Chromium Vapor Sensor for Monitoring Solid Oxide Fuel Cell Systems

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18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting

Pittsburgh, PA

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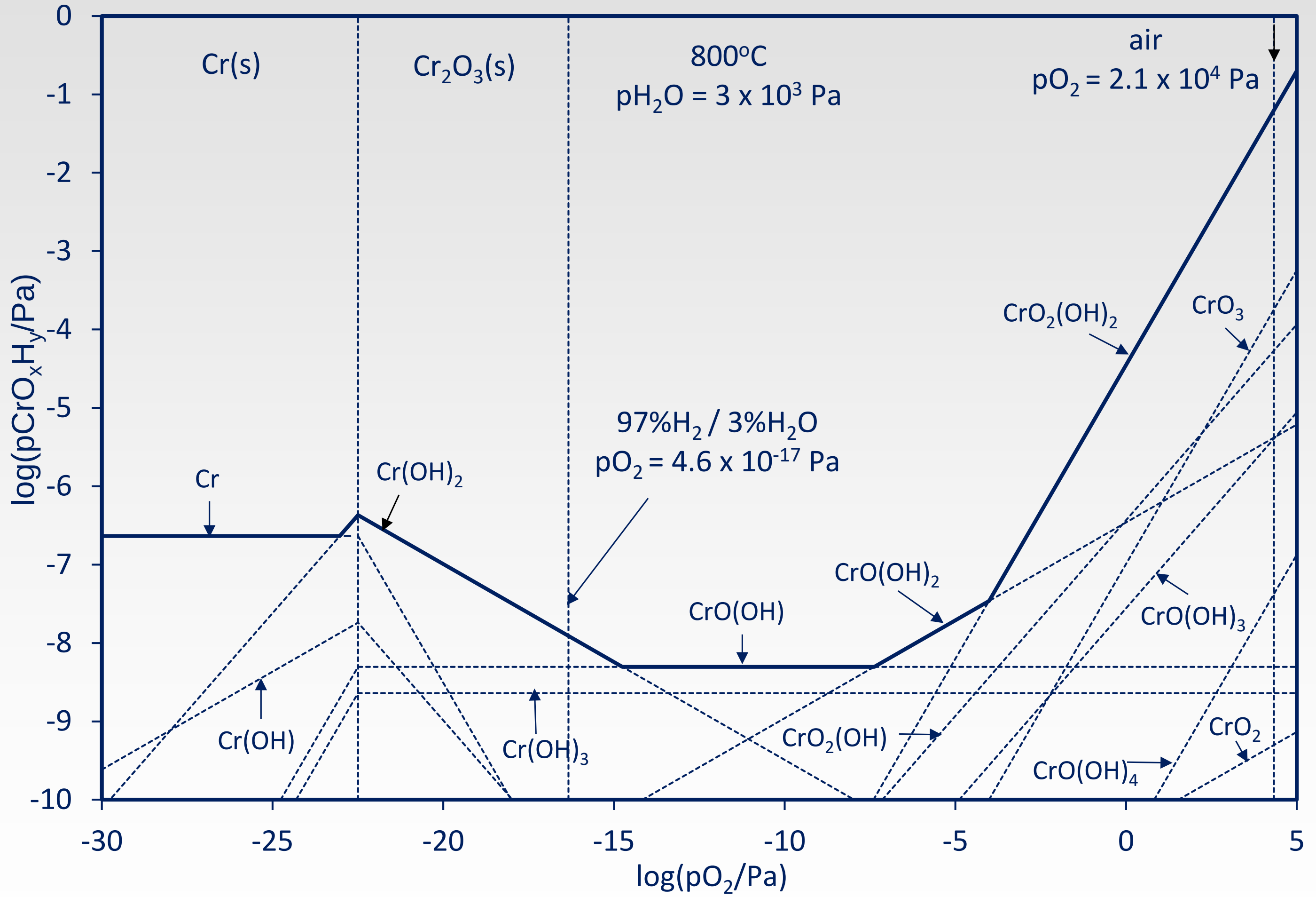
Project Team

- Phase I
  - PI: Jeffrey Fergus
  - Graduate student: Moaiz Shahzad
  - Undergraduate student: Tommy Britt
- Planned for Phase II
  - Fuel Cell Energy, Hossein Ghezel-Ayagh
  - Naval Research Lab, Fritz Kub
  - University of Connecticut, Prabhakar Singh

Background

- Source of Chromium
  - Chromia formers used for interconnect due to high electronic conductivity of Cr_2O_3 relative to Al_2O_3 and SiO_2
  - Oxidation of chromia scale (interconnect or balance of plant) to CrO_3 or $CrO_2(OH)_2$
- Chromium Deposition
  - Cr^{6+} reduced to Cr^{3+} (*i.e.* Cr_2O_3) on cathode

Cr-O-H Vapor Pressures



Vapor pressures higher in oxidizing conditions

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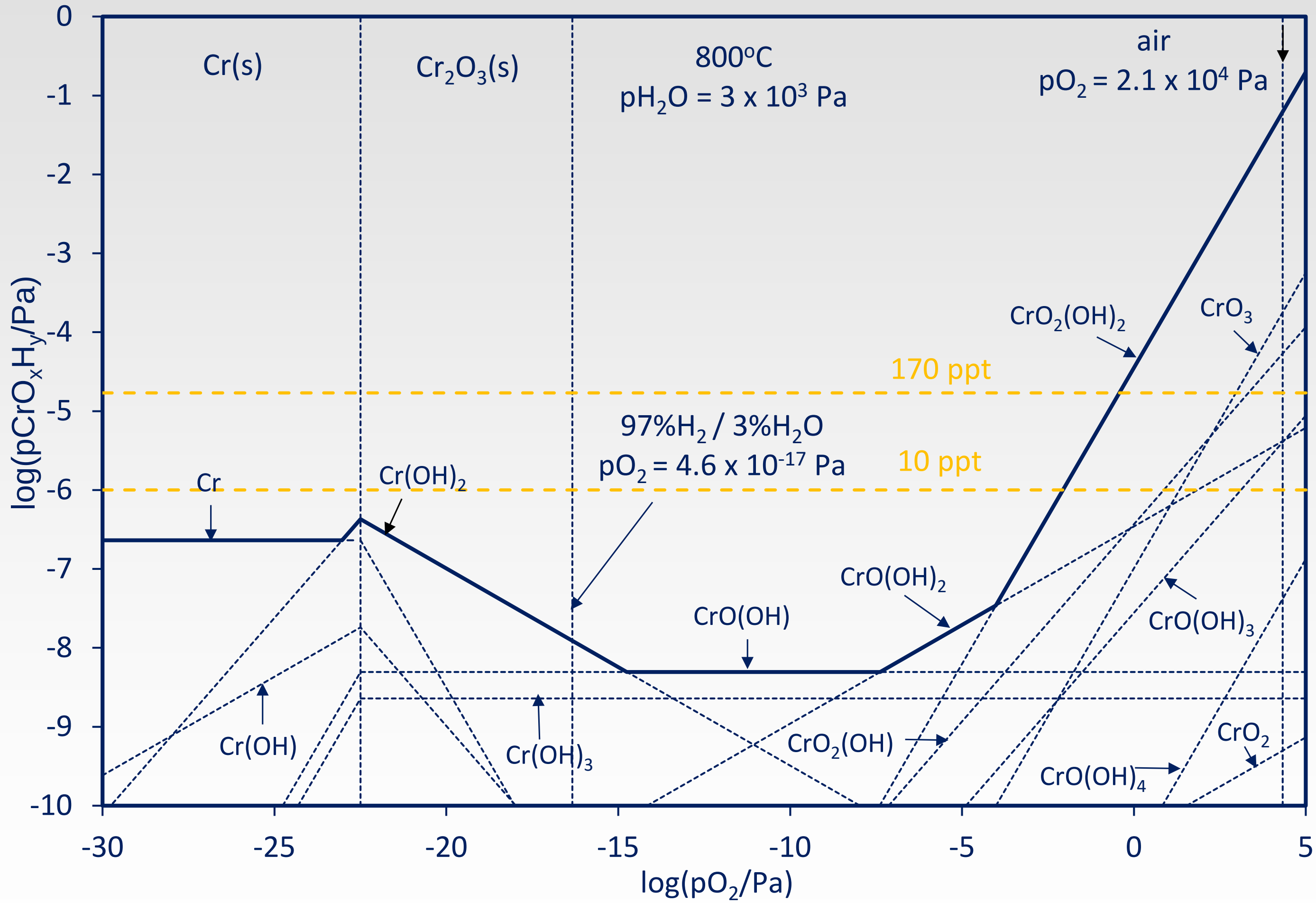
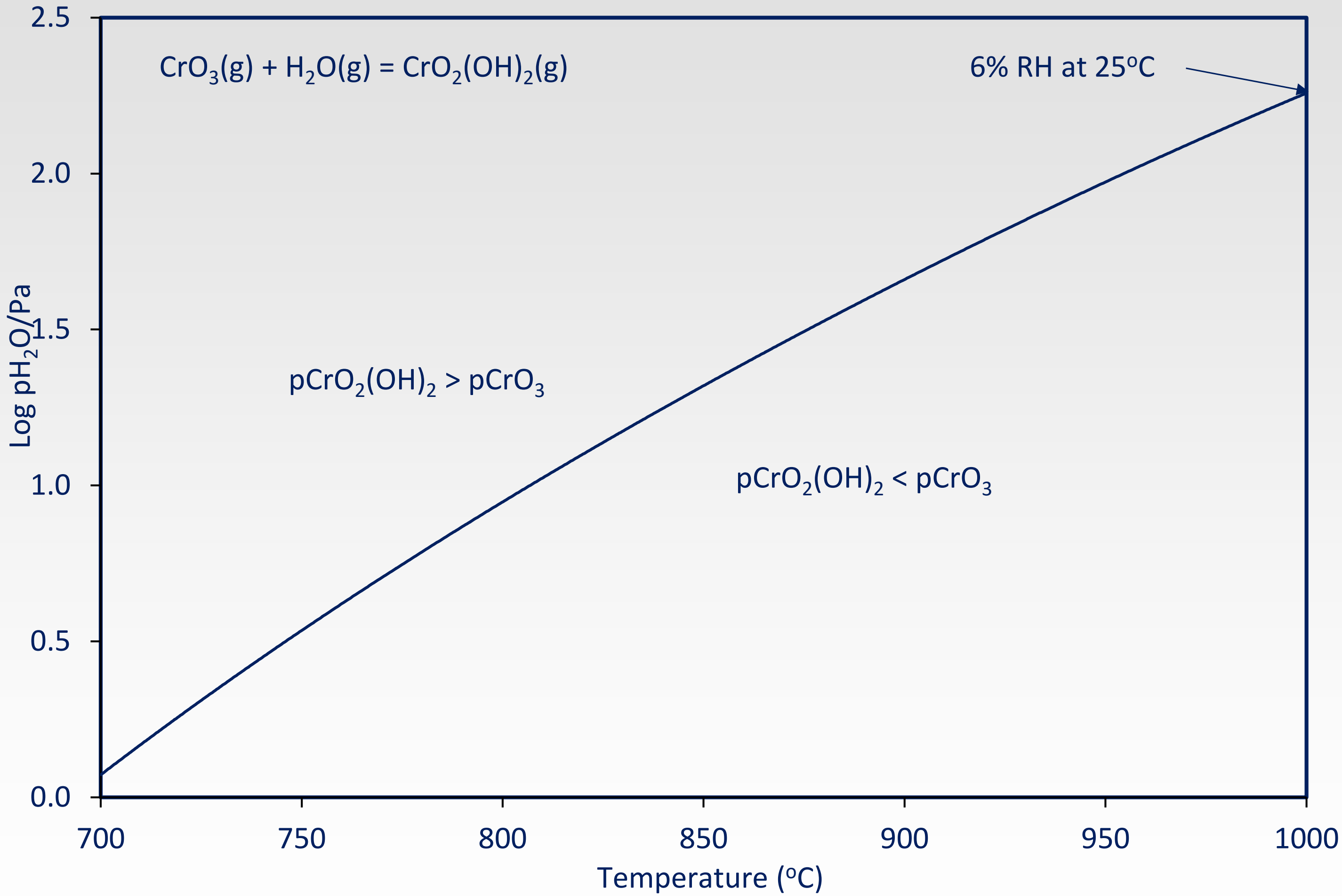
Cr-O-H Vapor Pressures



Vapor pressures higher in oxidizing conditions

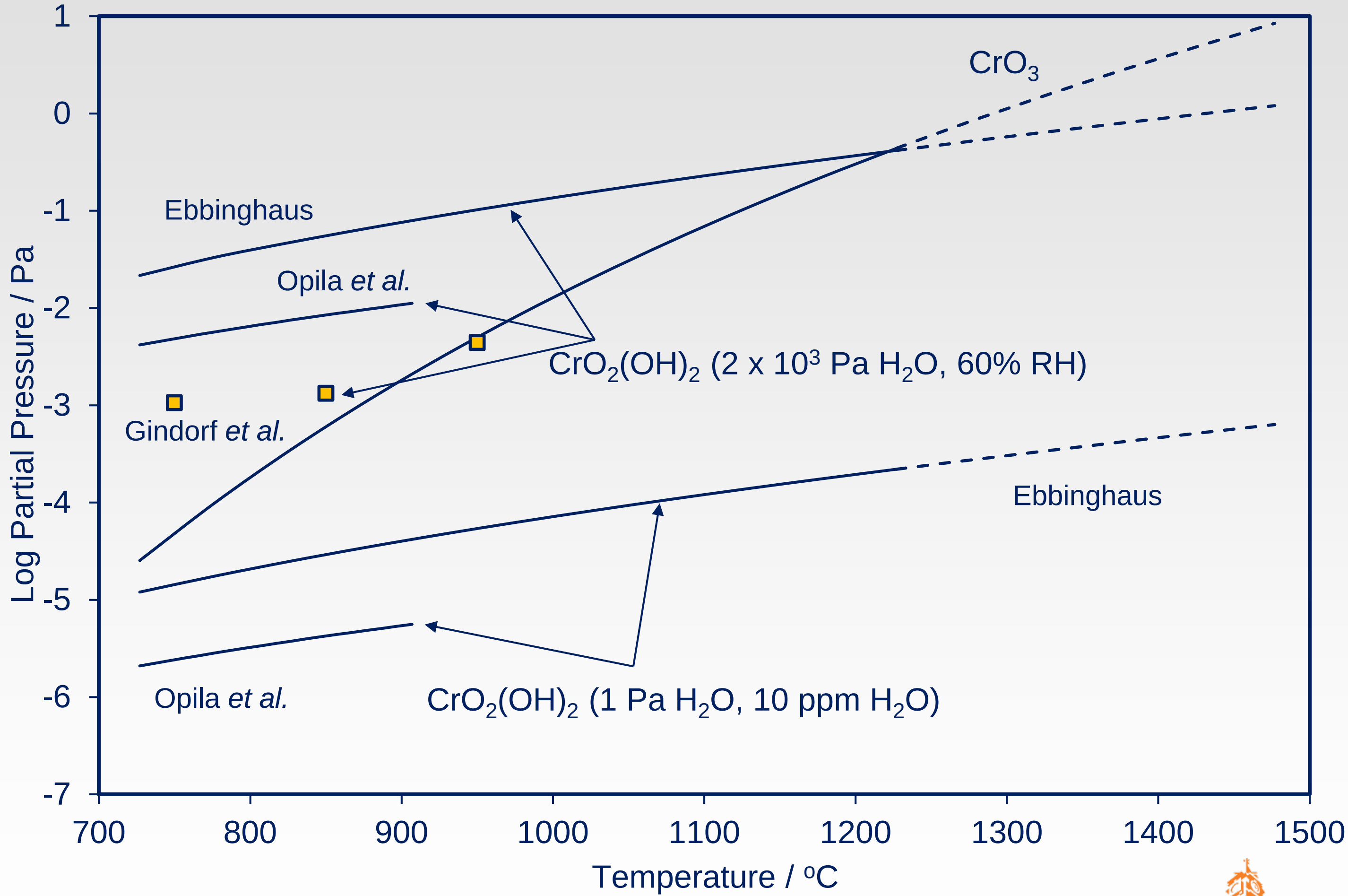
Stability of CrO_3 / $CrO_2(OH)_2$



$CrO_2(OH)_2$ predominant even in relatively dry conditions

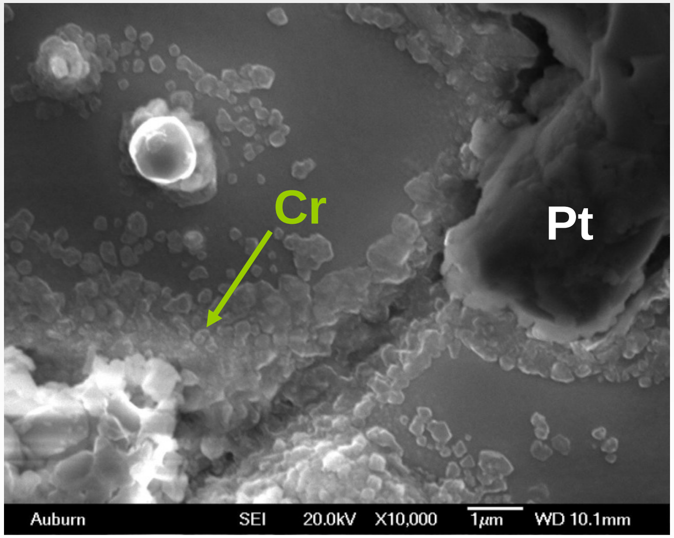
Vapor Pressure of CrO_3 / $CrO_2(OH)_2$

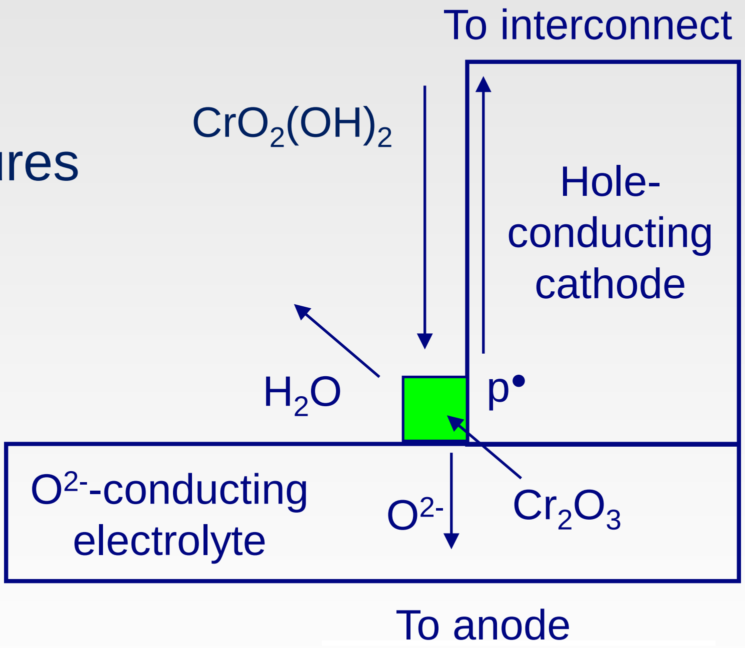
Vapor pressure of $CrO_2(OH)_2$ high at relatively low temperatures



Chromium Poisoning in SOFCs

- Chromium poisoning
  - Oxidation of Cr_2O_3 to Cr^{6+} species ($CrO_2(OH)_2$ or CrO_3)
  - Deposition of Cr_2O_3 on cathode
  - Occurs even at IT-SOFC temperatures





K. Wang and J. Fergus, *J. Electrochem. Soc.* **157**, B1008 (2010).

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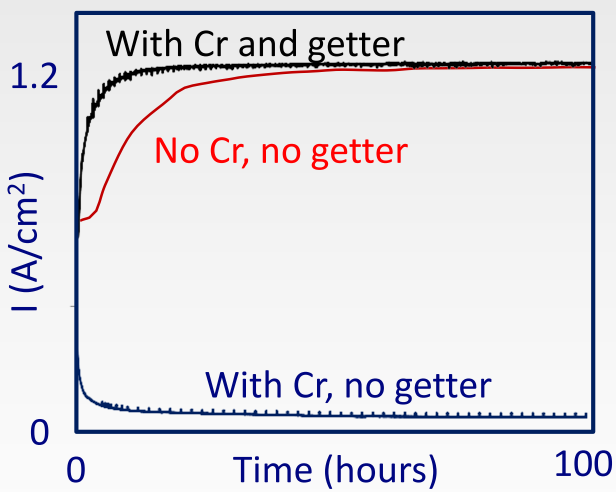
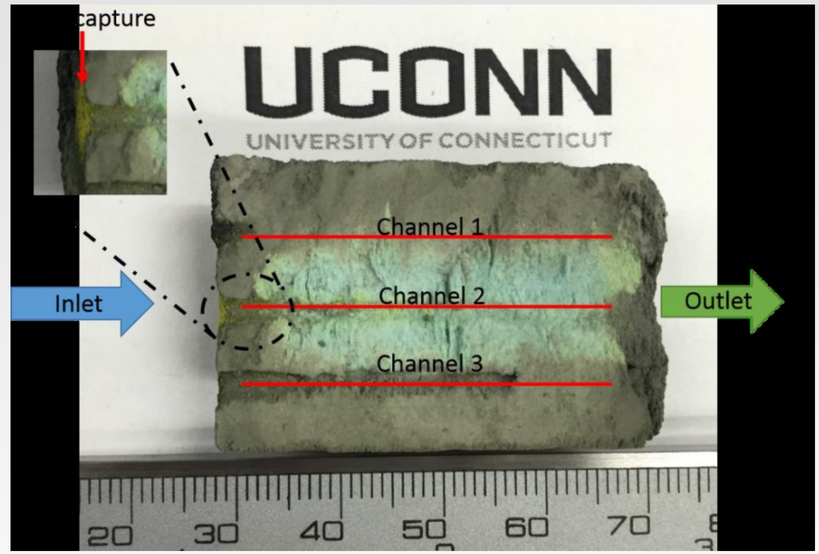
Reduce Chromium Poisoning

- 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

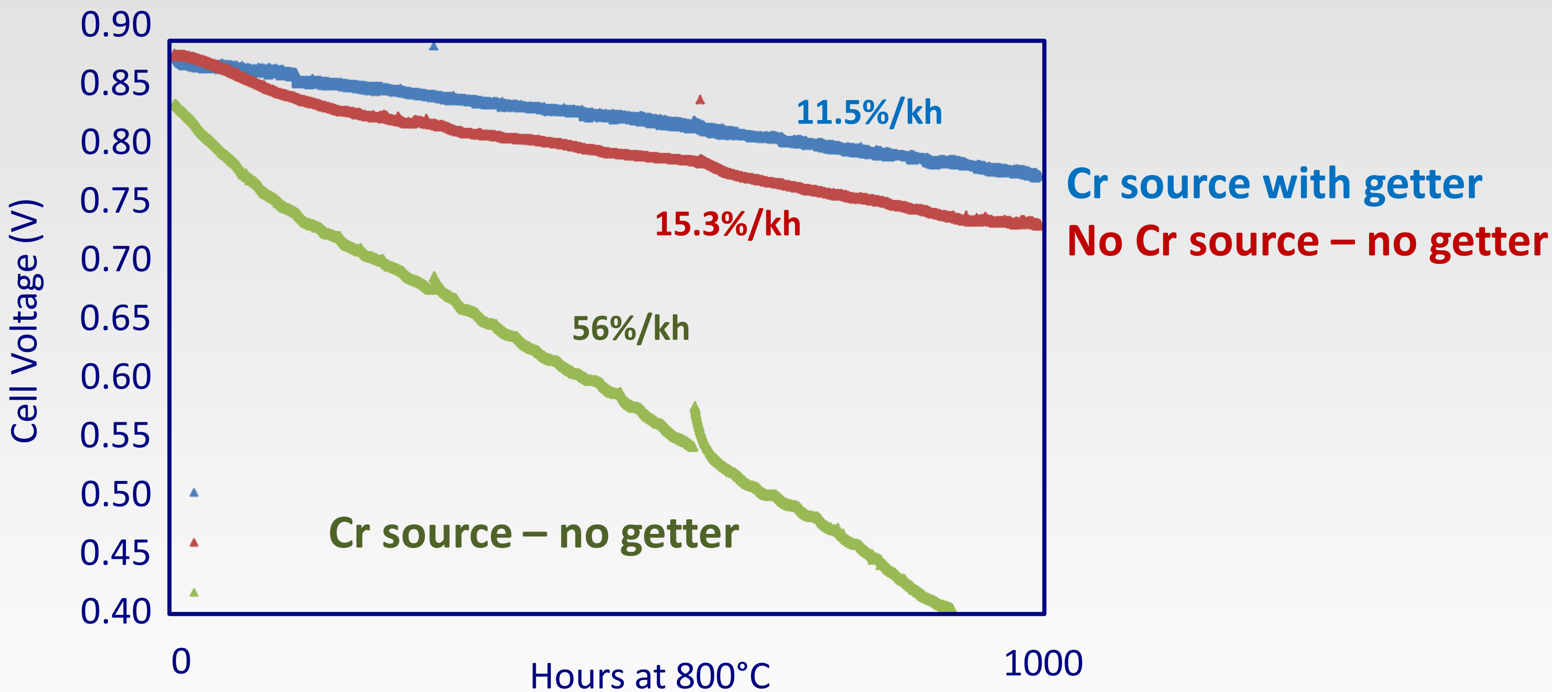
Chromium Getter





C. Liang et al., “Mitigation of Cathode Poisoning Using Chromium Getters,” 17th Annual Solid Oxide Fuel Cell Project Review Meeting July 19-21, 2016, Pittsburgh PA, https://www.netl.doe.gov/events/conference-proceedings/2016/2016sofc

Chromium Getter



J. Stevenson and B. Koeppel, SOFC Development at PNNL: Overview," 17th Annual Solid Oxide Fuel Cell Project Review Meeting July 19-21, 2016, Pittsburgh PA, https://www.netl.doe.gov/events/conference-proceedings/2016/2016sofc

Project Objective

- Phase I
  - To design, fabricate and test a chromium sensor for monitoring the chromium vapor produced during the operation of an SOFC
- Planned for Phase II
  - Evaluate the sensors in an operating fuel cell system in collaboration with FuelCell Energy
  - Evaluate sensor in chromium getter system developed at the University of Connecticut.
  - Develop of smaller sensors based on thin-film deposition techniques will involve collaboration with the Naval Research Laboratory.

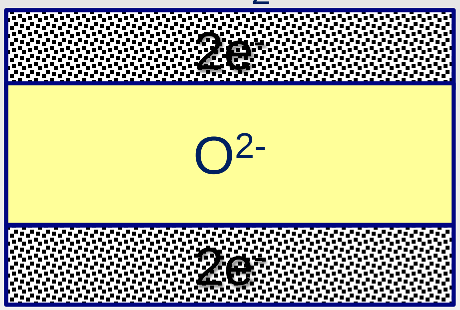
Chemical Sensor SOFC BOP / Stack

- Potentiometric Chemical Sensors
  - Solid electrolyte sensors have been demonstrated in aggressive environments
    - Oxygen dissolved in molten steel
    - Oxygen in exhaust gas form internal combustion engines
  - Thermodynamic – not kinetic
    - Stable
    - Not microstructure dependent
- 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

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

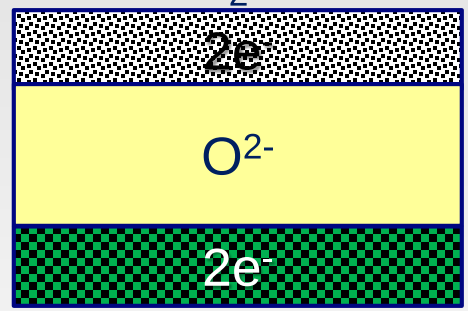
$2O^{2-} = O_2^S + 4e^-$



$2O^{2-} = O_2^R + 4e^-$

Gas reference
(e.g. Exhaust Gas Sensor)

$2O^{2-} = O_2^S + 4e^-$



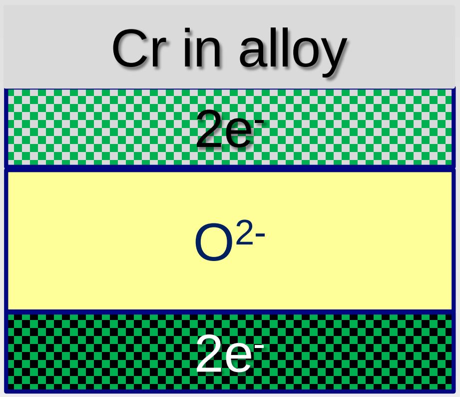
$2Cr + 3O^{2-} = Cr_2O_3 + 6e^-$

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

$2Cr + 3/2O_2 = Cr_2O_3$

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

Auxiliary Electrode



$2\underline{Cr} + 3O^{2-} = Cr_2O_3 + 6e^-$

Auxiliary Electrode

$2Cr + 3O^{2-} = Cr_2O_3 + 6e^-$

$$E = \frac{RT}{4F}\ln\left(\frac{pO_2^S}{pO_2^R}\right) = \frac{RT}{4F}\ln\left(\frac{\frac{a_{Cr_2O_3}}{a_{Cr}^2)_{alloy}\cdot K}}{\frac{a_{Cr_2O_3}}{a_{Cr}^2)_{ref}\cdot K}}\right) = \frac{RT}{4F}\ln\left(\frac{a_{Cr}^2)_{ref}}{a_{Cr}^2)_{alloy}}\right)$$

For Cr + Cr_2O_3 reference $\quad E = -\frac{RT}{2F}\ln(a_{Cr})$

Chemical Sensor SOFC BOP / Stack

- Sensor Parameters
  - Solid electrolytes
    - Yttria-stabilized zirconia
    - Beta" alumina
  - Auxiliary Electrodes
    - $YCrO_3$
      - Doping
    - $Na_2Cr_2O_4$
    - Composite electrodes
  - Geometries
    - Tubular
    - Planar
- Operational Parameters
  - Temperature
    - 500-800°C
  - Chromium
    - Temperature of Cr_2O_3
  - Water vapor

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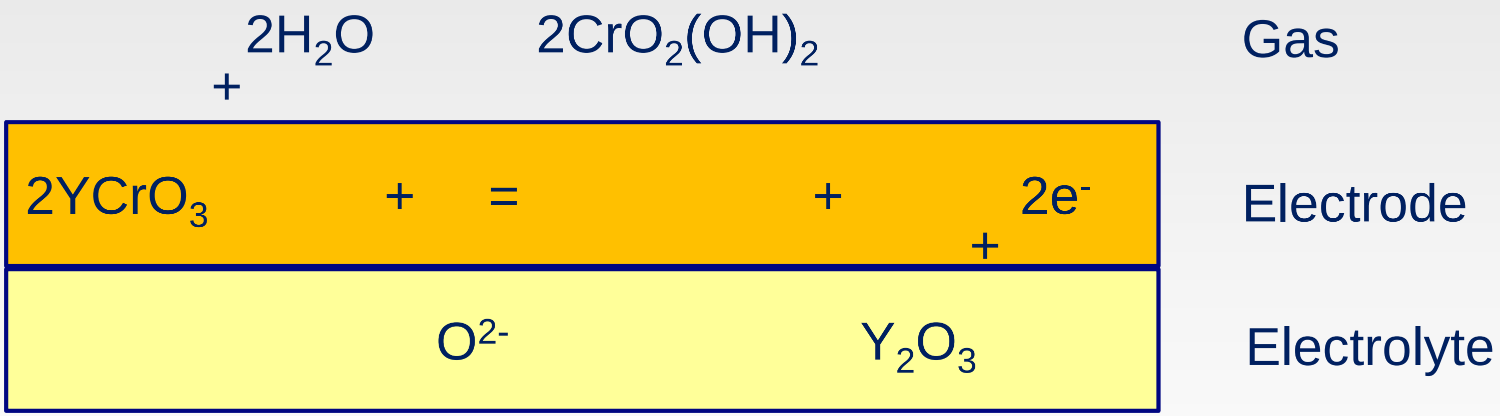
YSZ Auxiliary Electrode Reaction

$$2YCrO_3 + 2H_2O + O^{2-} = 2CrO_2(OH)_2 + Y_2O_3 + 2e^-$$



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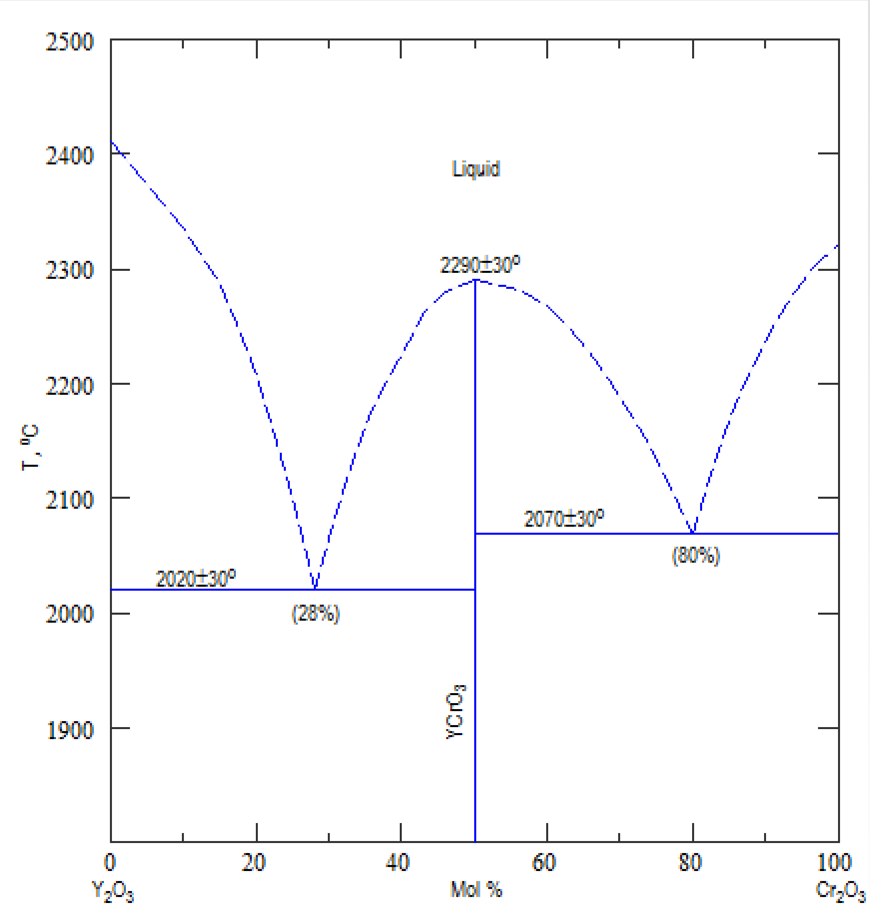
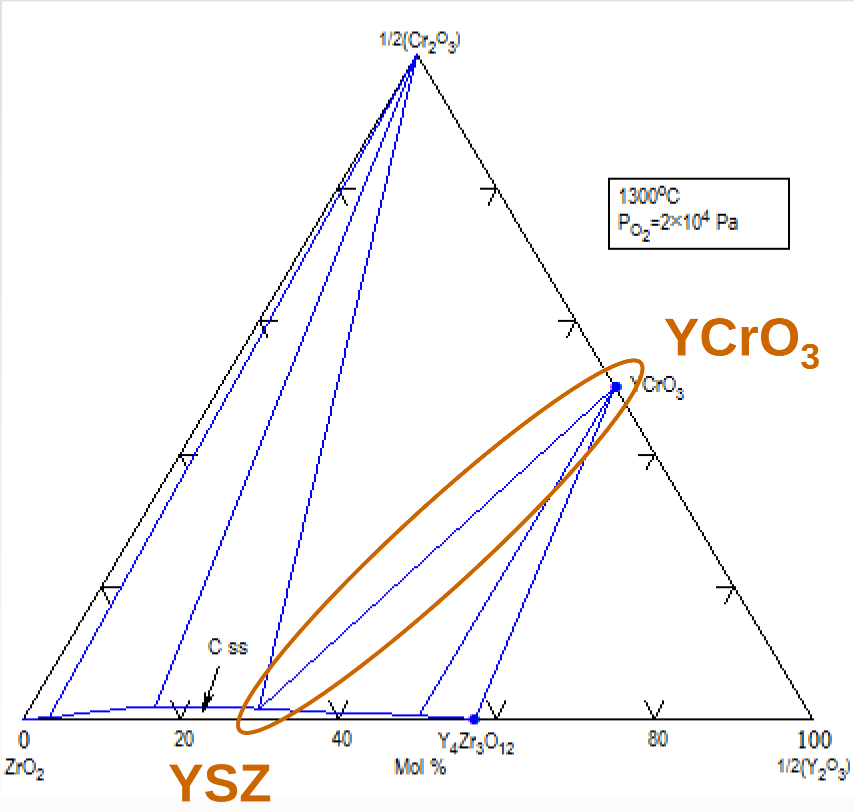
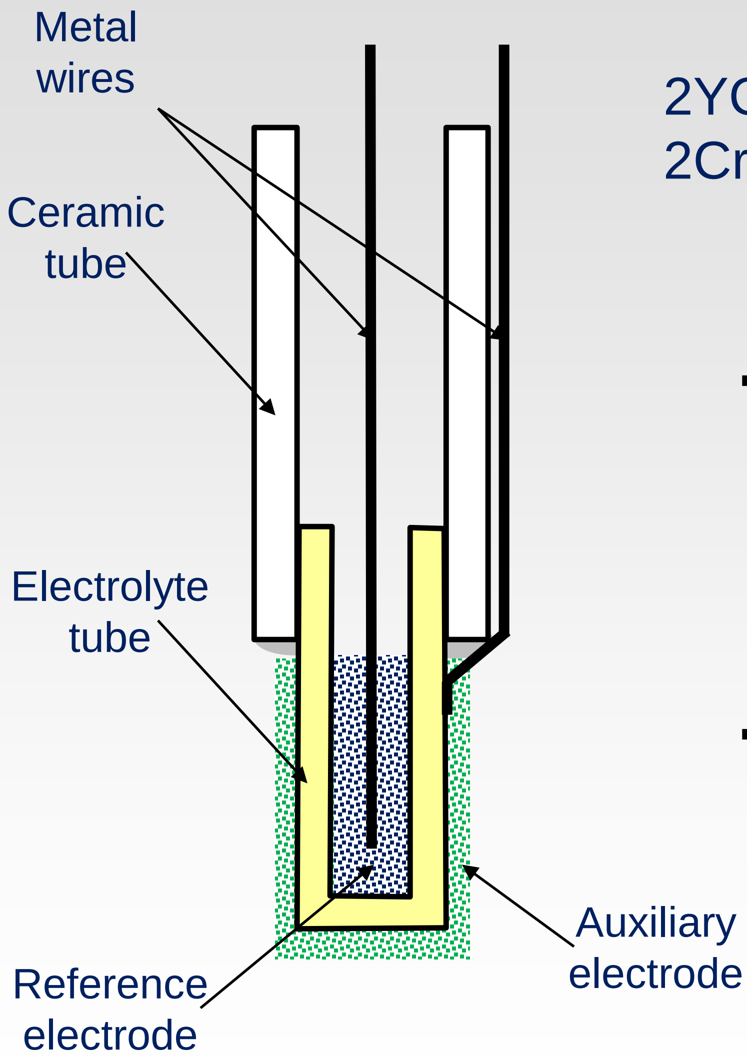
Zr-Y-Cr-O Phase Equilibria



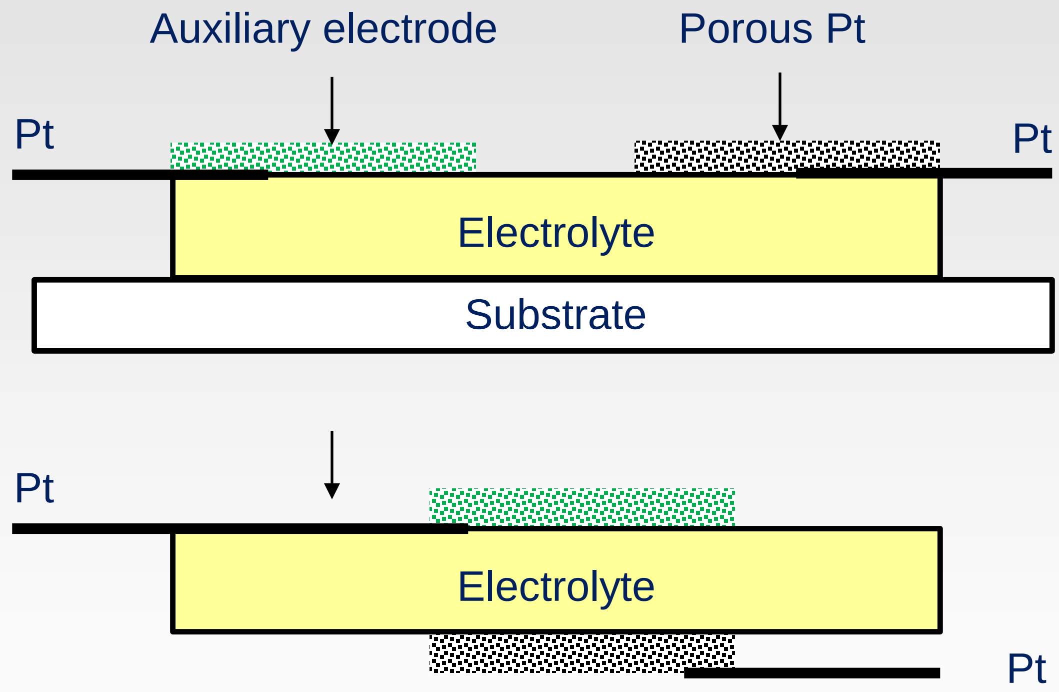


Sensor Schematics



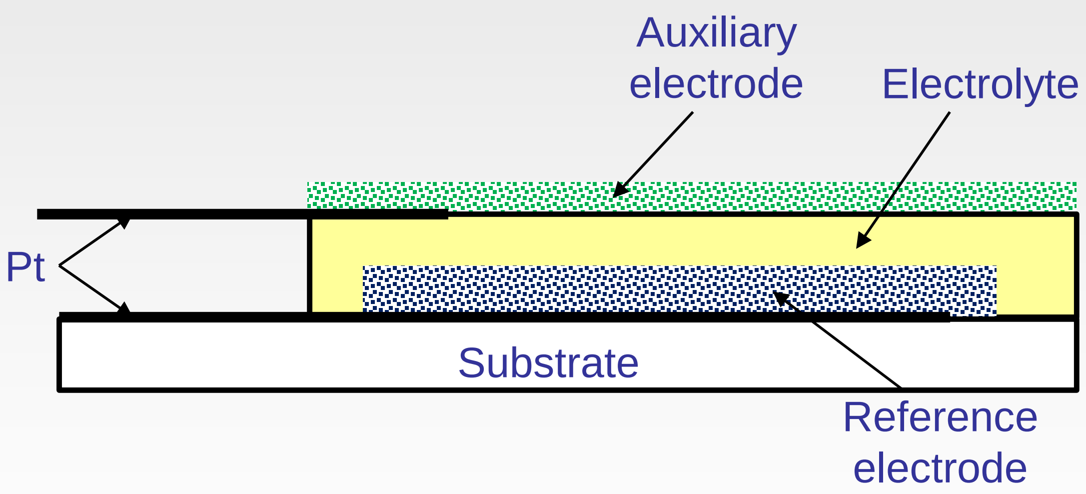
$$2YCrO_3 + 2H_2O + O^{2-} = 2CrO_2(OH)_2 + Y_2O_3 + 2e^-$$

$$O^{2-} = O_2 + 2e^-$$



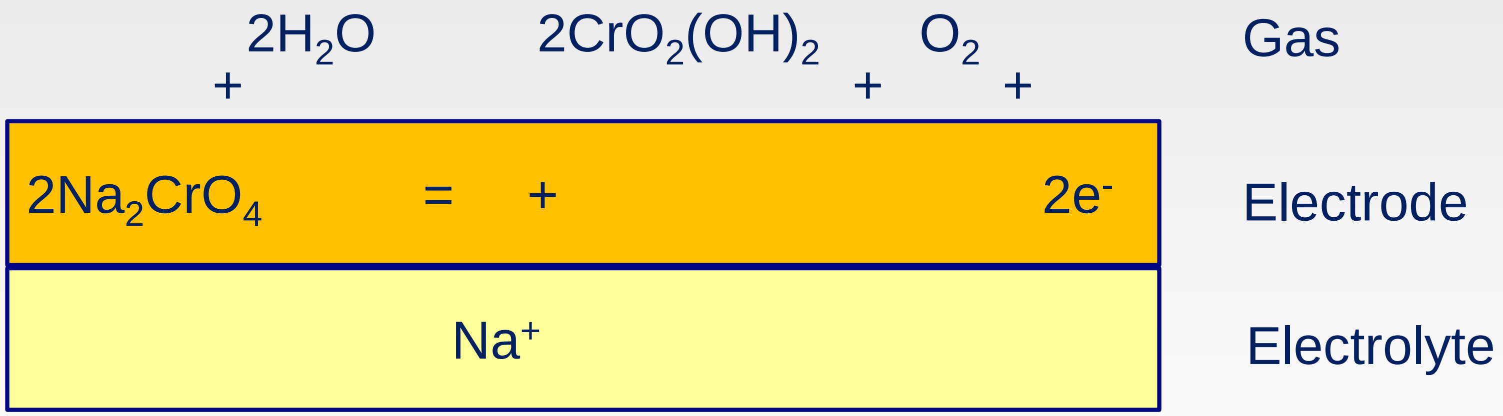
Sensor Miniaturization

- Thin film fabrication
- Measure of local Cr vapor concentrations



Beta Alumina Auxiliary Electrode Reaction

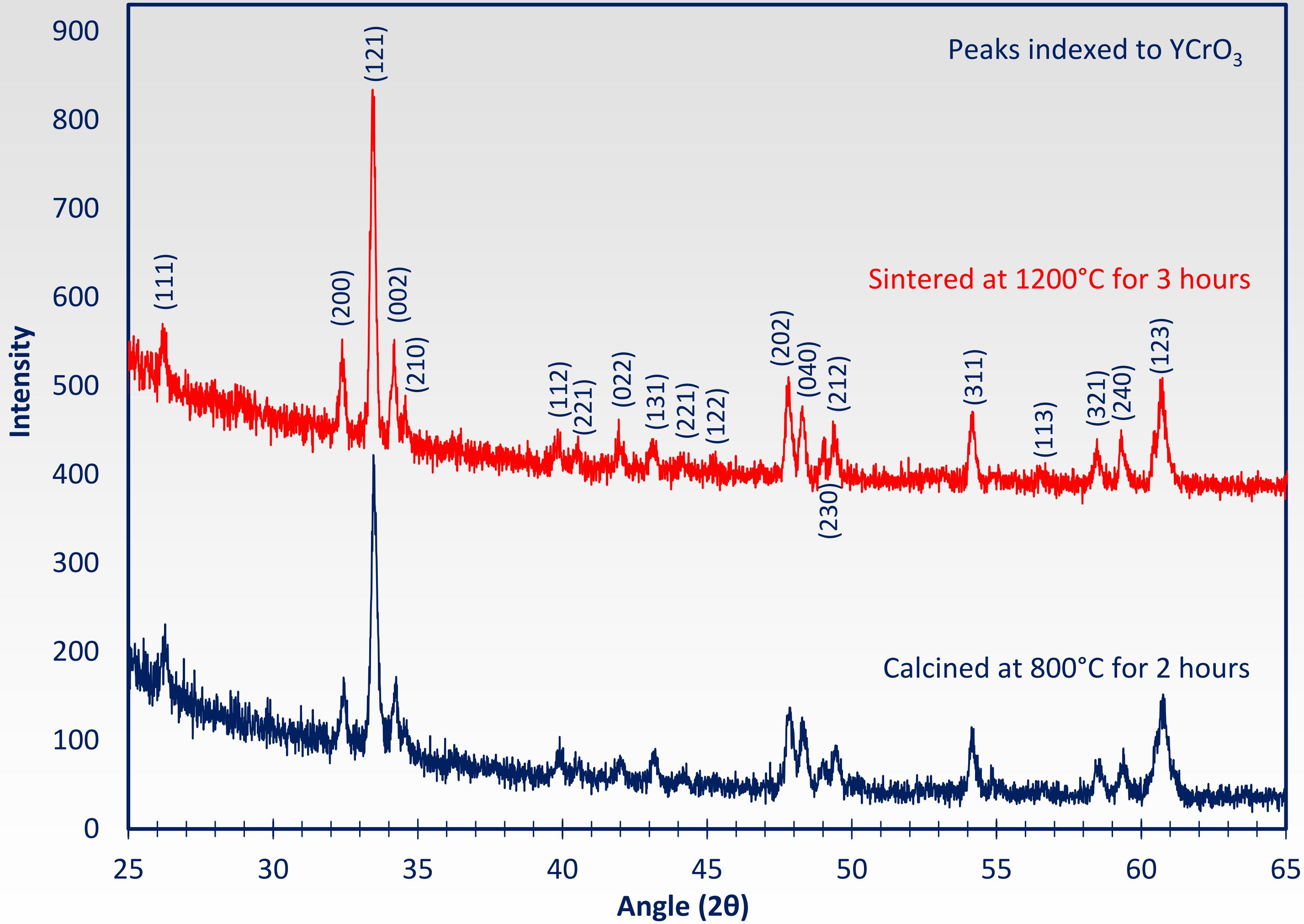
$$2Na_2CrO_4 + 2H_2O = 4Na^+ + 2CrO_2(OH)_2 + O_2 + 2e^-$$



Synthesis of $YCrO_3$

- Co-precipitation
- $Y(OH)_3$ and $Cr(NO_3)_3 \bullet 9H_2O$ dissolved in aqueous solutions of HNO_3 and NH_4OH
- Stirred overnight
- Dried for 24 hours at 80°C
- Calcined for 2 hours at 800°C
- Sintered for 3 hours at 1200-1500°C

Synthesis of $YCrO_3$



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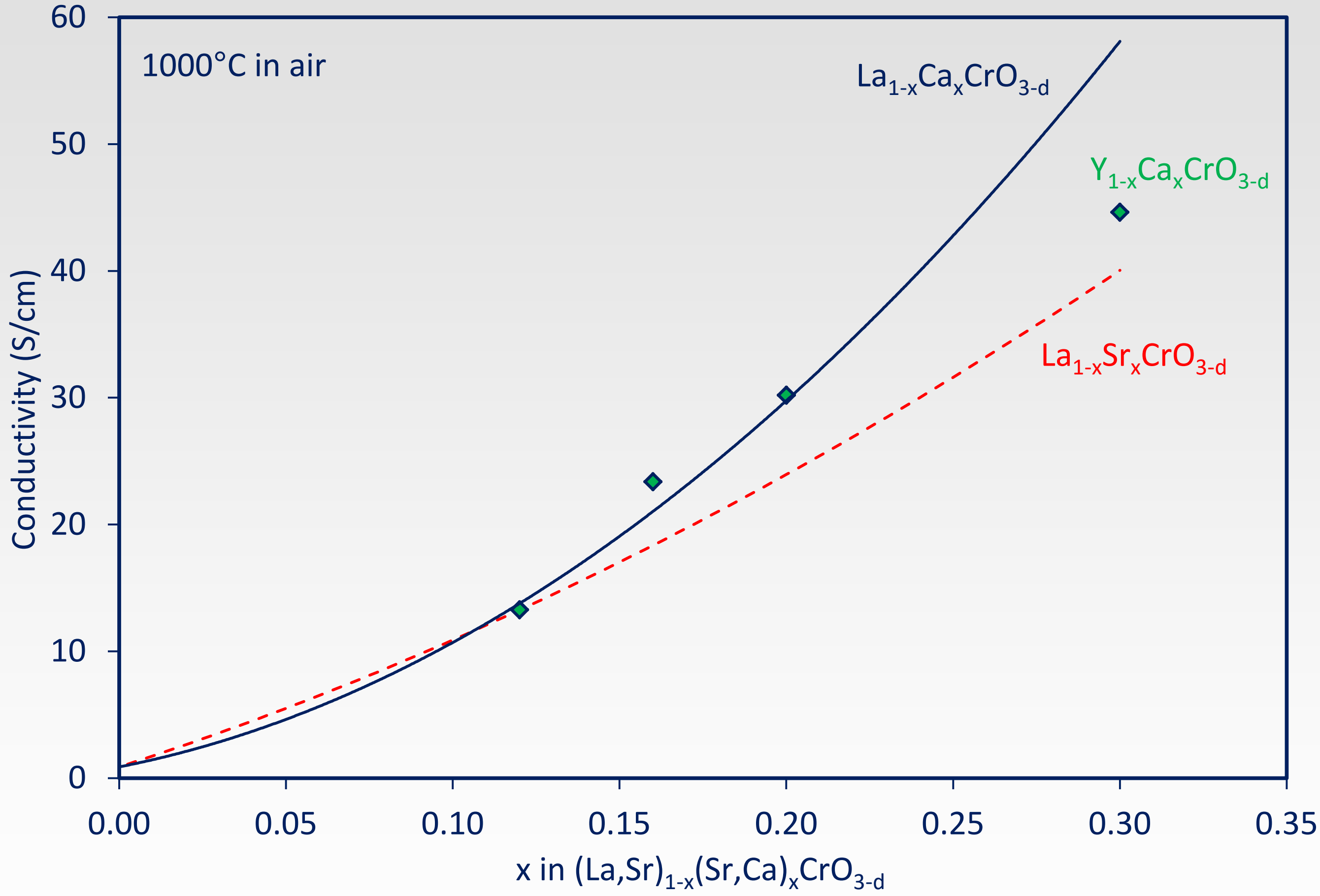
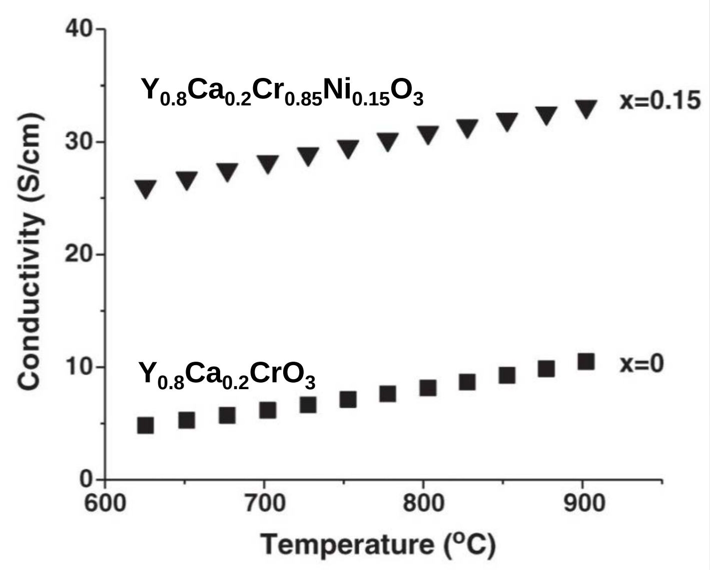
A-Site Doping of $YCrO_3$

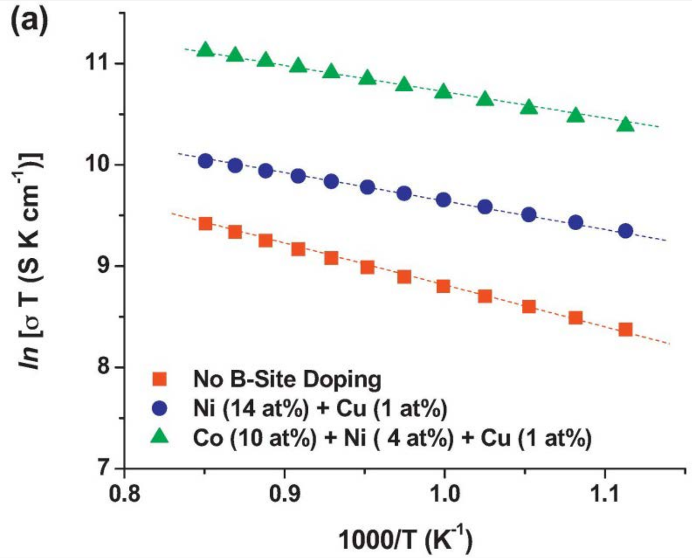


Doped chromites used as ceramic interconnects in SOFCs

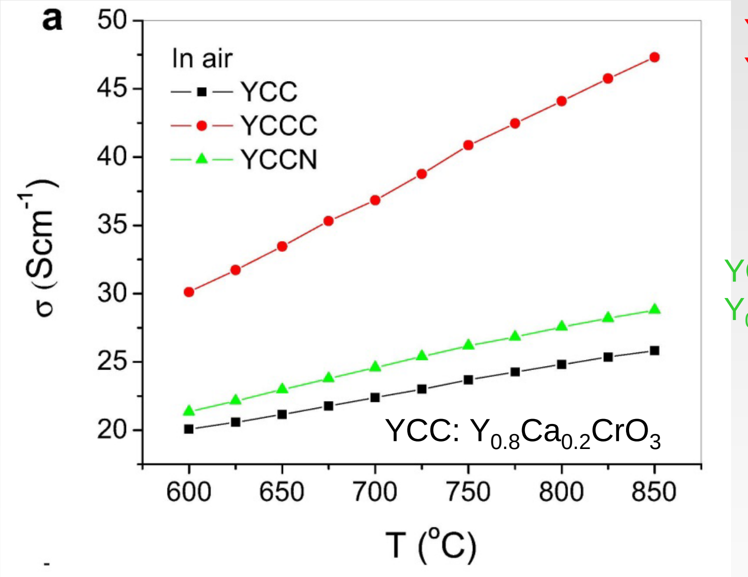
J.W. Fergus, *Solid State Ionics* **171** (2004) 1.
J.L. Bates, L.A. Chick and W.J. Weber, *Solid State Ionics* **52** (1992) 235.

B-Site Doping of $YCrO_3$





K.J. Yoon, J.W. Stevenson and O.A. Marina, *Solid State Ionics* **193** (2011) 60; *J. Power Sources* **196** (2011) 8531.

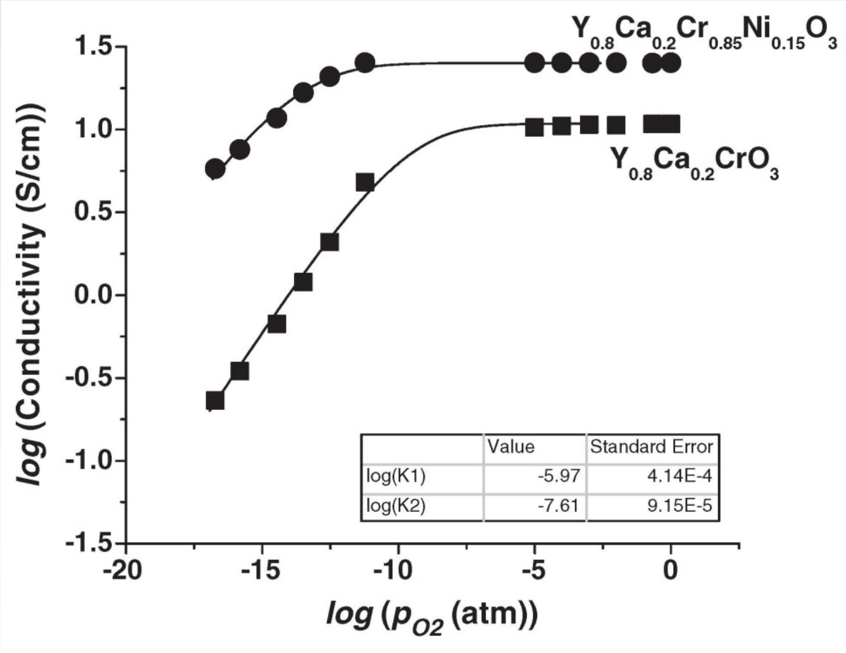


YCCC: $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_3$

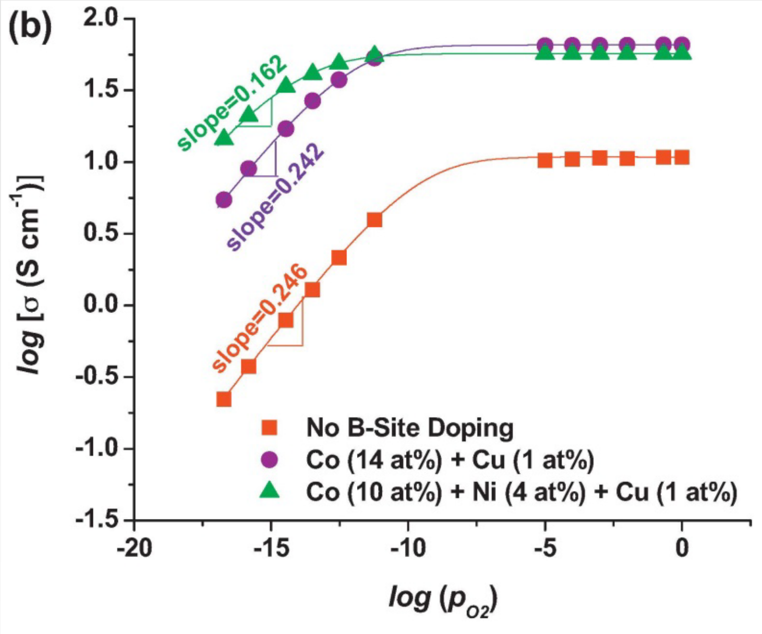
YCCN: $Y_{0.8}Ca_{0.2}Cr_{0.9}Ni_{0.1}O_3$

W. Li, M. Gong and X. Liu, *J. Power Sources* **241** (2013) 494.

B-Site Doping of $YCrO_3$



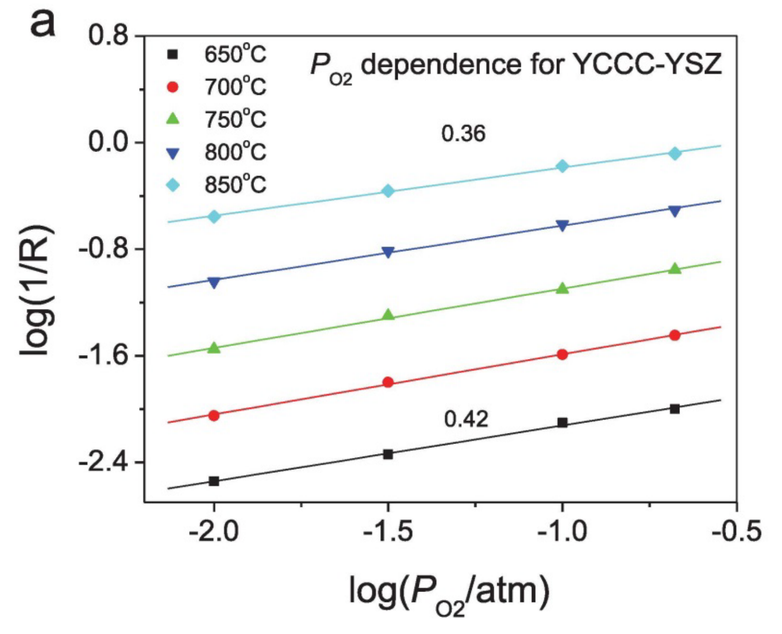
	Value	Standard Error
log(K1)	-5.97	4.14E-4
log(K2)	-7.61	9.15E-5



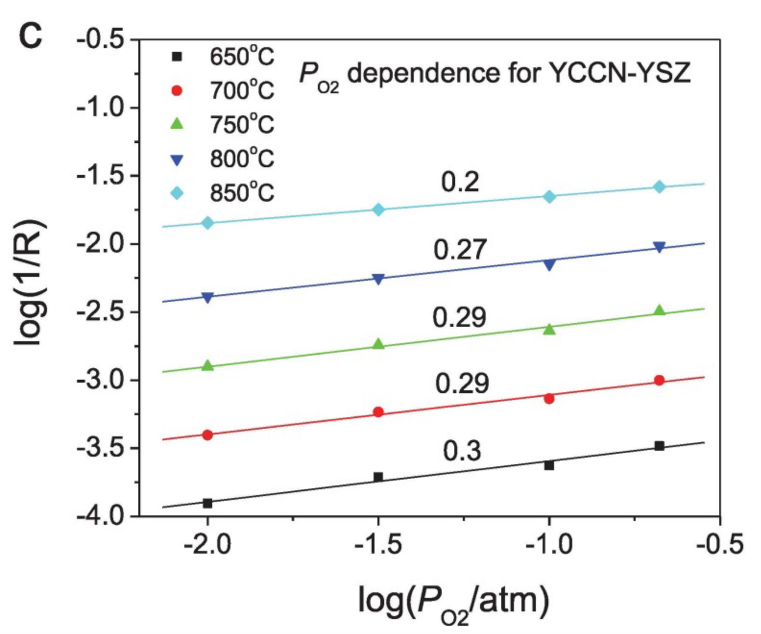
K.J. Yoon, J.W. Stevenson and O.A. Marina, *Solid State Ionics* **193** (2011) 60; *J. Power Sources* **196** (2011) 8531.

Doped $YCrO_3$ as Electrode

YCCC: $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_3$



YCCN: $Y_{0.8}Ca_{0.2}Cr_{0.9}Ni_{0.1}O_3$



W. Li, M. Gong and X. Liu, *J. Electrochem. Soc.* **161** (2014) F551.

Summary

- Chromium sensor for health monitoring in SOFC balance of plant
  - Solid electrolyte potentiometric
    - Demonstrated performance in aggressive environments
    - Potential for miniaturization
  - Auxiliary electrode for Cr sensitivity

Acknowledgment

- DOE NETL Solid Oxide Fuel Cell Core Technology and Innovative Concepts award number DE-FE0028183 (Arun C. Bose)

Thank you for your attention