro)

Leak rates of samples at 973 K

Leak rate of 904 cement at 973 K during cycle test

Leak rate of 904 cement at 973 K during cycle test
Metal Supported Tubular SOFC w/Infiltrated Electrodes

Porous stainless steel

Dense YSZ

Ni/Ceria

Porous YSZ

LSM/YSZ

H₂+3%H₂O/Air at 700 °C

300 mA/cm² @ 0.85 V

400 mA/cm² @ 0.7 V

Current Density (mA/cm²)

Power Density (mW/cm²)
Metal Supported vs. Ceramic SOFCs

Metal SOFC

Ceramic SOFC

Porous stainless steel
Dense YSZ
Ni/Ceria
LSM/YSZ

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY
Summary

• SOFC Applications
  – Degradation rates of cells/stacks continue to decrease but further work is needed for stationary power applications
  – Transportation is near term but issues with thermal cycling must be addressed.
  – Feedback on failure mechanisms in stacks is needed

• Corrosion
  – The SOFC community is accumulating the necessary knowledge and understanding
  – More work on long term oxidation (effect of Si, etc) is needed
  – Basic research on interdiffusion, effects of g.b. etc is needed

• Protection
  – Coatings appear to resolve many issues with interconnect, if they can be cost effective
Team:

Investigators:
Steven Visco          P.I. Program Lead
Lutgard De Jonghe   Co-PI

Scientists:
Peggy Hou            High temperature corrosion
Velimir Radmilovic   NCEM FIB/SEM/TEM

Post Doc:
Hideto Kurokawa       Cr transport phenomena
Ken Lux                Air electrode stability

Senior Technical Staff:
Craig Jacobson        Processing and characterization
Mike Tucker           Metal supported SOFC development
Grace Lau             Processing and analysis
Inna Belogolovsky    Processing and testing

Graduate Students:
Tal Sholklapper       Nano-particulate catalysts
Liming Yang           Novel anode catalysts
Xuan Chen              Infiltration of cathode catalysts
Acknowledgements

• This work was supported by SECA through NETL
• Thanks to Lane Wilson for helpful discussions on Cr issues and model stack construction