Electrode Contamination Studies

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The Chromium Contamination Issue

- Metallic bipolar plates for planar SOFCs contain chromium

- Chromium forms a volatile oxy-hydroxide

- The oxy-hydroxide is reduced to chromium oxide at the cathode

- The chromium oxide deposits affect the cell performance

\[
\text{Cr}_2\text{O}_3 + 1.5\text{O}_2 + 2\text{H}_2\text{O} = 2\text{CrO}_2(\text{OH})_2
\]

\[
2\text{CrO}_2(\text{OH})_2 + 6e^- + 3\text{V}_o^{--} = \text{Cr}_2\text{O}_3 + 3\text{O}^{2-} + 2\text{H}_2\text{O}
\]
Three Cell Configurations Were Tested

E-Brite

E-Brite, Au Separation

Au

With and without external dosing
**Cells Run at 800°C Effect of Contact**

The graph shows the effect of contact on cell potential over time at 800°C. The data is divided into three categories:

- **Au Interconnect**: Exhibits a significant decrease in cell potential with a drop of 5% per 1000 hours.
- **E-Brite/Au Wrapped Channels Exposed**: Shows no degradation over the observed time period.
- **E-Brite**: Also shows no degradation over the observed time period.

The x-axis represents time in hours, ranging from 0 to 500, while the y-axis represents cell potential in volts, ranging from 0 to 1.0.
Effects of Alkali Metals at 800°C

- Macor Fixture Aremco 569 and 685 Cement
- Macor Fixture Extra Au/Al2O3 wash Aremco 569 and 685 Cements
- Alumina Fixture/Alumina Cement/5%KOH in LSM
- Alumina Fixture/Aremco 571 Cement
- Alumina Fixture/Alumina Cement
Vapor pressure of $\text{K}_2\text{CrO}_4$

![Graph showing the vapor pressure of $\text{K}_2\text{CrO}_4$ and $\text{CrO}_2\text{(OH)}_2$ as a function of reciprocal temperature. The graph plots log(P_v) (atm) against 1000/T (K⁻¹). The data points for $\text{K}_2\text{CrO}_4$ are shown with a blue line, while the data points for $\text{CrO}_2\text{(OH)}_2$ are shown with a black line. The graph indicates a decrease in vapor pressure with increasing temperature.](image-url)
**Incremental Chromium Transport Mechanisms**

Surface of interconnect

- Normal: \[ \text{Cr}_2\text{O}_3(s) + \frac{3}{2} \text{O}_2(g) + 2\text{H}_2\text{O} \rightarrow 2\text{CrO}_2(\text{OH})_2(g) \]
- Incremental: \[ \text{Cr}_2\text{O}_3(s) + \frac{3}{2} \text{O}_2(g) + 4\text{KOH} \rightarrow 2\text{K}_2\text{CrO}_4(g) + 2\text{H}_2\text{O}(g) \]

Cathode interface

- \[ 2\text{CrO}_2(\text{OH})_2(g) + 6\text{e}^{-} \rightarrow \text{Cr}_2\text{O}_3(s) + 2\text{H}_2\text{O}_2(g) + 3\text{O}^{2-} \]
- \[ 2\text{K}_2\text{CrO}_4(g) + 6\text{e}^{-} \rightarrow \text{Cr}_2\text{O}_3(s) + 2\text{K}_2\text{O}(g) + 3\text{O}^{2-} \]
Degradation of cell potentials at 800°C and different current densities

No Degradation

2.5% per 1000 hrs

5% per 1000 hrs

21% per 1000 hrs

Cell Potential (V)

Time (Hrs)

0 mA/cm²

184 mA/cm²

367 mA/cm²

735 mA/cm²
Effect of Current Density at 800°C

### Steady State Degradation (%V Decrease/1000hrs)

- **Current Density (mA/cm²)**: 0, 200, 400, 600, 800
- **wt% Cr in Active Cathode**: 0, 2, 4, 6, 8

- **Graph 1**: Steady State Degradation vs. Current Density
- **Graph 2**: wt% Cr in Active Cathode vs. Current Density

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Effect of Cell Potential at 800°C
Factors affecting Chromium Migration

- Rate of oxyhydroxide formation
- Hydrodynamics
- Diffusion in cathode pores
- Rate of reduction
800°C

Potential
Controlled

Diffusion Controlled

- 0 mA/cm^2
- 184 mA/cm^2
- 367 mA/cm^2
- 735 mA/cm^2

Cell Potential (V)

Time (Hrs)
Phase distribution from 0.5 micron beam x-ray diffraction at APS
Cathode (LSM + YSZ) layer

Very weak diffraction peaks of MnCr$_2$O$_4$ and Cr$_2$O$_3$ phases were observed. Cr$_2$O$_3$ is relatively more abundant in the contact paste.
Strain Distribution
Cr$_2$O$_3$ Growing on YSZ
in cell operated at 800°C, 500 Hours, 1.15A

- Cr$_2$O$_3$ particles grow on YSZ.
- Traces of Mn associated with.
- LSM Typically clean.
- Some trances of spinel, but limited.
- Pores still open.
Cells Run at 700°C Effect of Contact

- **Au Interconnect**: No Degradation, 6% per 1000 hrs
- **E-Brite/Au Wrapped Channels Exposed**: 40% per 1000 hrs
- **E-Brite**: Degradation observed
Degradation at 700°C

- No Degradation
- 50% per 1000 h
- 40% per 1000 h
- 380% per 1000 h

Cell Potential (V)

Time (Hrs)

- 0 mA/cm²
- 184 mA/cm²
- 367 mA/cm²
- 735 mA/cm²
Effects of temperature on cell potentials after 500 hours of operation
$\text{MnCr}_2\text{O}_4$ Growing on YSZ
in cell operated at 700°C, 500 Hours, 1.15A
(Mn,Cr)$_3$O$_4$ Nano-particles Filling Pores in cell at 700°C, 500 Hours, 1.15Å

YSZ Particle

(Mn,Cr)$_3$O$_4$ Nano-Particles

Decomposed
The vacancy concentration affects the $\text{Cr}^{6+}/\text{Cr}^{3+}$ equilibrium potential and also the degree of blockage.

\[
2\text{CrO}_2(\text{OH})_2 + 3\text{V}_\text{O}^{\bullet\bullet} + 6e^- \leftrightarrow \text{Cr}_2\text{O}_3 + 3\text{O}_\text{O}^x + 2\text{H}_2\text{O}
\]

\[
E = E^\circ - \frac{RT}{nF} \ln \left( \frac{(a_{\text{H}_2\text{O}})^2}{(a_{\text{CrO}_2(\text{OH})_2})^2 * (a_{\text{V}_\text{O}^{\bullet\bullet}})^3} \right)
\]

\[
E = E^\circ - 0.03 * \ln \left( 10^6 * \left[ \text{V}_\text{O}^{\bullet\bullet} \right]^{-3/2} \right)
\]

\[\therefore \text{Doubling} \ [\text{V}_\text{O}^{\bullet\bullet}] \text{ increases} \ E \text{ by} \sim 32 \text{ mV} \]
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