Interactions of Silicon in Metallic Interconnect Materials with Perovskite Protective Coatings

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Outline

• **Effects of silicon impurities on the performance of coated metallic interconnects**
  – Background
  – What lead us to look into this issue.
  – Some initial results (ASR and SEM)

• **Electro-deposition of interconnect coatings**
  – Plans and initial results

• **Goals and plans of coal syngas work**
Interconnects for Planar SOFCs

**Interconnect Function**- electrically connect the cells in a stack, provide separation and flow control of gases, and provides mechanical stability.

**Interconnect Requirements:**
- Gas impervious
- Electrically conducting
- Stable in both oxidizing and reducing atmospheres
- CTE
- Non-reactive
- High thermal conductivity
- Good strength
- Low cost

- $\text{Cr}_2\text{O}_3$ layer continues to grow - increases resistance.

- Migration of Cr within the stack contaminates the SOFCs.
Technical Approach

A conductive and protective coating seemed like the best option given what we knew, from our own work and from reviewing literature reports, about the effects of chromia on cell performance.

Coating Techniques
1) magnetron sputtering deposition (test coating possibilities)
2) low cost technique (electrodeposition of alloys or multilayers, or electrophoretic deposition)

Substrates
1) Stainless 446  CTE=11μm/m-°C
2) CROFER APU22  CTE=11μm/m-°C

Conductive oxides
LaCrO$_3$
La$_{0.9}$Ca$_{0.1}$CrO$_3$
La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$Co$_{0.1}$O$_3$
La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$O$_3$
MnCo Spinell
### Background

The sputtered films were amorphous as deposited and slightly substoichiometric in O, but upon heating in air transform first to LaCrO₄ and then subsequently to LaCrO₃. Doing the initial crystallization in H₂/N₂ avoids the LaCrO₄ phase.

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**ASR values of sputtered LaCrO₃ and Ca doped LaCrO₃ on SS446 substrates with different initial crystallization environments**

<table>
<thead>
<tr>
<th>Initial treatment</th>
<th>La0.9Ca0.1Cr03 Air 800°C</th>
<th>La0.9Ca0.1Cr03 Forming gas 800°C</th>
<th>LaCr03 air 800°C</th>
<th>LaCrO3 Forming gas 800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>After formation</td>
<td>0.011 Ω•cm²</td>
<td>0.014 Ω•cm²</td>
<td>0.044 Ω•cm²</td>
<td>0.013 Ω•cm²</td>
</tr>
<tr>
<td>Additional 100 hours At 800°C in Air</td>
<td>0.036 Ω•cm²</td>
<td>0.44 Ω•cm²</td>
<td>0.108 Ω•cm²</td>
<td>0.21 Ω•cm²</td>
</tr>
</tbody>
</table>
Each film was exposed to 100hrs in air at 800C after the initial crystallization treatment. The composition of the layers was confirmed by EDS analysis. Note that the LaCrO3 coating annealed initially in H2/N2 showed improved resistance to oxidation. However, The SiO2 layer becomes more continuous.
**Crofer APU22 Substrate Compositions and coating compositions**

<table>
<thead>
<tr>
<th>batch</th>
<th>Chemical Composition (wt%)</th>
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<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>JGP</td>
<td>Bal.</td>
</tr>
<tr>
<td>JXW</td>
<td>Bal.</td>
</tr>
<tr>
<td>JZF</td>
<td>Bal.</td>
</tr>
<tr>
<td>KCB</td>
<td>Bal</td>
</tr>
</tbody>
</table>

LaCrO$_3$, La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$O$_3$, La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$Co$_{0.1}$O$_3$

The substrates have variable silicon and aluminum content and the coatings have different ionic and electronic conductivities.
Area Specific Resistance of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.9}\text{Co}_{0.1}\text{CrO}_3$
sputter coated film on Crofer substrates with varying
silicon content (heated to 900°C in air)
TEM and EDS analysis of amorphous grain boundary phase
Area Specific Resistance of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.9}\text{Co}_{0.1}\text{CrO}_3$ sputter coated film on Crofer substrates with varying silicon content.
ASR as a function of time at 800°C in air for La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$Co$_{0.1}$CrO$_3$ (initial heat treatment in air) sputter coated film on Crofer alloy substrates with different silicon contents
SEM images of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.9}\text{Co}_{0.1}\text{CrO}_3$ sputtered coatings after 1000 hrs at 800°C

JGP 0.11 wt% Si

JXW 0.01 wt% Si
SEM images of La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$Co$_{0.1}$O$_3$ sputtered coatings after 1000 hrs at 800C

JGP 0.11 wt% Si

JXW 0.01 wt% Si

EDS analysis indicates that the surface crystallites are MnCr spinel
Summary silicon content work

The work needs to be completed.

- Obtain cross sectional SEM images of the La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$Co$_{0.1}$O$_3$ samples initially treated in air and in H$_2$/N$_2$ after 1000 hours at 800°C in air.
  - Determine if silica layers are continuous
  - Investigate the formation of substrate grain boundary phases
- Compare with LaCrO$_3$ and La$_{0.7}$Sr$_{0.3}$Cr$_{0.9}$O$_3$ sputtered coatings and possibly MnCo spinel

Determine the acceptable level of silicon impurities allowable for interconnect substrates coated with dense films.
Electroplating of Alloys as Precursors for Oxide Protective Layers

Targeting MnCo spinel formation

Form Mn/Co alloy coating by electroplating

Convert to oxide

Form Mn/Co multilayer coating by electroplating

First form alloy in reducing environment

Followed by oxidation

Directly oxidize multilayers

This technique should be useful for coating complex geometries. It should also be adaptable to many compositions.
Mn and Co Alloy deposition

- For alloy deposition the deposition potentials for the metals must be close
- $E^\circ$ for Mn$^{2+}$ to Mn(s) is -1.18, $E^\circ$ for Co$^{2+}$ to Co(s) is -0.277
  - Using the Nernst equation and assuming dilute solutions. The difference in concentration between Mn$^{2+}$ and Co$^{2+}$ would need to be 30 Orders of magnitude different.

$$E = E^\circ + \frac{RT}{\nu F} \ln a$$

$E$=deposition potential, $E^\circ$= standard reduction potential, $R$ = ideal gas constant, $T$= temperature, $\nu$= # of electrons, $F$= Faradays constant, $a$= activity

For 0.01M Mn$^{2+}$ a concentration of $1\times10^{-32}$M Co$^{2+}$ is required to have a similar deposition potential.
Mn and Co Alloy deposition

- 0.008M CoSO$_4$, 0.008M EDTA, 0.075M Saccharin, 0.032M MnSO$_4$
  - EDTA was added to the CoSO$_4$ solution and heated to achieve chelation
- pH was varied over a range from 1-9.
- Current densities of 50mA/cm$^2$ and 100mA/cm$^2$ were used
- Platinum counter electrodes
- Substrates (CROFER APU22) were sanded with 600 grit sandpaper and cleaned ultrasonically in ethanol
- 50°C
Effect of Saccharin addition on Co morphology

Simple electroplating of Co

Electro-plating of Co with Saccharin addition 0.025M
Deposition from Co\(^{2+}\) and Mn\(^{2+}\) solutions with Saccharin and EDTA additions

pH 1.04-6.35

- EDS shows only Co deposition

pH of 8.3

- EDS shows an approximately 47/53 Mn/Co ratio

At pH=9.26 solid formation in solution occurred
Possible effect of pH

- LogK for Mn$^{2+}$+2H$_2$O→HMnO$_2^-$+3H$^+$ is -32.6529

$$K = \frac{[HMnO_2^-][H^+]^3}{[Mn^{2+}]} = 1.6 \times 10^{-32}$$

$$K = \frac{[HMnO_2^-][5 \times 10^{-9}]^3}{[0.032]} = 1.6 \times 10^{-32}$$

$$[HMnO_2^-]=4.1 \times 10^{-10}$$

Using the Nernst equation to calculate the deposition potential at that concentration, then gives -0.43865V for deposition of Manganese from HMnO$_2^-$. 
Coal Syngas with Solid Oxide Fuel Cells

The combination of coal syngas and solid oxide fuel cells represents an economical, efficient power source for future power generation. However there are many questions regarding these systems.

Questions

- What problems may be associated with the use of coal syn-gas in SOFCs?
  - Coal syngas composition-high CO levels
  - Coal syngas contaminants-what clean up is necessary?
- Particulate matter
- BOP/Interconnects
- To be determined

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Concentration (ppmv)</th>
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<tbody>
<tr>
<td>Fe(CO)₅</td>
<td>0.05-6.0</td>
</tr>
<tr>
<td>Ni(CO)₄</td>
<td>0.01-1.0</td>
</tr>
<tr>
<td>Sb</td>
<td>0.03-1.0</td>
</tr>
<tr>
<td>Cd</td>
<td>0.01-0.2</td>
</tr>
<tr>
<td>Be</td>
<td>0.03-2.3</td>
</tr>
<tr>
<td>Cr</td>
<td>0.03-6.0</td>
</tr>
<tr>
<td>K</td>
<td>0-550</td>
</tr>
<tr>
<td>Se</td>
<td>0.15-1.0</td>
</tr>
<tr>
<td>Na</td>
<td>0-300</td>
</tr>
<tr>
<td>Pb</td>
<td>0.25-3.0</td>
</tr>
<tr>
<td>Zn</td>
<td>0-100</td>
</tr>
</tbody>
</table>
Coal Syn Gas with Solid Oxide Fuel Cells

Current Research Activities

Baseline Operations (FY06-FY07)
- SOFC operation on various gasified coal compositions is being completed

Coal Contaminant Issues (FY06-FY07)
- Major coal syn gas contaminants (H₂S and Cl) are being tested.
- Thermodynamic evaluation of trace coal syn gas contaminants are being completed.

Future Research Activities

Trace Contaminant Testing (FY07-FY08)
Test trace coal syn gas contaminants that may be detrimental to SOFC operation based on thermodynamic analysis.

Anode Development (FY08-FY09)
Develop SOFC anodes better suited for operation with coal syn gas that will reduce the clean up processing needed.

Long Term Testing (FY10)
Complete 8000hr SOFC stack test with coal syn gas.
Conclusions

• Si (or other impurities) can affect the ASR for coated ferritic interconnect materials.
  – Substrate impurity levels, coating thickness, specific synthesis routes, or coating composition may play a role in this interaction

• Mn/Co electrodeposited alloys can be obtained from complexed Co and Mn sulphate solutions. Solution pH plays a role in allowing the deposition of Mn.
Future Work

- Investigate the mechanism of MnCr spinel formation at coated metallic interconnect substrate grain boundaries
- Complete cross-sectional SEM analysis of perovskite coated samples
- Optimize the Mn/Co alloy deposition
- Oxidize the films to get the MnCo spinel
- Test coated samples on cells
- Base-line coal syngas tests

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