Chromium Vapor Sensor for Monitoring Solid Oxide Fuel Cell Systems

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• Students
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Background

• Source of Chromium
  – Chromia formers used for interconnect due to high electronic conductivity of $\text{Cr}_2\text{O}_3$ relative to $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$
  – Oxidation of chromia scale (interconnect or balance of plant) to $\text{CrO}_3$ or $\text{CrO}_2(\text{OH})_2$

• Chromium Deposition
  – $\text{Cr}^{6+}$ reduced to $\text{Cr}^{3+}$ (i.e. $\text{Cr}_2\text{O}_3$) on cathode
Cr-O-H Vapor Pressures

Vapor pressures higher in oxidizing conditions

[Graph showing vapor pressures of Cr-O-H complexes under different conditions, including Cr(s), CrO(OH), CrO(OH)₂, CrO(OH)₃, and CrO(OH)₄.]

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Cr-O-H Vapor Pressures

10 ppm does not cause degradation

Stability of CrO$_3$ / CrO$_2$(OH)$_2$

CrO$_2$(OH)$_2$ predominant even in relatively dry conditions

CrO$_3$(g) + H$_2$O(g) = CrO$_2$(OH)$_2$(g)

pCrO$_2$(OH)$_2$ > pCrO$_3$

pCrO$_2$(OH)$_2$ < pCrO$_3$

6% RH at 25°C
Vapor pressure of CrO$_2$(OH)$_2$ high at relatively low temperatures

Vapor Pressure of CrO$_3$ / CrO$_2$(OH)$_2$
Reduce Chromium Poisoning

- **Source**
  - Non-chromia forming alloys
    - Alumina, silica high electrical resistance
    - NiO fast growth rate
  - Alloying additions
    - Mn to form outer spinel layer reduces chromia activity and thus vapor pressure
  - Coatings

- **Cell**
  - Cr poisoning resistant electrodes

- **System**
  - Cr getter
Chromium Getter

J. Stevenson and B. Koeppel, SOFC Development at PNNL: Overview,” 17th Annual Solid Oxide Fuel Cell Project Review Meeting

Cr source – no getter
No Cr source – no getter
Cr source with getter

Cell Voltage (V)

56%/kh
15.3%/kh
11.5%/kh

0 1000 Hours at 800°C
**Chemical Sensor SOFC BOP / Stack**

- **Potentiometric Chemical Sensors**
  - Solid electrolyte based
  - Thermodynamic – not kinetic
    - Stable
    - Not microstructure dependent
  - Used in ICE exhaust gas sensors, molten steel oxygen probes

- **Auxiliary Electrode**
  - Relate activity of target (Cr) to that of the mobile species ($O^{2-}$ or $Na^+$)
    - $Cr / O^{2-}: 2Cr + 3O^{2-} = Cr_2O_3 + 6e^-$
    - $Cr / Na^+: 5Cr + 3Na_2CrO_4 = 6Na^+ + 4Cr_2O_3 + 6e^-$
Potentiometric Chemical Sensors

\[ E = \frac{RT}{4F} \ln \left( \frac{pO_2^S}{pO_2^R} \right) = \frac{RT}{4F} \ln \left( \frac{1}{pO_2^R} \right) + pO_2^S \]

2O\(^2\)\(^-\) = O\(_2\)\(^S\) + 4e\(^-\)

2O\(^2\)\(^-\) = O\(_2\)\(^R\) + 4e\(^-\)

Gas reference
(e.g. Exhaust Gas Sensor)

2Cr + 3/2O\(_2\) = Cr\(_2\)O\(_3\)

K = \frac{a_{Cr_2O_3}}{a_{Cr} \cdot p_{O_2}^{3/2}} \rightarrow p_{O_2}^{3/2} = \left( \frac{a_{Cr_2O_3}}{a_{Cr}^2 \cdot K} \right)^{2/3}

2Cr + 3O\(^2\)\(^-\) = Cr\(_2\)O\(_3\) + 6e\(^-\)

Metal + oxide reference
(e.g. Molten Steel Oxygen Probe)

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2Cr + 3O^{2-} = Cr_{2}O_{3} + 6e^{-}

\[ E = \frac{RT}{4F} \ln \left( \frac{pO_{2}^S}{pO_{2}^R} \right) = \frac{RT}{4F} \ln \left( \frac{a_{Cr_{2}O_{3}}}{\frac{a_{Cr}^2}{a_{Cr_{2}O_{3}}} \cdot K} \right) = \frac{RT}{4F} \ln \left( \frac{a_{Cr_{2}O_{3}}^2}{a_{Cr}^2} \right) \]

For Cr + Cr_{2}O_{3} reference

\[ E = -\frac{RT}{2F} \ln(a_{Cr}) \]
YSZ Auxiliary Electrode Reaction

\[ 2\text{YCrO}_3 + 2\text{H}_2\text{O} + \text{O}^{2-} = 2\text{CrO}_2(\text{OH})_2 + \text{Y}_2\text{O}_3 + 2\text{e}^- \]
Zr-Y-Cr-O Phase Equilibria

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Sensor Schematics

\[2\text{YCrO}_3 + 2\text{H}_2\text{O} + \text{O}^{2-} = 2\text{CrO}_2(\text{OH})_2 + \text{Y}_2\text{O}_3 + 2\text{e}^-\]

\[\text{O}^{2-} = \text{O}_2 + 2\text{e}^-\]

Reference electrode
Electrolyte tube
Ceramic tube
Metal wires

Electrolyte
Substrate
Porous Pt

Pt

Auxiliary electrode

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Sensor Miniaturization

- Thin film fabrication
- Measure of local Cr vapor concentrations
Sensor Testing
Resistance measurement applies small current which disturbs cell.
Low Temperature Response

- τ_{400°C} = 19 min
- τ_{425°C} = 17 min
- τ_{425°C} = 33 min
- τ_{450°C} = 30 min
- τ_{375°C} = 65 min
- τ_{400°C} = 50 min
Response Time

Pt, Pt paste | YSZ | YCrO$_3$, Ag

Time Constant (min)

Temperature (°C)

with Cr (dry)

no Cr (dry)
Sensor Response

Pt, Pt paste | YSZ | YCrO$_3$, Ag

- no Cr (dry)
- with Cr (dry)
- no Cr (wet)
- with Cr (wet)

Voltage (mV) vs. Temperature (°C)

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Beta Alumina Auxiliary Electrode Reaction

$$2\text{Na}_2\text{CrO}_4 + 2\text{H}_2\text{O} = 4\text{Na}^+ + 2\text{CrO}_2(\text{OH})_2 + \text{O}_2 + 2\text{e}^-$$
Synthesis of Na₂CrO₄

- Cr₂O₃ + Na₂CO₃
- Vapor phase deposit
Summary

• Mitigation of chromium poisoning
  – Alloy design
  – Ceramic coatings
  – Chromium getter

• Chromium sensor for health monitoring
  – Solid electrolyte based
  – YSZ or β alumina
Thank you for your attention