Chromium Vapor Sensor for Monitoring Solid Oxide Fuel Cell Systems

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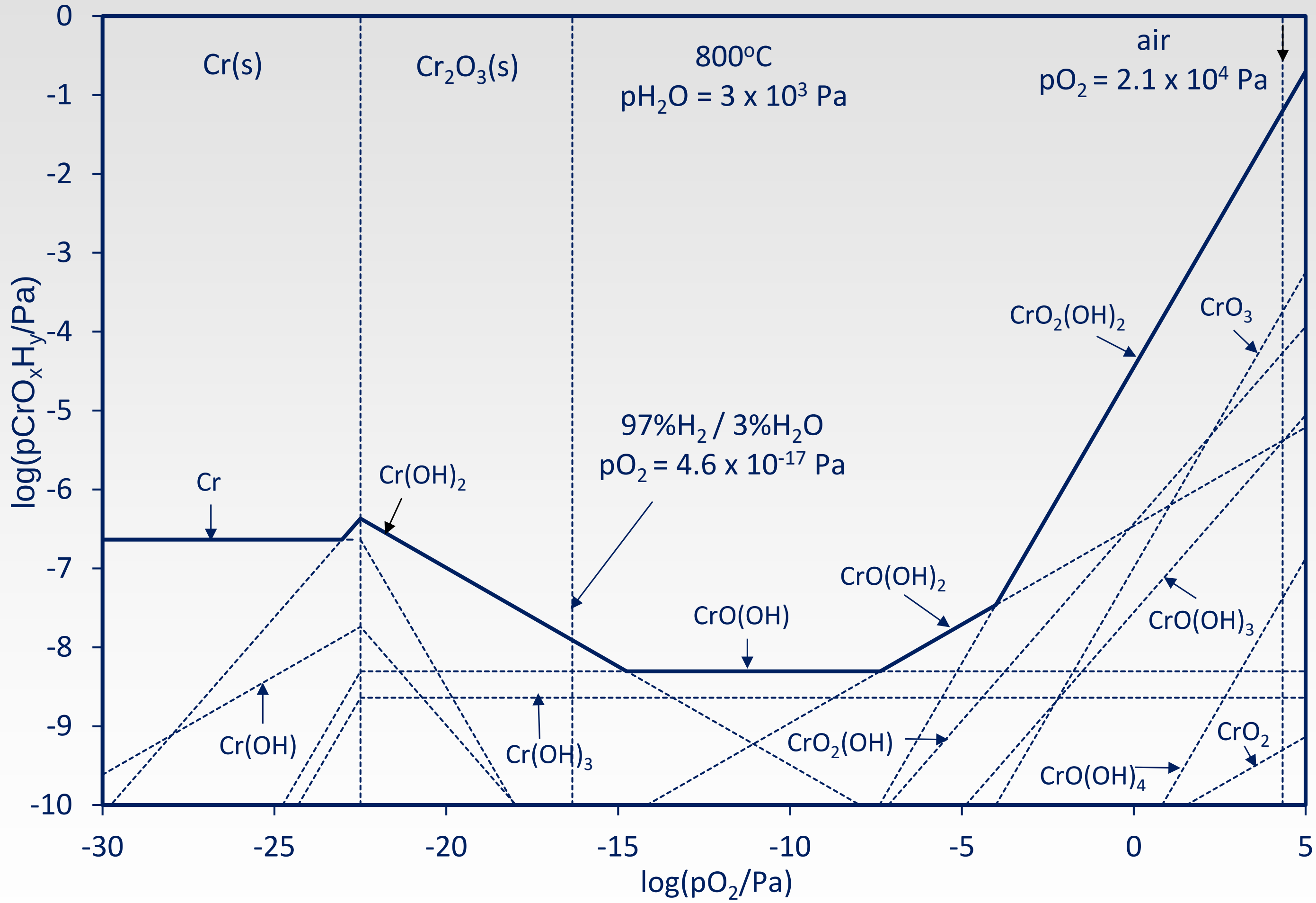
Acknowledgments

- Funding
  - DOE NETL Solid Oxide Fuel Cell Core Technology and Innovative Concepts, DE-FE0028183
- Students
  - Graduate student: Moaiz Shahzad
  - Undergraduate student: Tommy Britt

Background

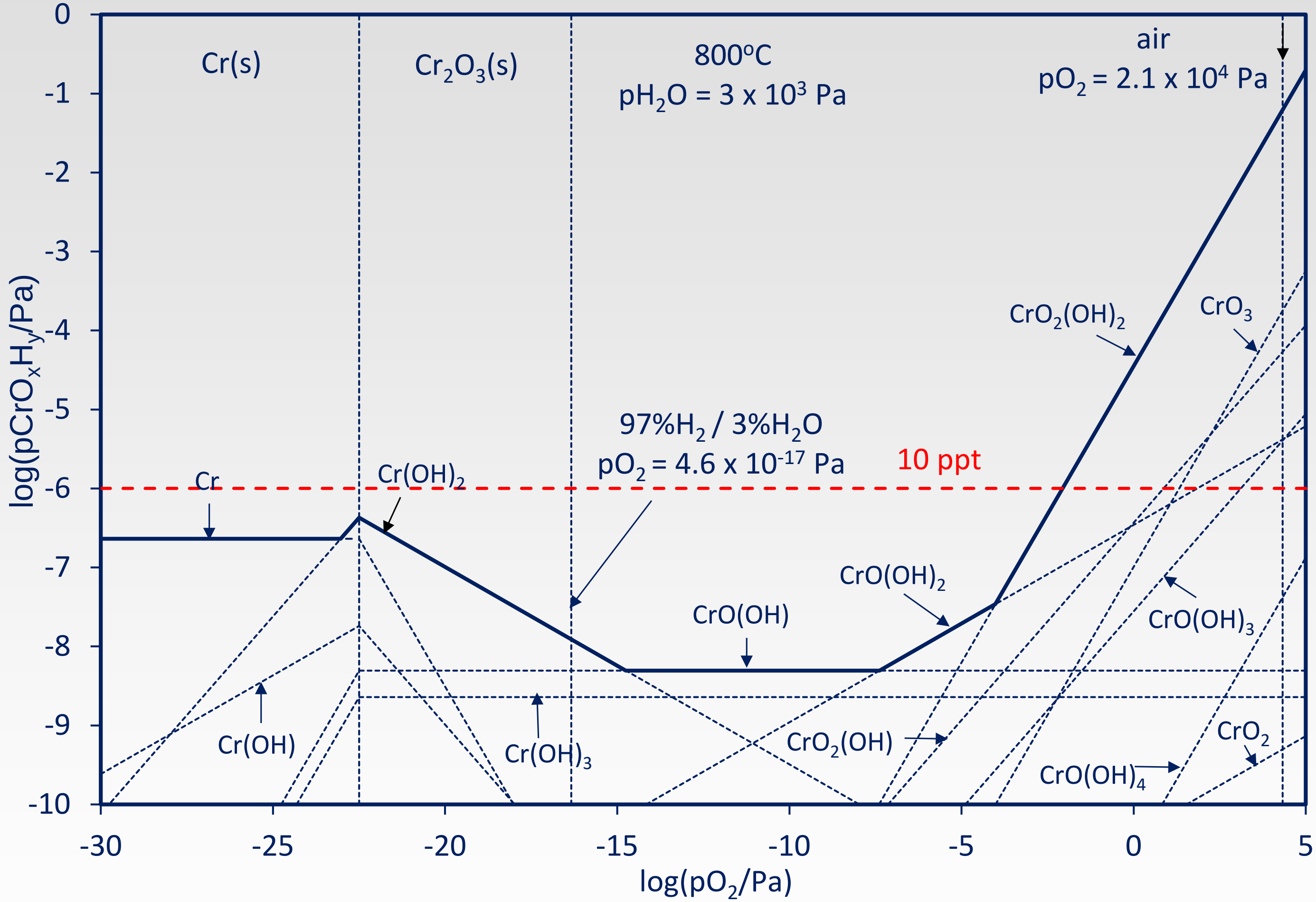
- Source of Chromium
  - Chromia formers used for interconnect due to high electronic conductivity of Cr_2O_3 relative to Al_2O_3 and SiO_2
  - Oxidation of chromia scale (interconnect or balance of plant) to CrO_3 or $CrO_2(OH)_2$
- Chromium Deposition
  - Cr^{6+} reduced to Cr^{3+} (*i.e.* Cr_2O_3)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

Cr-O-H Vapor Pressures



Vapor pressures higher in oxidizing conditions

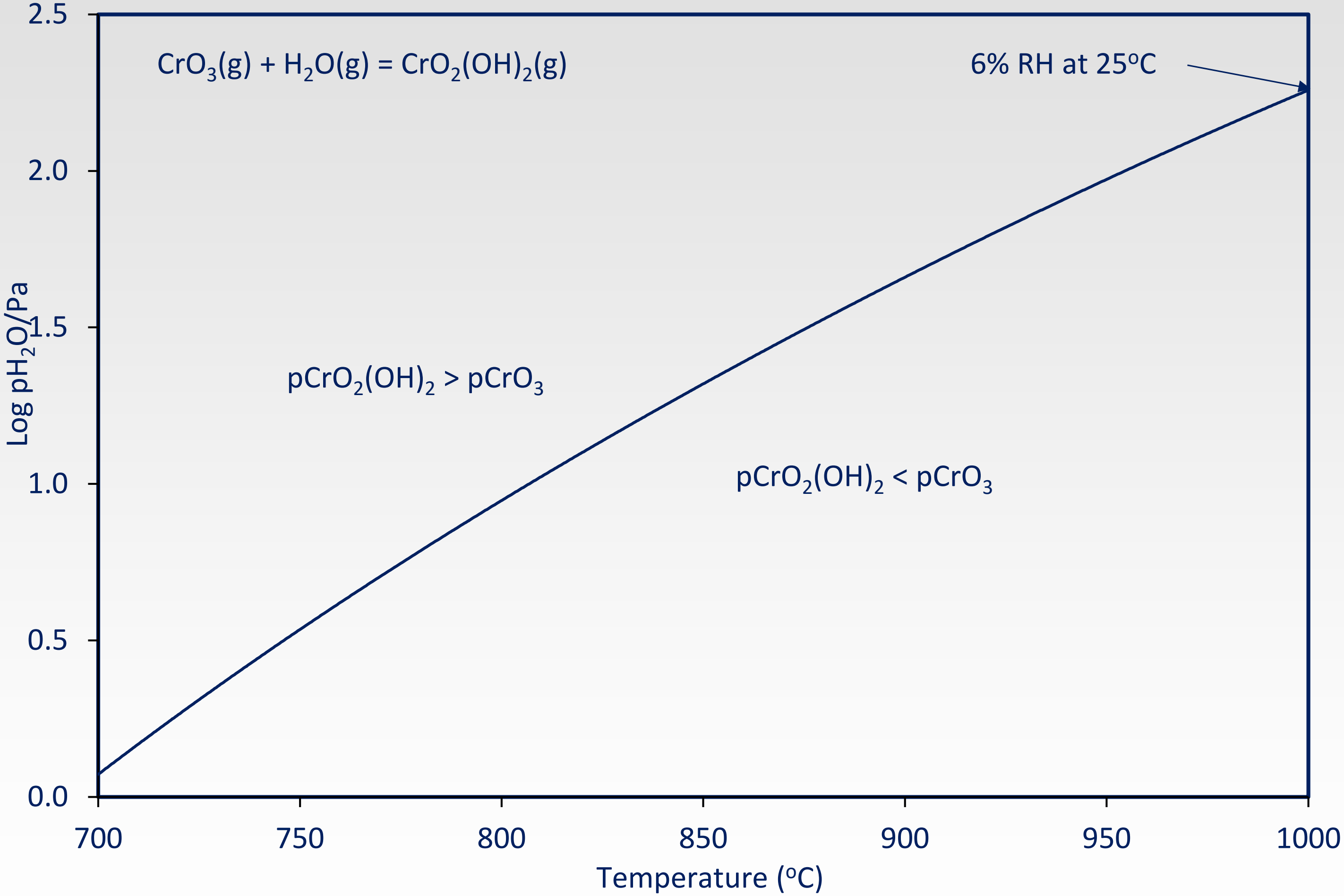
Cr-O-H Vapor Pressures



10 ppm does not cause degradation

J.S.Hardy *et al.*, "Button Cell Tests with LSM/YSZ Cathodes with Quantified Cr Concentrations," 17th Annual Solid Oxide Fuel Cell Project Review Meeting, June 12-14, 2017, Pittsburgh PA, https://www.netl.doe.gov/events/conference-proceedings/2017/sofc

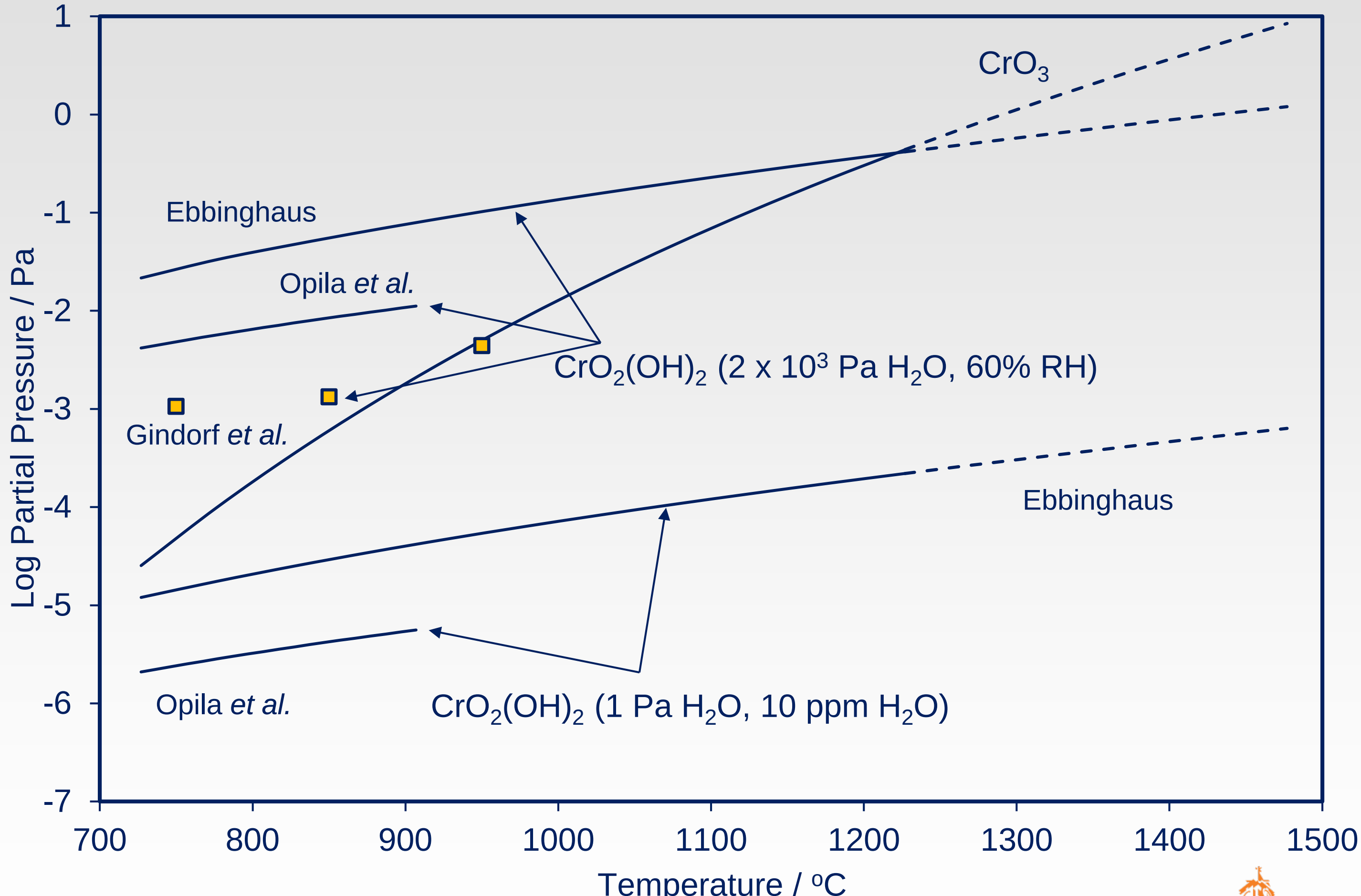
Stability of CrO_3 / $CrO_2(OH)_2$



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

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

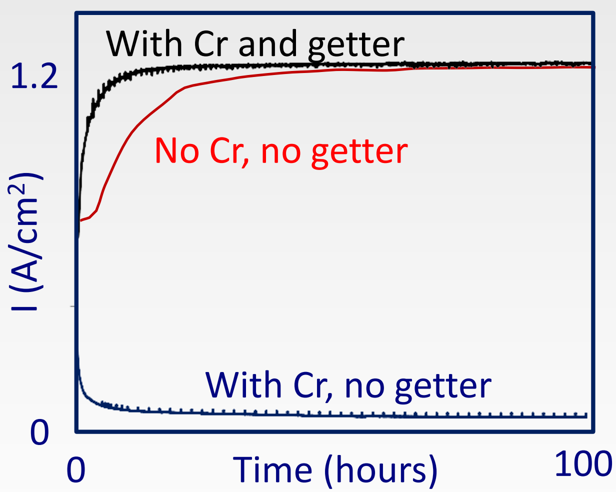
Vapor pressure of $CrO_2(OH)_2$ high at relatively low temperatures

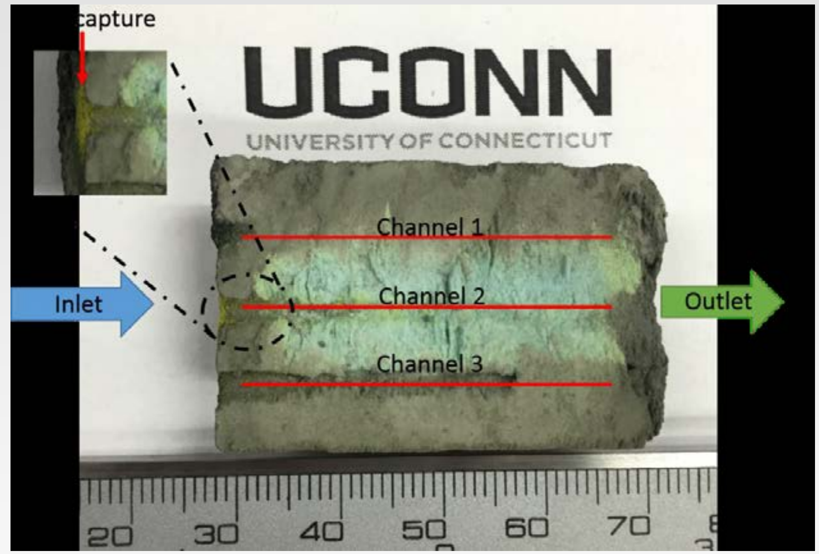


Reduce Chromium Poisoning

- 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

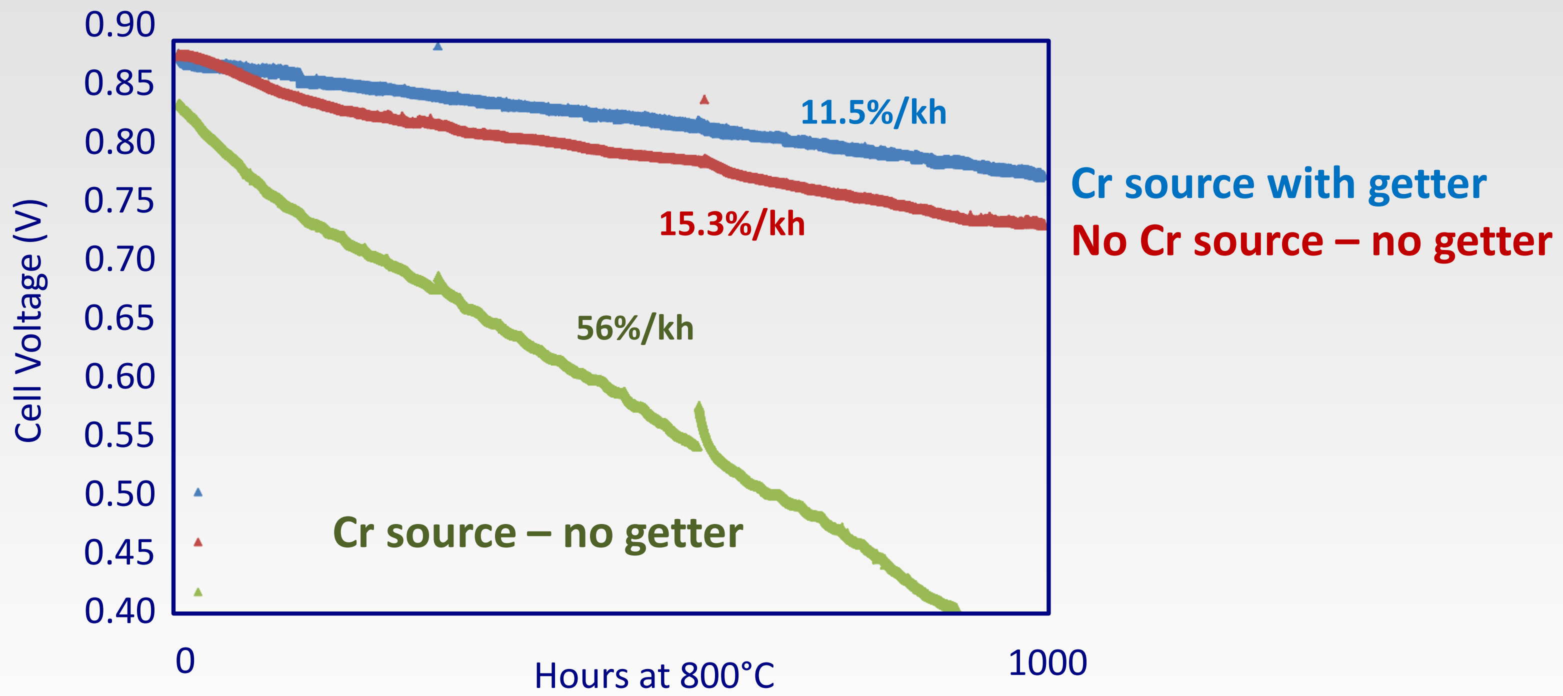
Chromium Getter





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

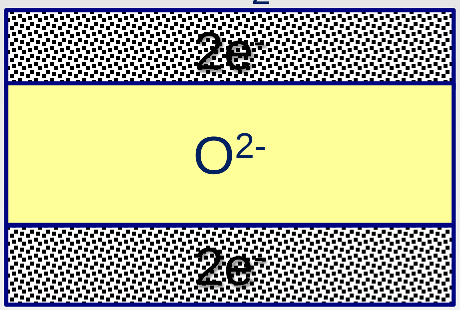
Chemical Sensor SOFC BOP / Stack

- 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)

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

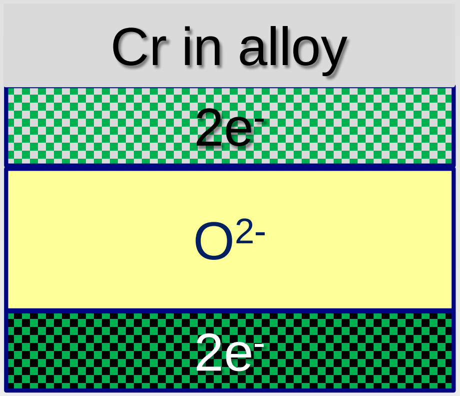
$2Cr + 3O^{2-} = Cr_2O_3 + 6e^-$

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

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

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

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

YSZ Auxiliary Electrode Reaction

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

$2H_2O$ $2CrO_2(OH)_2$ Gas

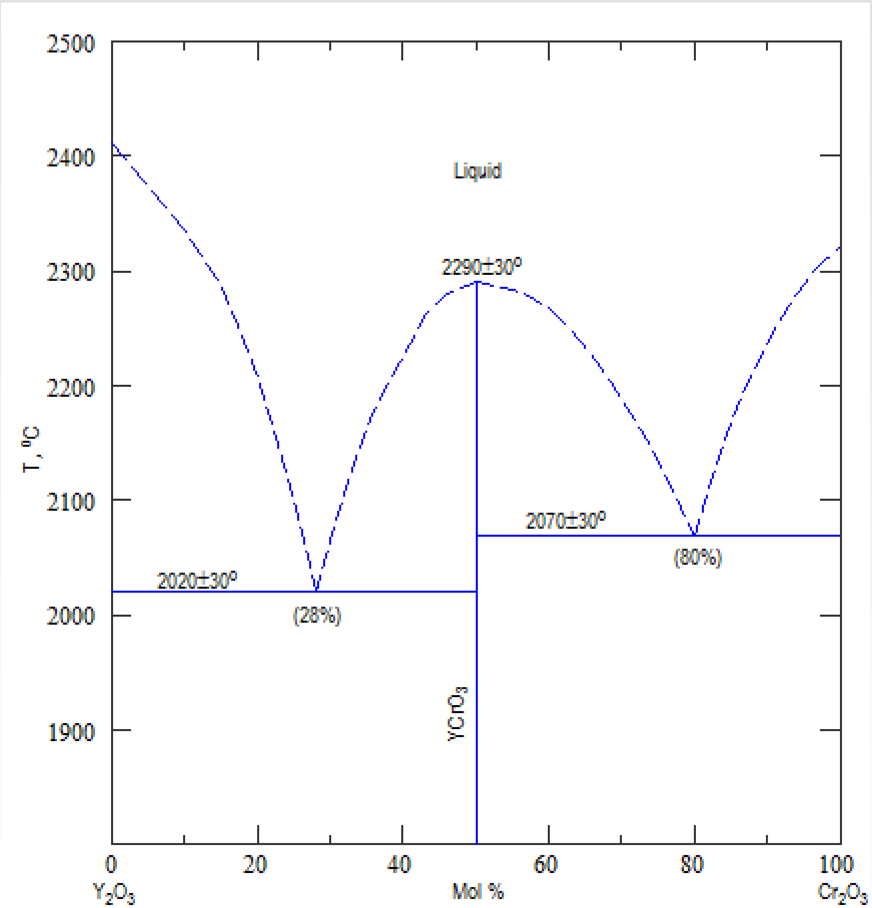
\+

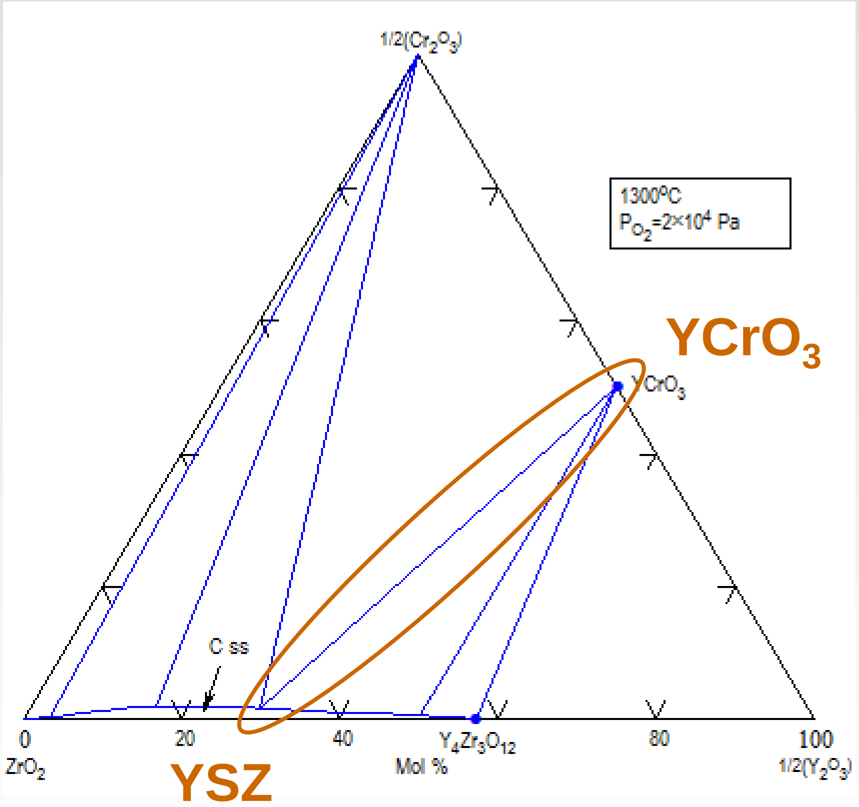
$2YCrO_3$ + = + $2e^-$ Electrode

\+

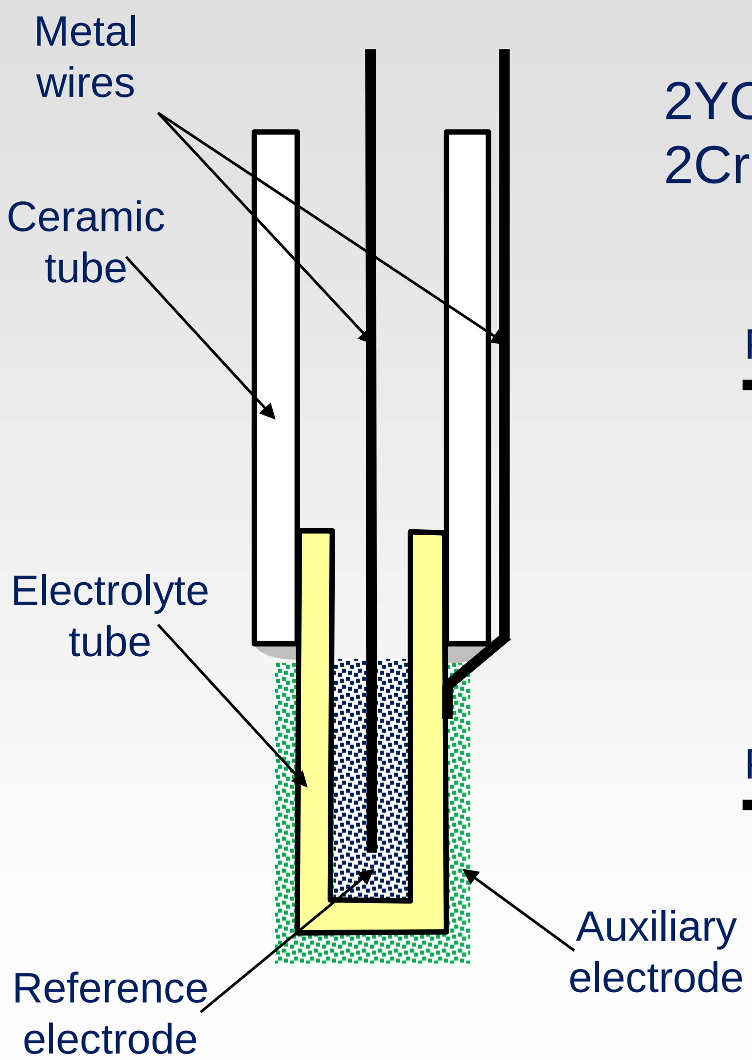
O^{2-} Y_2O_3 Electrolyte

Zr-Y-Cr-O Phase Equilibria



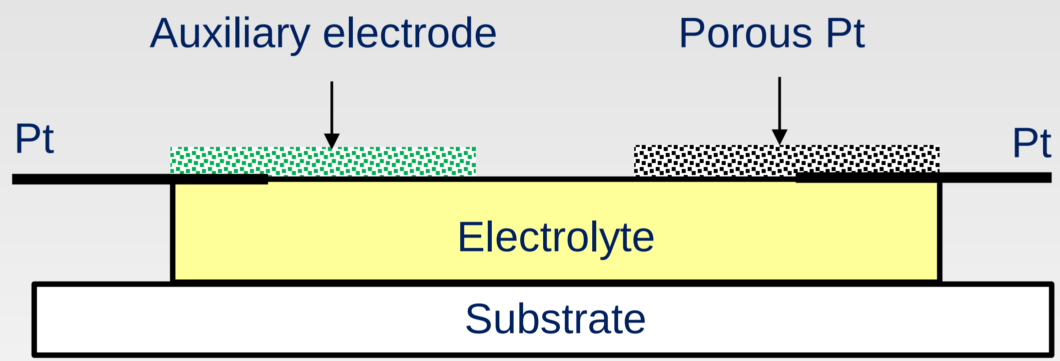


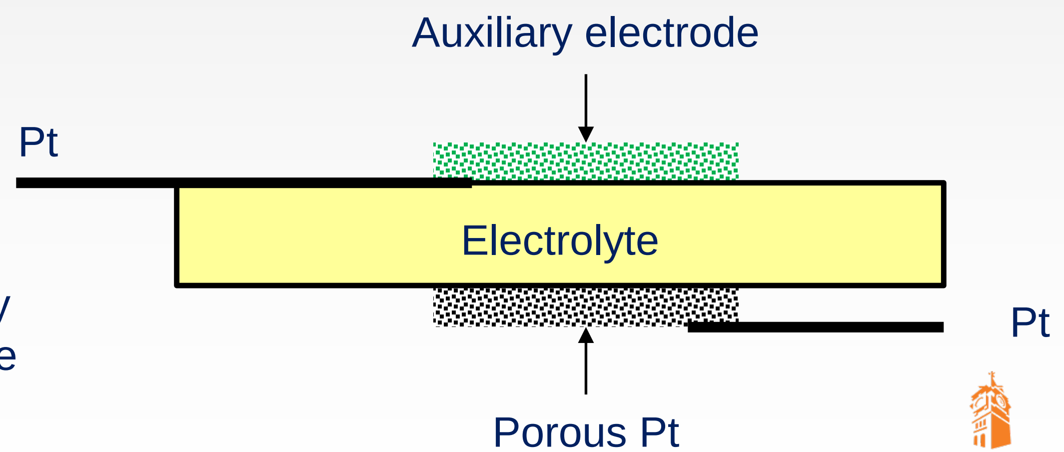
Sensor Schematics



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

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





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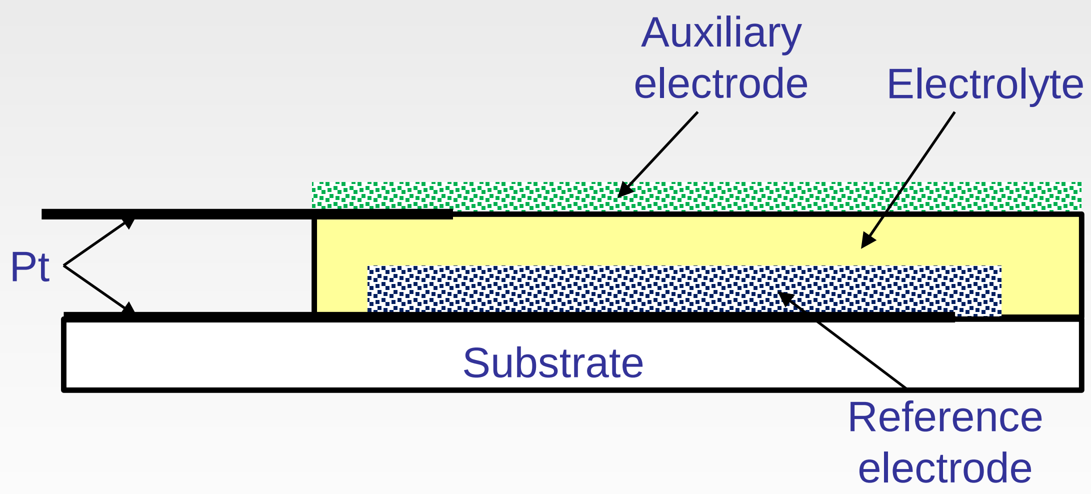
Sensor Miniaturization

- Thin film fabrication
- Measure of local Cr vapor concentrations



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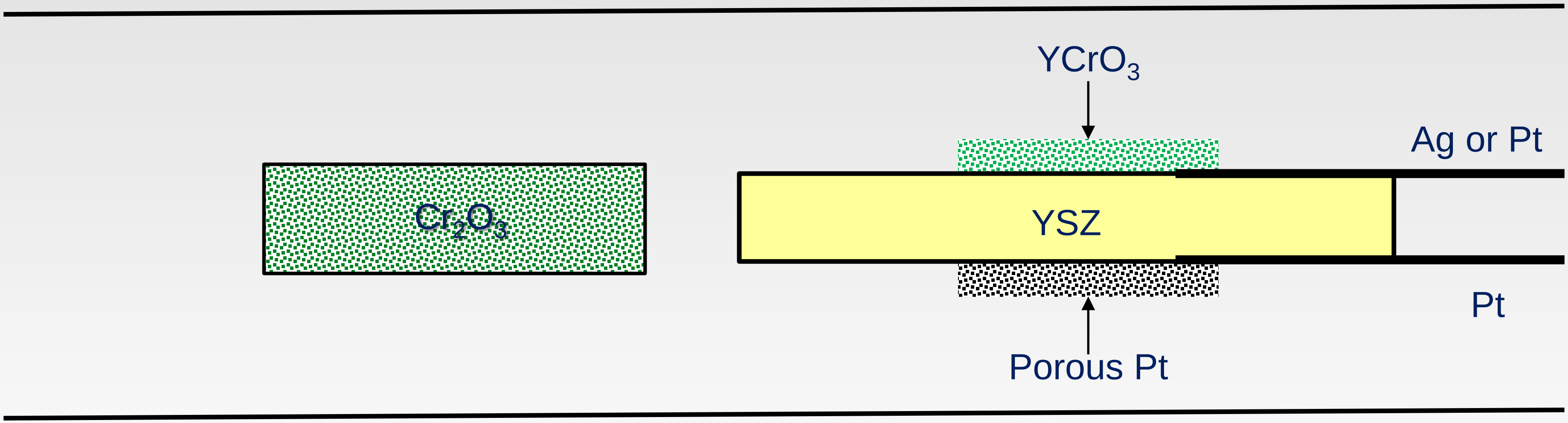
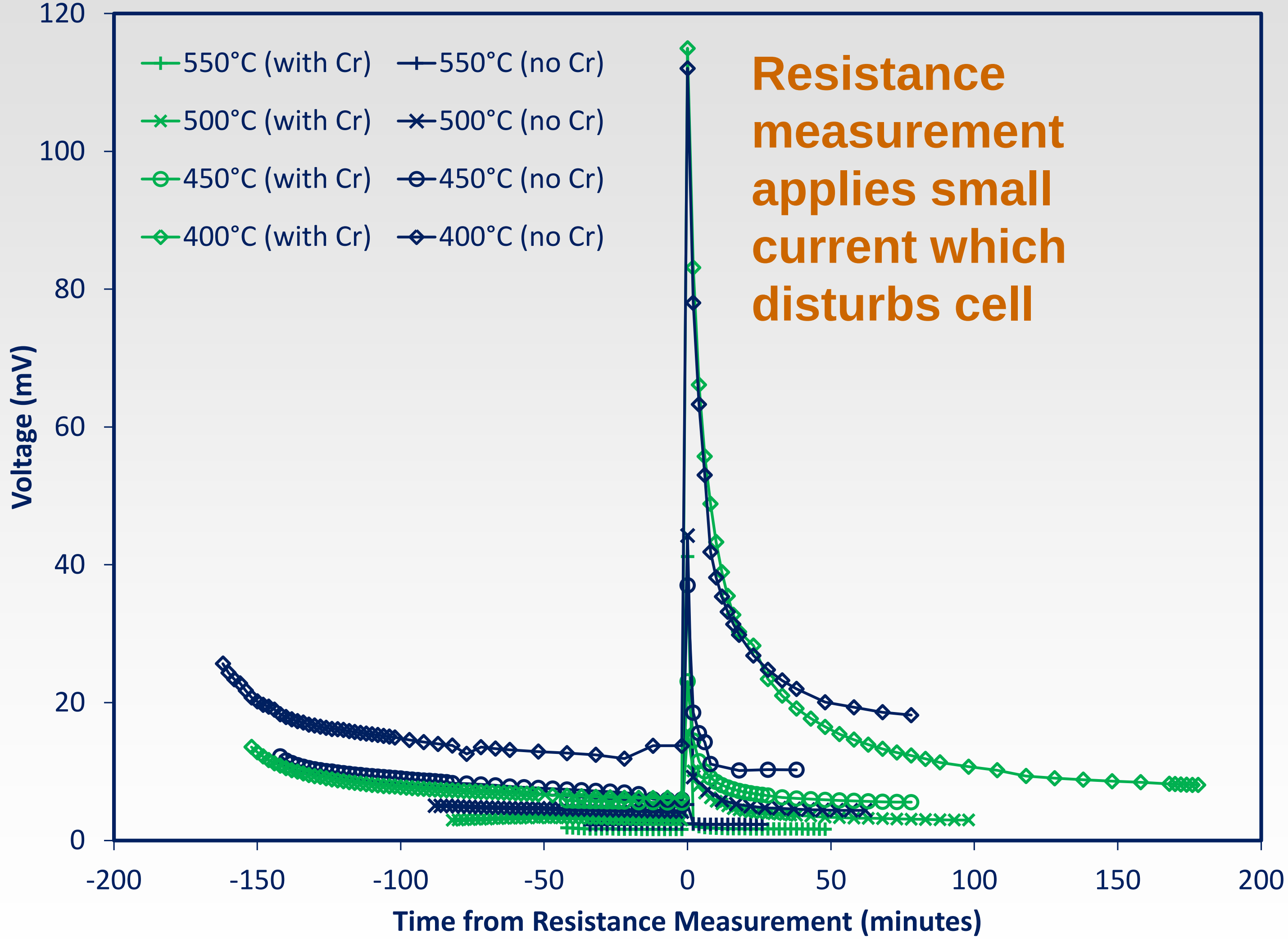
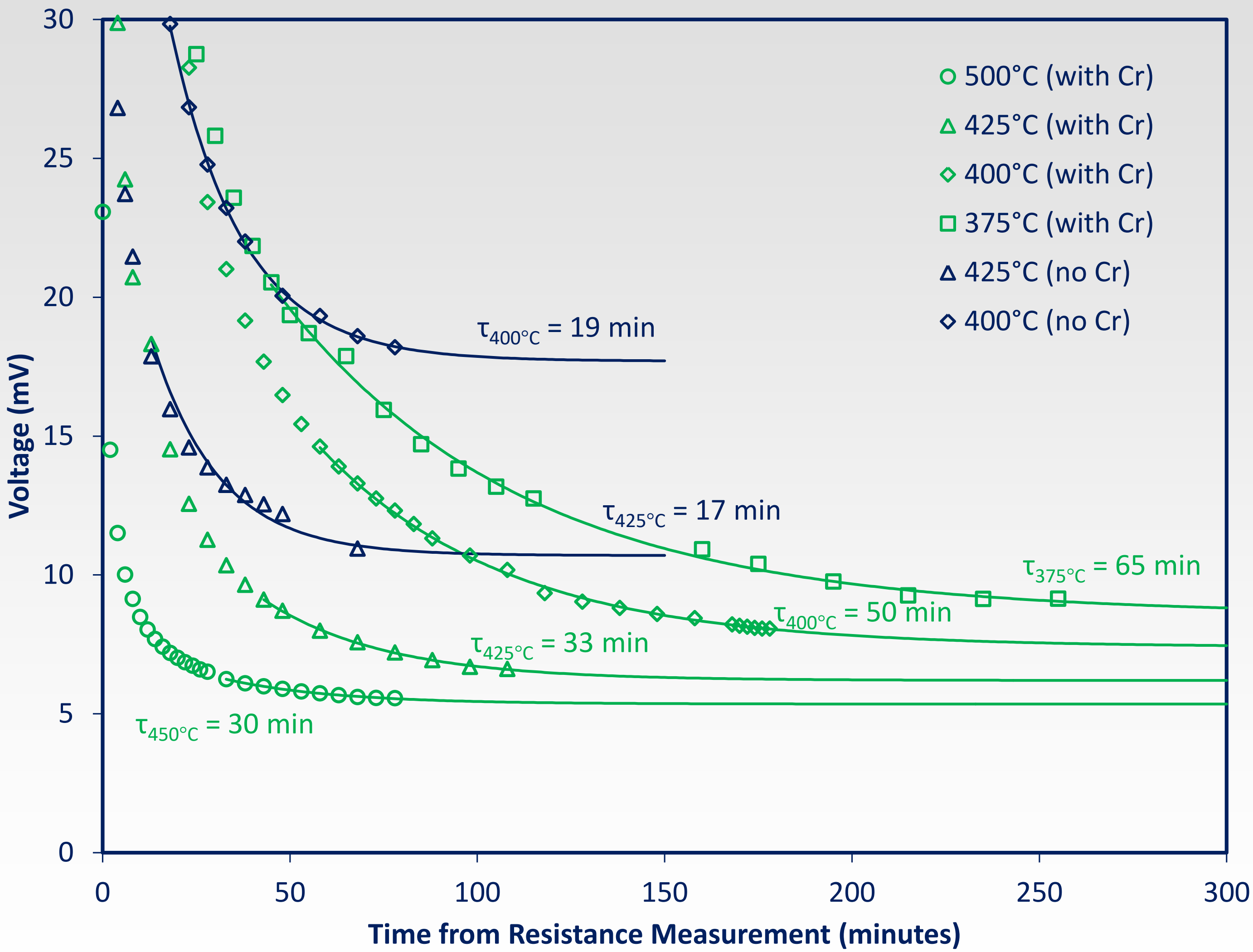
Sensor Testing



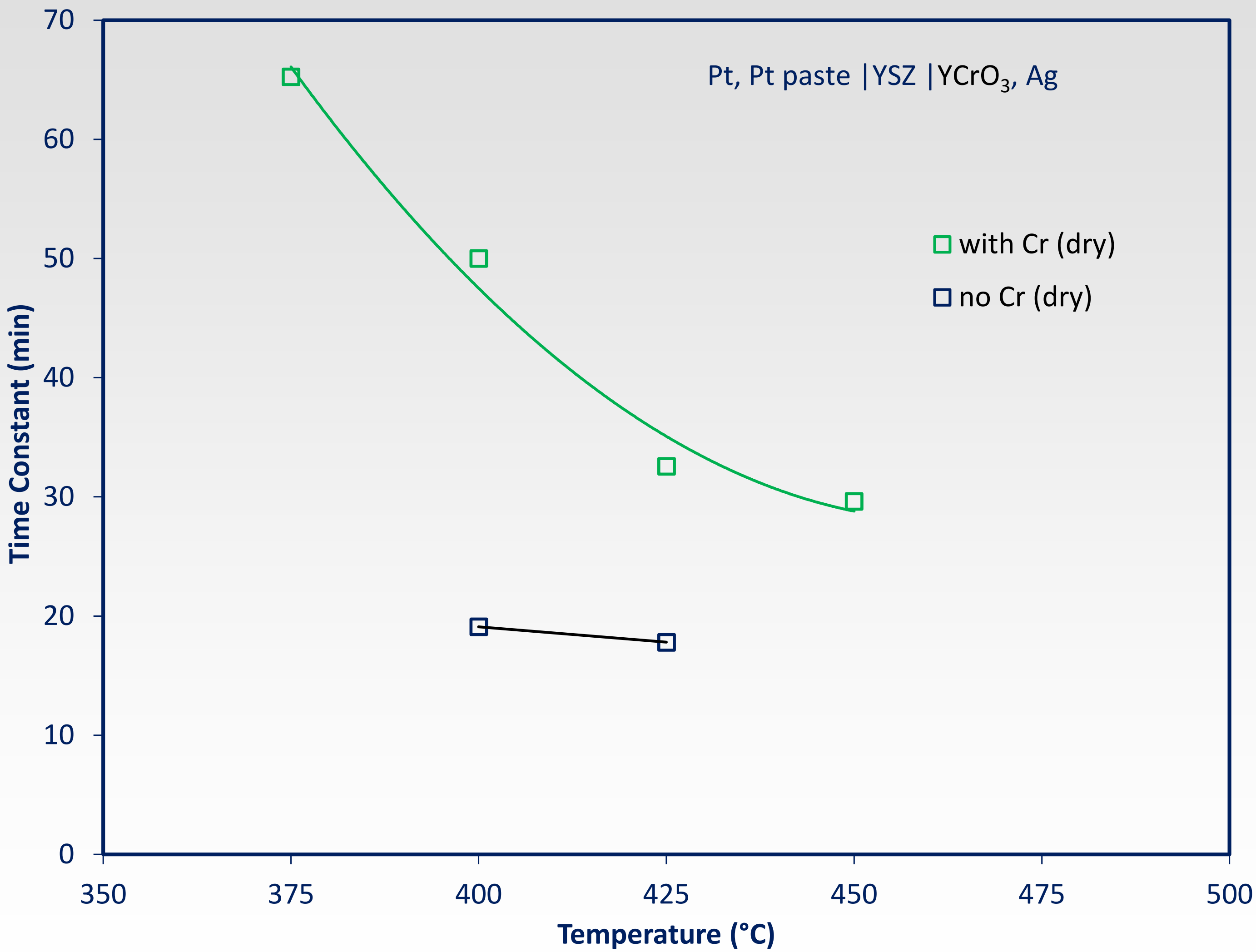
Sensor Response



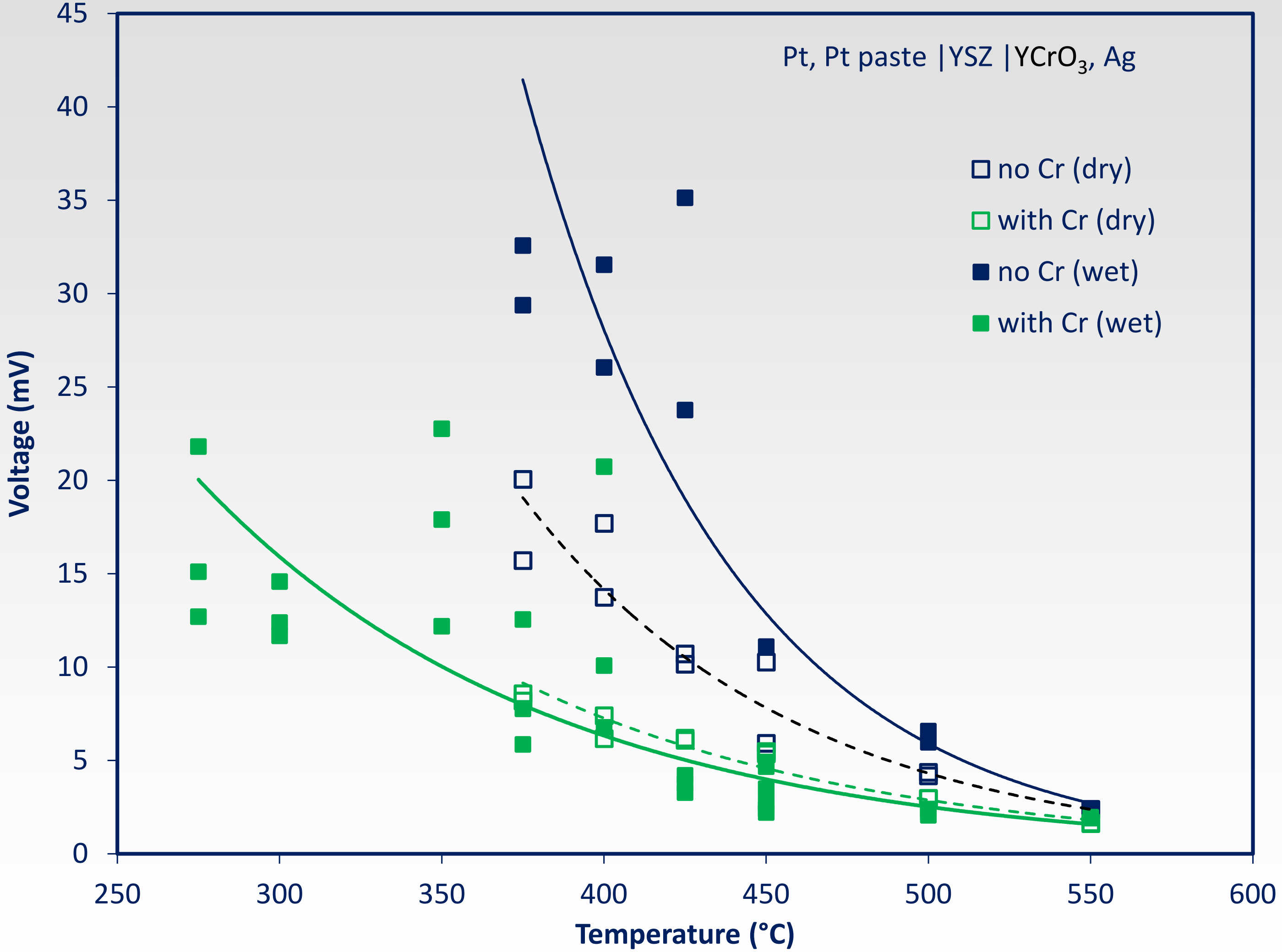
Low Temperature Response



Response Time



Sensor Response



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Beta Alumina Auxiliary Electrode Reaction

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

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

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Synthesis of Na_2CrO_4

- $Cr_2O_3 + Na_2CO_3$
- 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