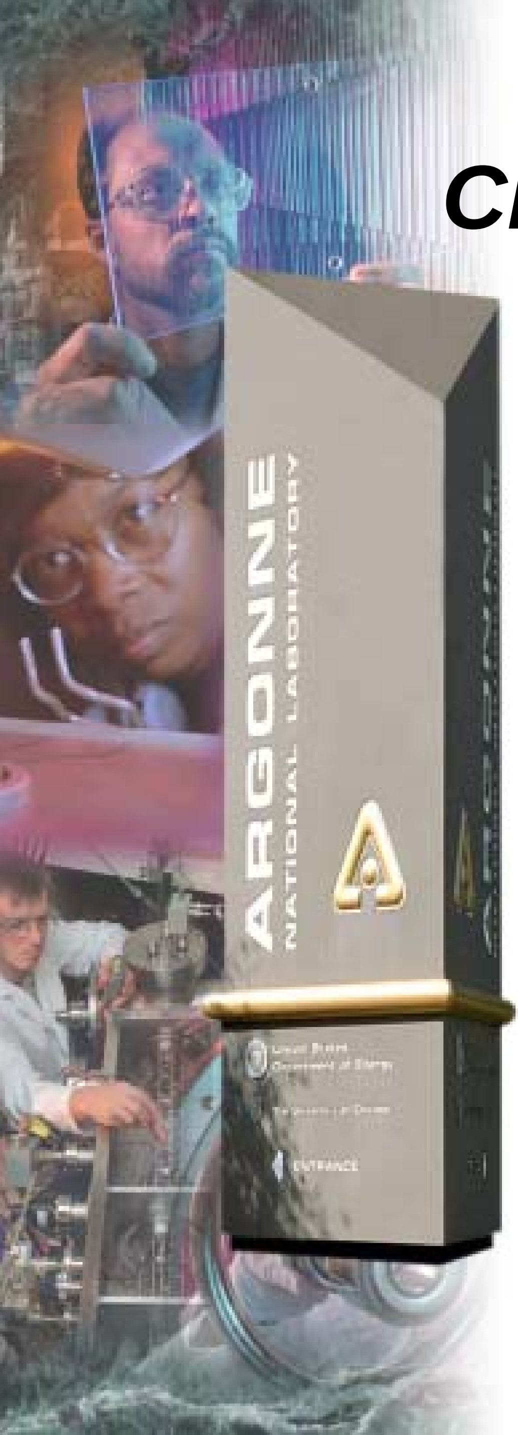

Chromium Poisoning and Diesel Reforming

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Terry Cruse, and
Cécile Rossignol

SECA Core Technology Review
Albany, NY
September 30 – October 1, 2003

Argonne National Laboratory

Office of Science
U.S. Department of Energy

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Office of Science Laboratory
Operated by The University of Chicago

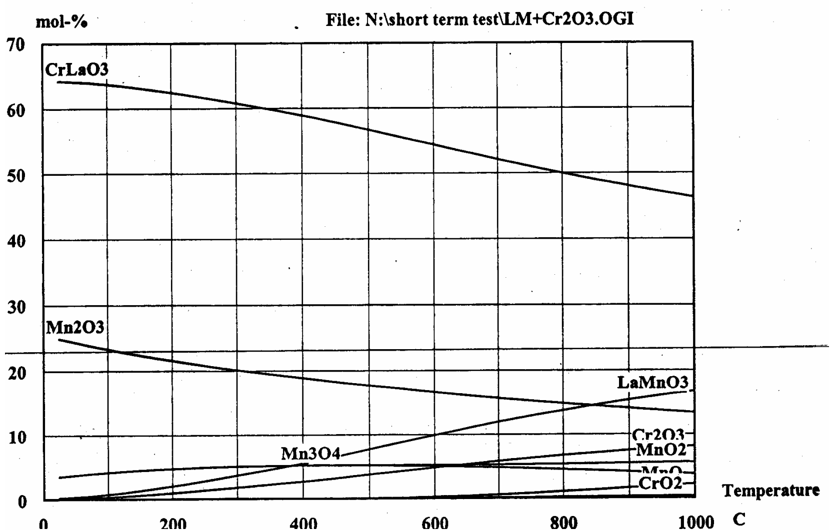
The Chromium Issue

- **In cells with metallic bipolar plates, chromium accumulates in anodes and cathodes**

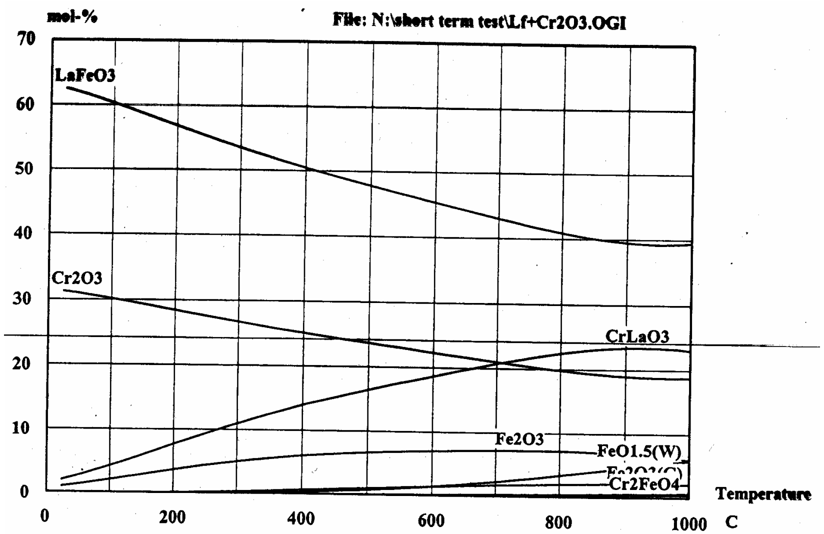
- **In some cases, the problem appears to become worse at lower temperature**

Thermodynamics:

- **Chromia protective scale can have a solid state reaction with $LaMnO_3$ and $LaFeO_3$**



HSC plot with chromia, $LaMnO_3$ and $LaCrO_3$



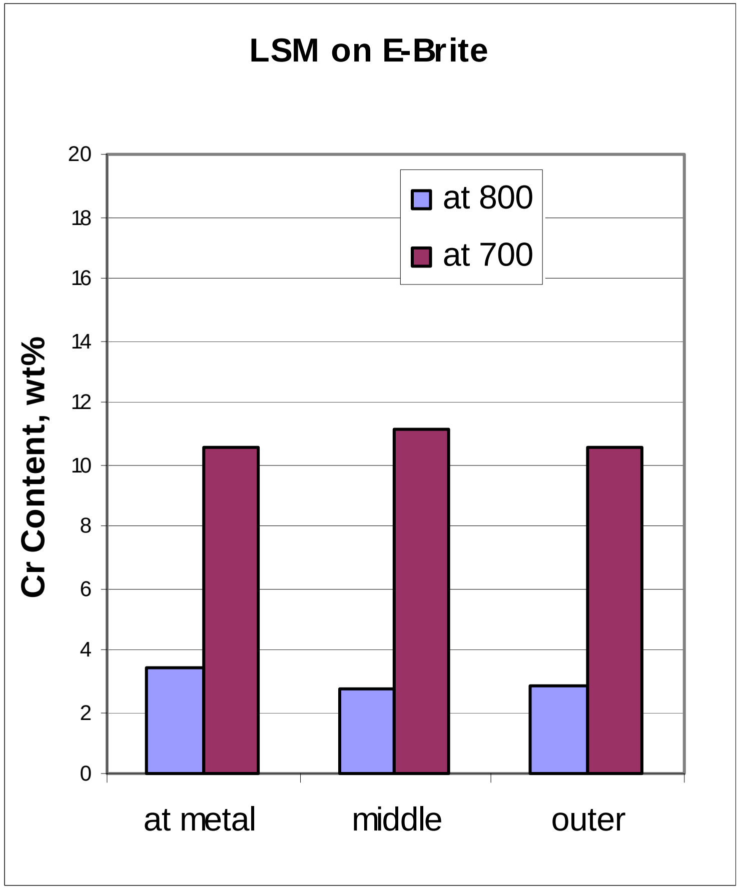
HSC plot with chromia, $LaFeO_3$ and $LaCrO_3$

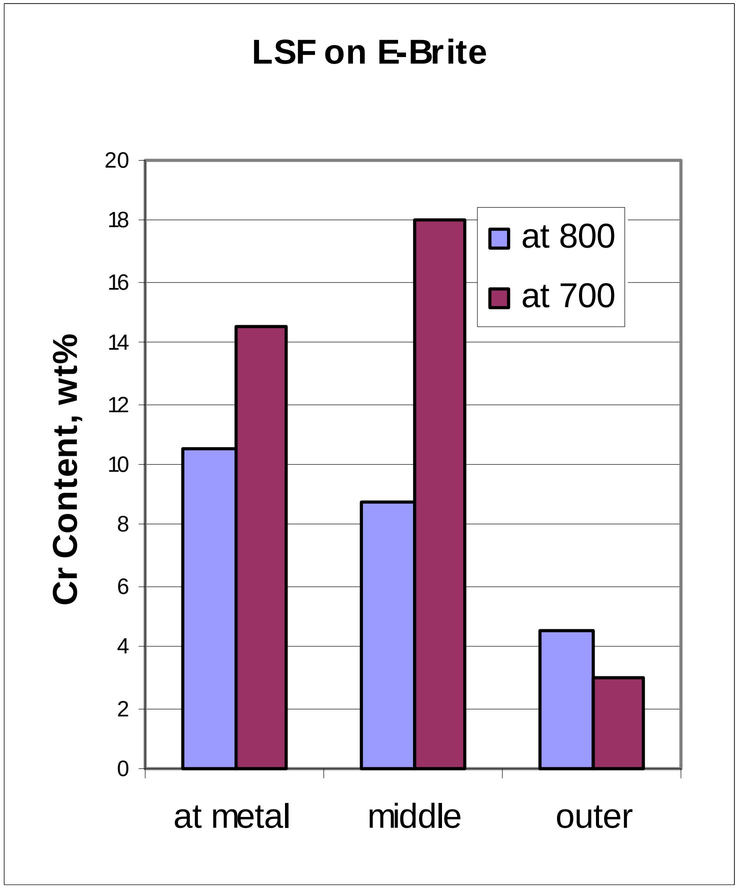
Approach to Determining Reactivity of Chromia Scale and Cathode

- **Coupon samples of metal interconnect are coated with cathode material and held at 700-800^{o}C in air with 25% water for 400h**

- **Measure Cr migration: Cr loss at metal surface and Cr collection in cathode layer examined by SEM/EDS**

Cr Content of Cathode Layers on E-Brite Coupons at 800ºC and 700ºC (using SEM/EDS) after 400 hours in 25% Humid Air

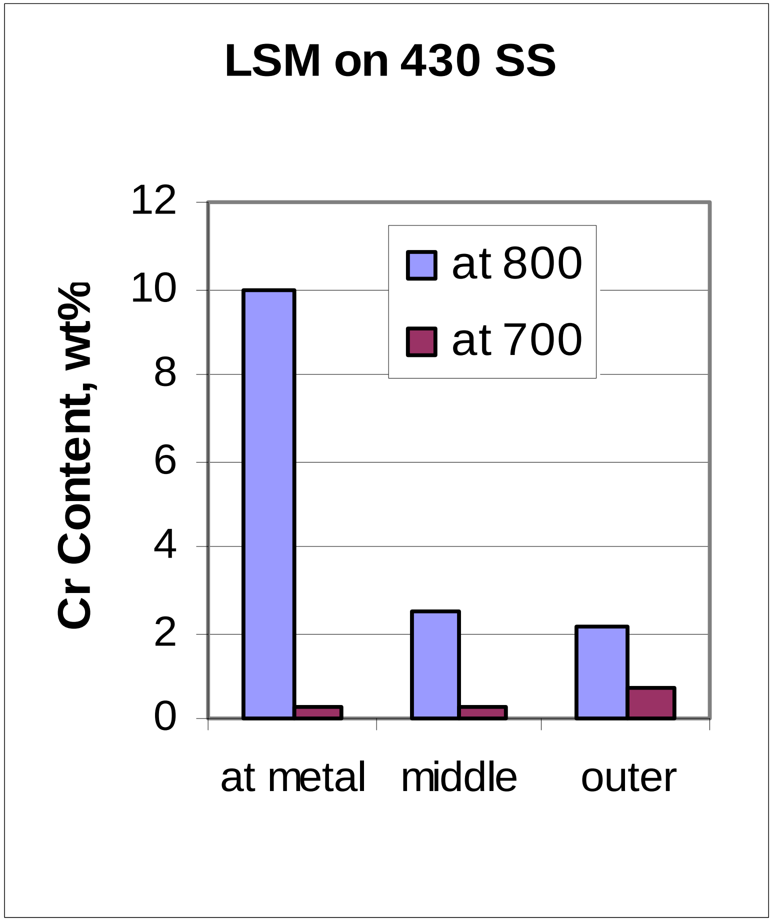




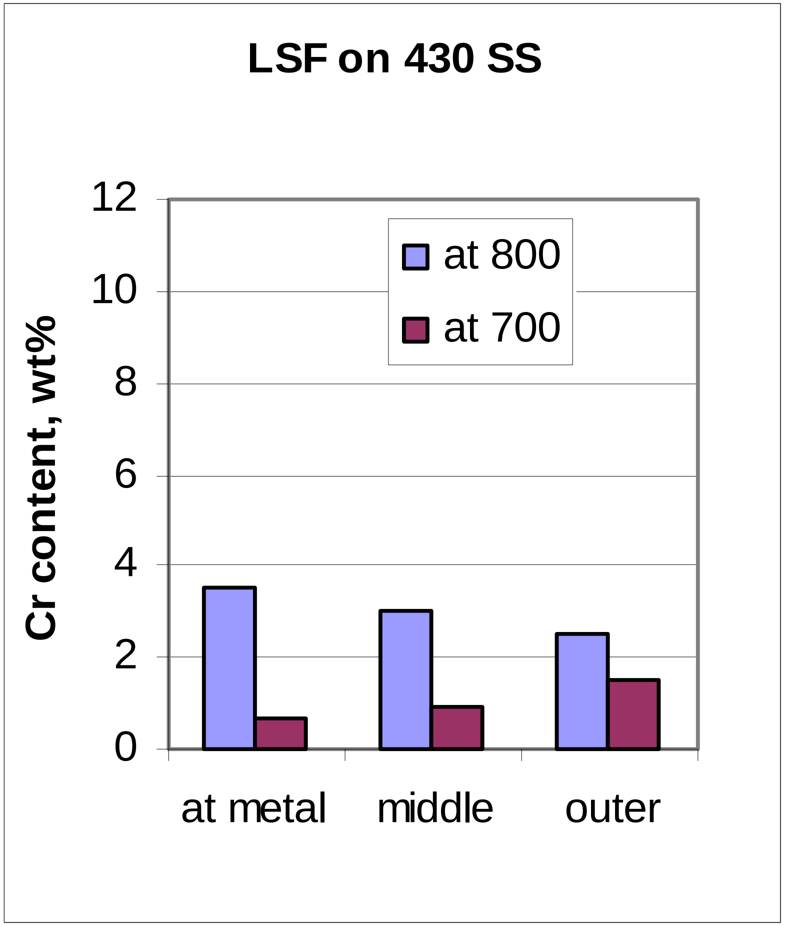
E-Brite chromia scale at 800C is 0.5 micron vs. 1 micron at 700C

E-Brite chromia scale at 800C is 10 Micron vs. 1 micron at 700C

Cr content of cathode layers on 430 SS Coupons at 800^{o}C and 700^{o}C (using SEM/EDS)



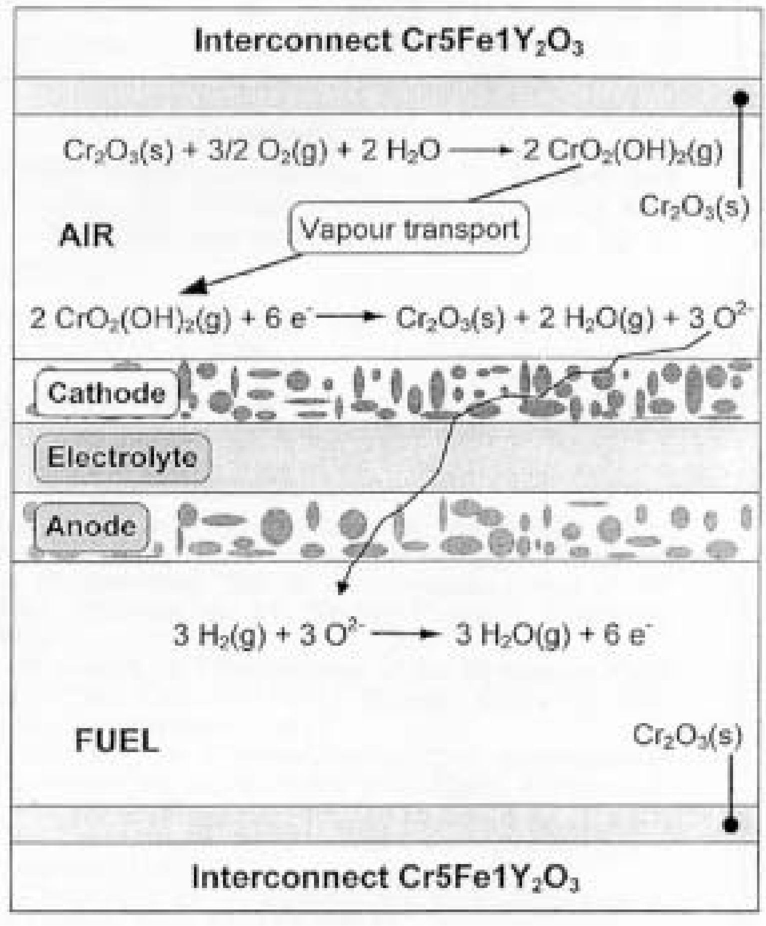
430 SS has a 1 micron chromia scale at 800^{o}C and Cr depletion at 700^{o}C, 10 micron Fe layer



430 SS has a incomplete chromia scale at 800^{o}C and Cr depletion at 700^{o}C, 6-8 micron Fe layer

Issue:

- **Chromia reacts with O_2 and H_2O to form volatile $Cr(OH)_2O_2$ (g), $Cr(OH)_2O$ (g), or $Cr(OH)O_2$ (g)**



From: Hilpert, K., D. Das, M. Miller D.H. Peck and R. Wei, *J. Electrochem. Soc*., vol. 143, no. 11, pp. 3642-3647 (1996).

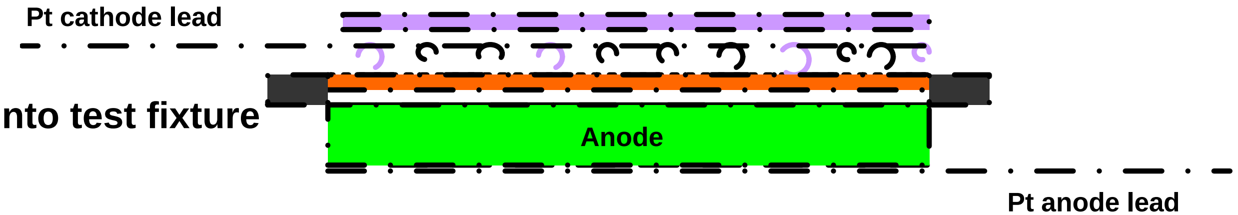
Approach to Volatility Issue

- **Measure SOFC performance degradation (current at 0.7 volts), polarization and impedance spectroscopy .**

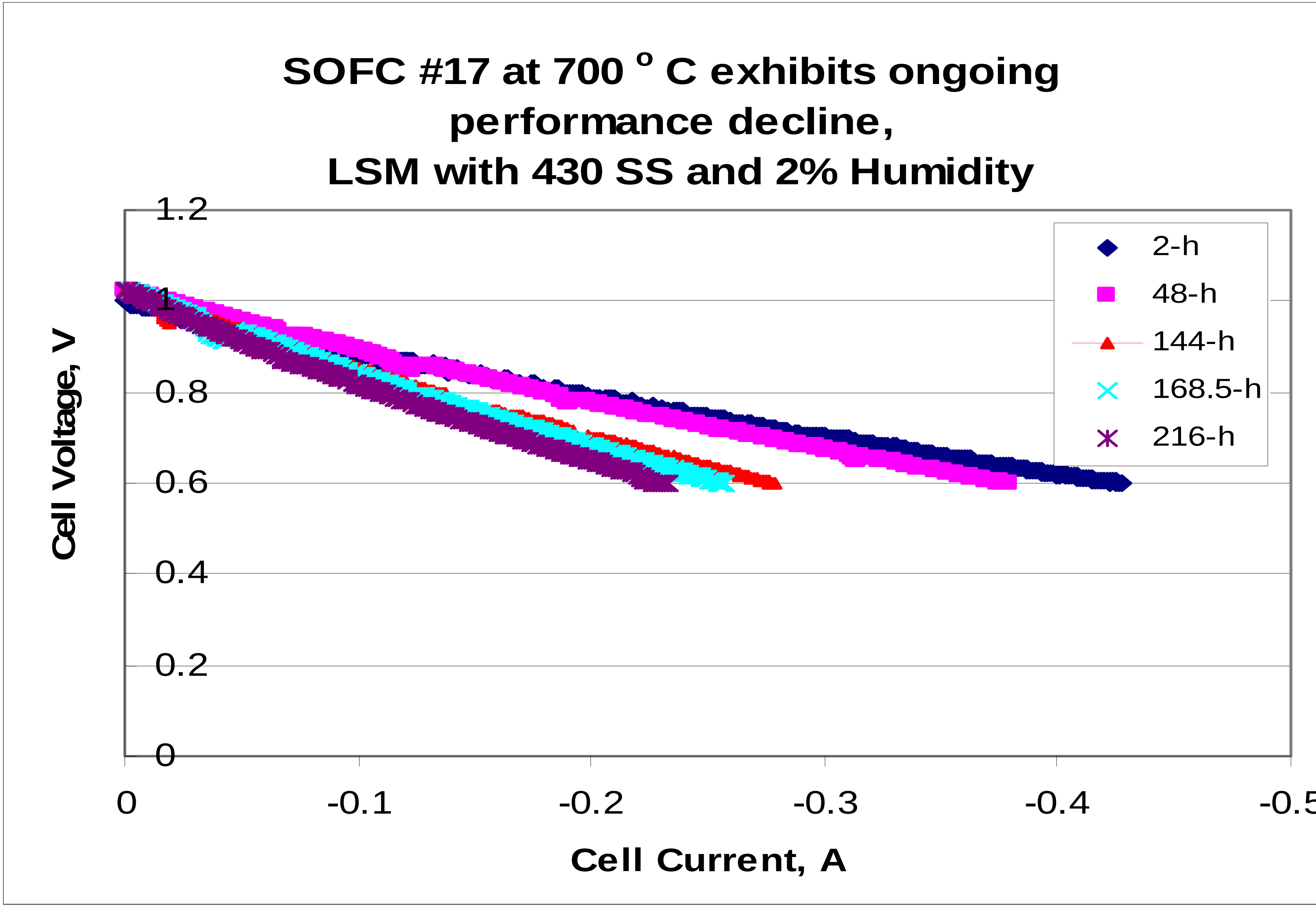
- **Post operative examination for Cr migration using SEM/EDS**

Metal interconnect plate and shavings onto cathode

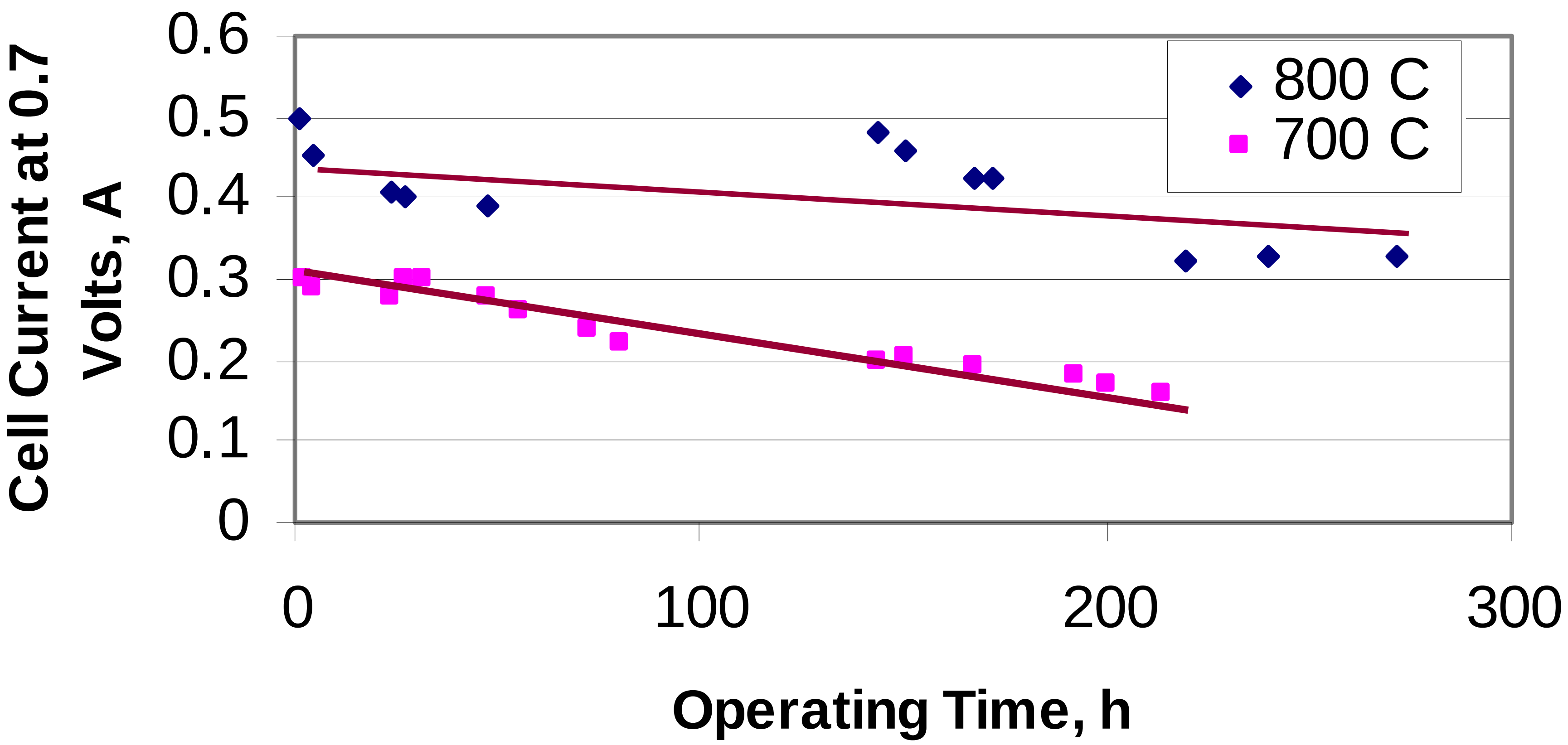
SOFC tri-layer sealed into test fixture



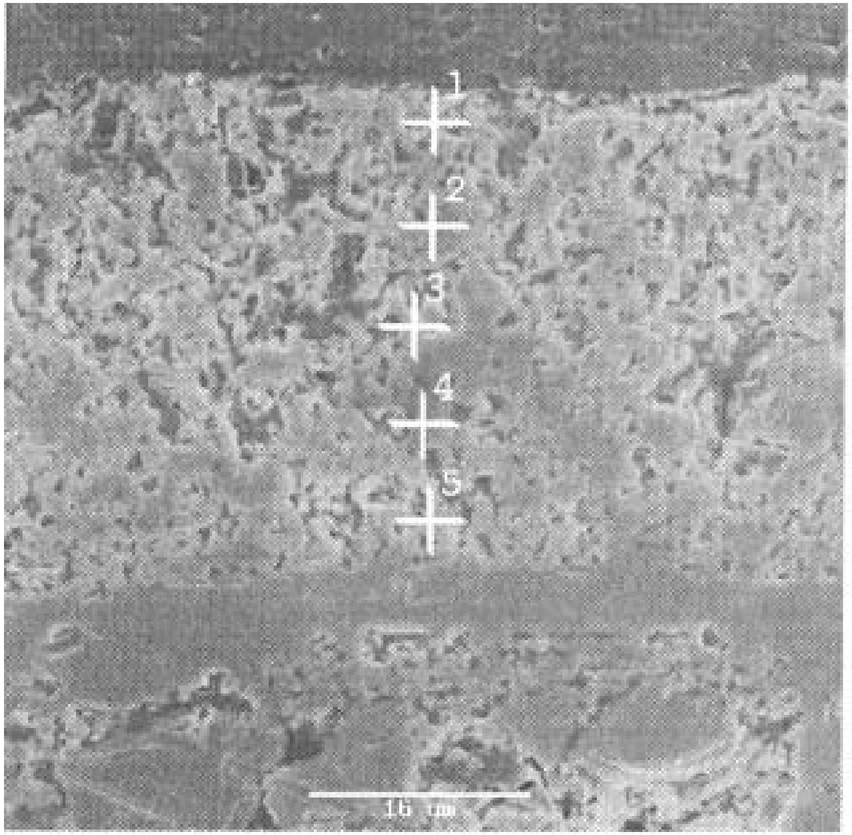
Cross-section of SOFC Test Cell (6 cm^2)


SOFC #17 at 700 ° C exhibits ongoing performance decline,
LSM with 430 SS and 2% Humidity
Cell Voltage, V
Cell Current, A
1.2
1
0.8
0.6
0.4
0.2
0
-0.1
-0.2
-0.3
-0.4
-0.5
2-h
48-h
144-h
168.5-h
216-h

SOFC Performance at 800^{o}C (#16) and 700^{o}C (#17) with LSM cathode and 430 SS



SEM of LSM Cathode Cross-section from SOFC (#16) with 430 SS at 800C

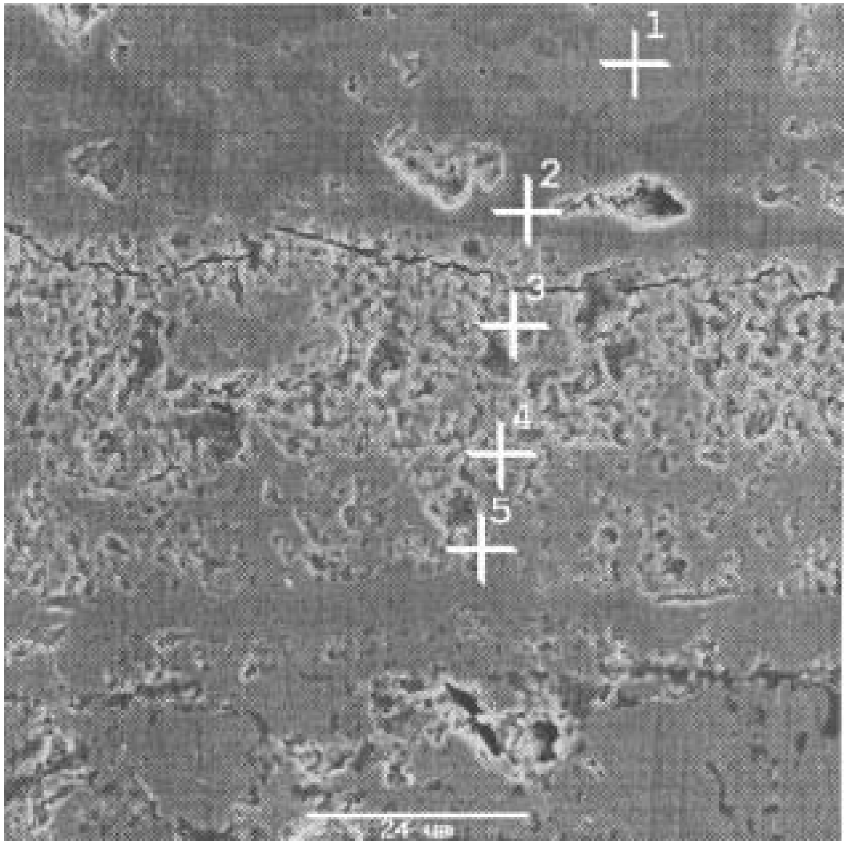


Cr Content by EDS at Sites 1-5:

- **0.4 wt% Cr**
- **0 wt% Cr**
- **0 wt% Cr**
- **0 wt% Cr**
- **0 wt% Cr**

Sites 1-5 are cathode thickness under 430 SS particle

SEM of LSM Cathode and 430 SS Interconnect from SOFC (#17) at 700^{o}C



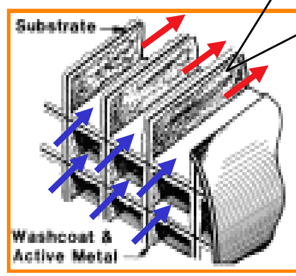
Cr Content at Sites by EDS

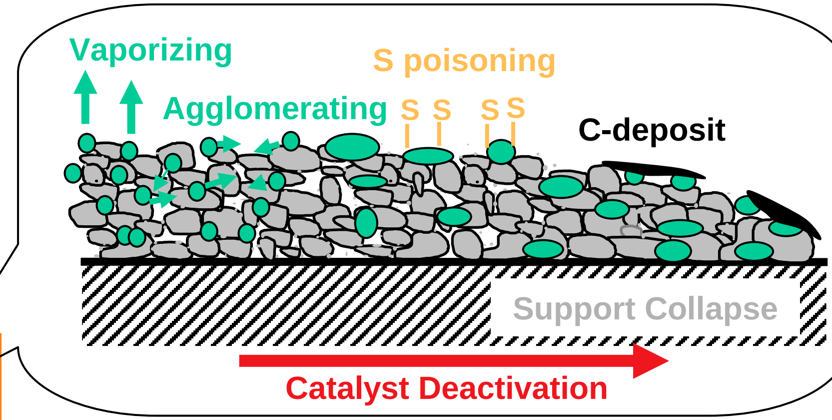
Sites 1-2: Cr depletion of 430 SS:
7.8 and 8.2 wt% Cr from 17 wt % Cr

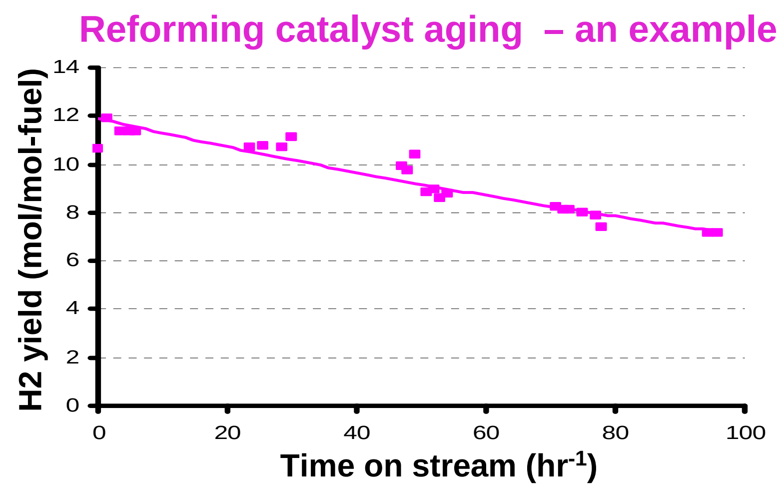
Sites 3-5 Cr level with cathode:
0, 1.50, 015 wt% Cr

Key Technical Challenges Facing Current Diesel Reforming Catalyst Development

- **Cost**
  - Costly Rh usage
- **Durability**
  - Metal vaporization
  - Metal agglomeration
  - Support stability
  - Sulfur poisoning
  - Coke formation



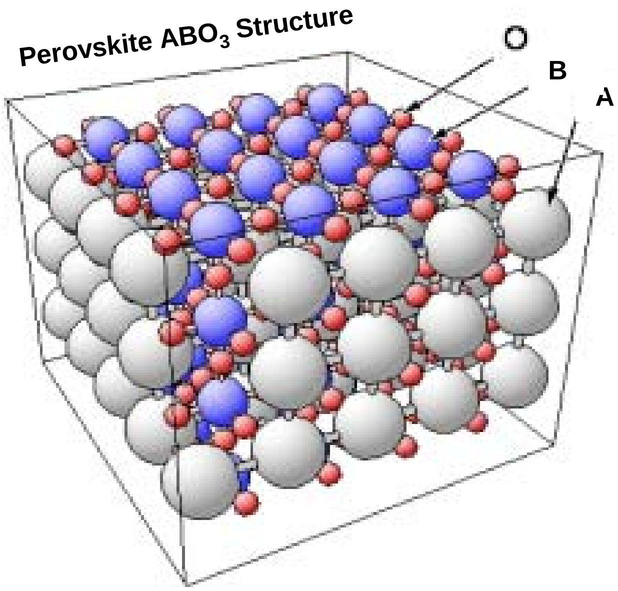




Catalyst activity and cost were rated as the top program need by SECA Vertical Team

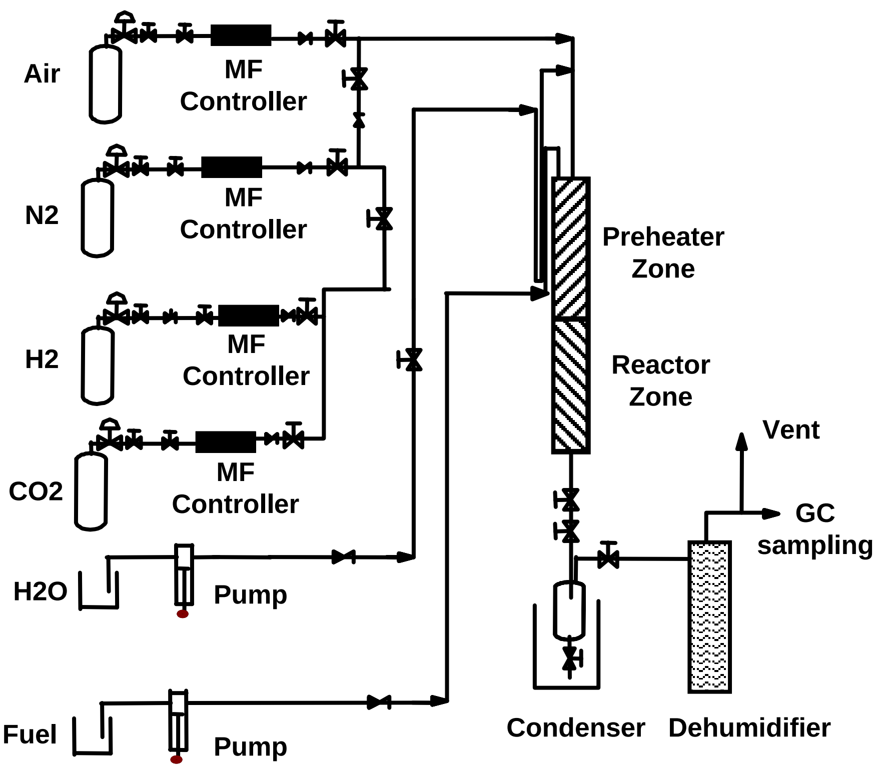
Approach to Diesel Reforming Catalyst

- **The Perovskite Catalyst…**
  - Consists of low cost material
  - Stable under high temperature
  - Stable in strong redox environment
  - Has adjustable cationic vacancy
  - Has exchangeable *A & B* site for activity improvement
  - Has mild catalytic oxidation activity
  - Contains transition metals active in SR such as Ni, Co, Mn, Cr, etc.



Argonne Catalytic ATR Reactor & Test Conditions

Test Plant Schematics



Catalyst Test Conditions

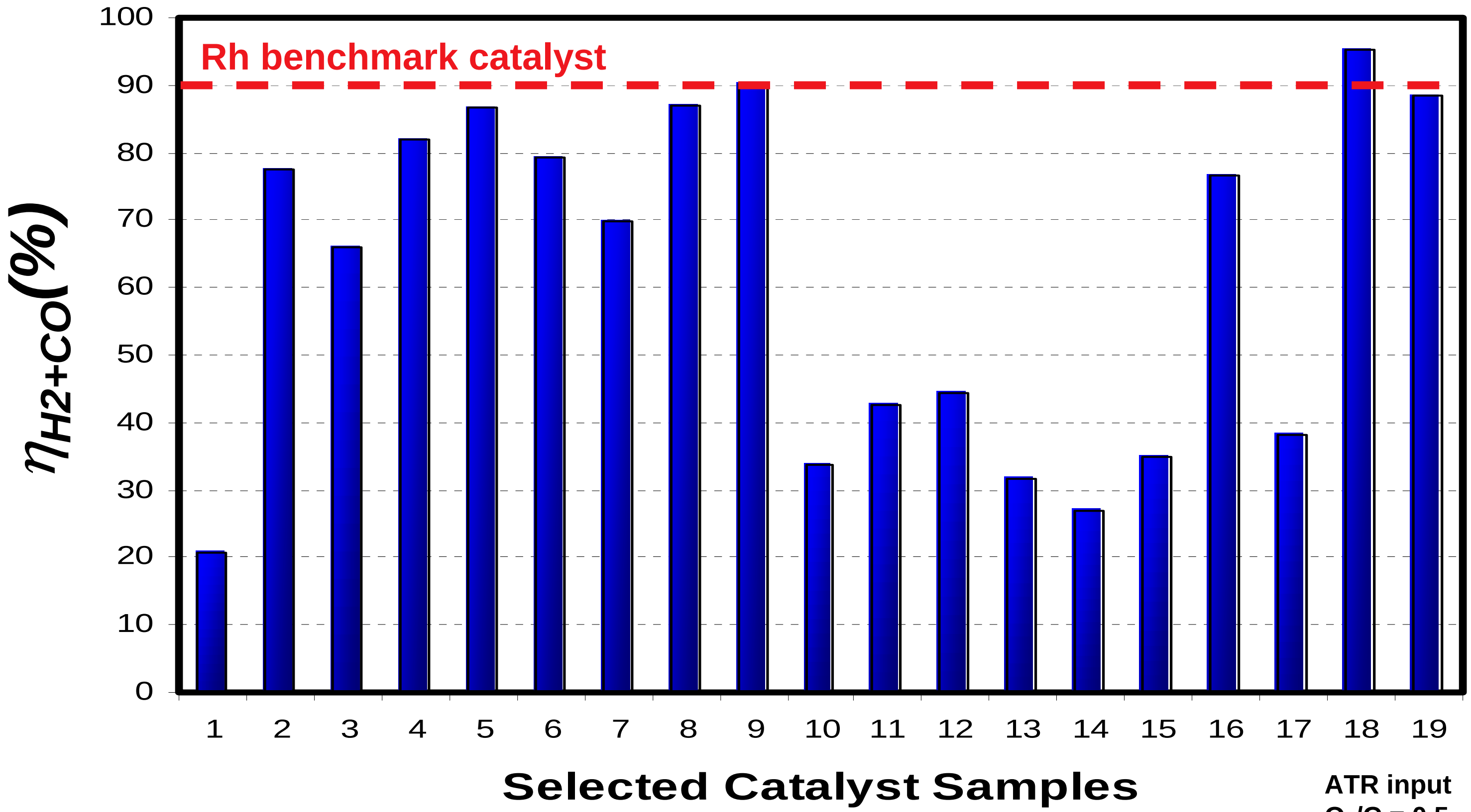
- **Reforming Input Mixture**
  - **ATR: O/C = 0.6 ~1, H2O/C = 1 ~ 3**
  - **SR: H2O/C = 3 ~ 6**
- **Temperature & Space Velocity**
  - **Reactor Temperature = 725 °C**
  - **Fuel Flow Rate = 2.8×10^{-3} gfuel/gCat•sec,**
  - **GHSV = 50 K ~ 100 K hr^{-1},**

Catalyst Characterization

- **Microreactor study**
  - Lightoff Temperature, TPR, TPD
- **Material characterization**
  - ICP, XRD, BET etc.

Diesel Reforming Catalyst Development at Argonne – Reforming Efficiency of Selected Samples

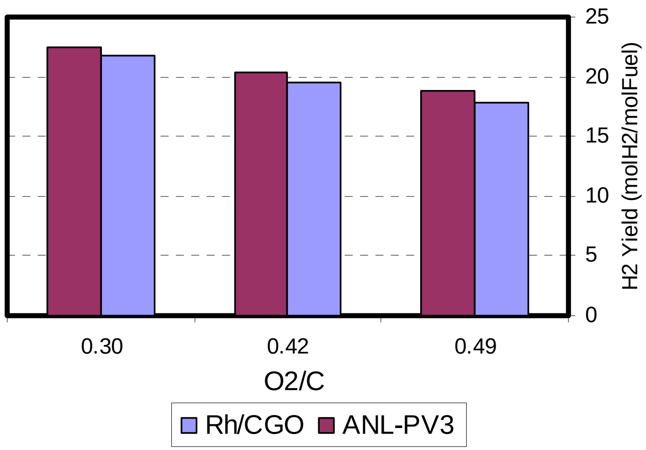
- Over 20 catalyst formulation with different combination of metals in A & B.
- The catalyst activity depends highly on formulation and preparation conditions.

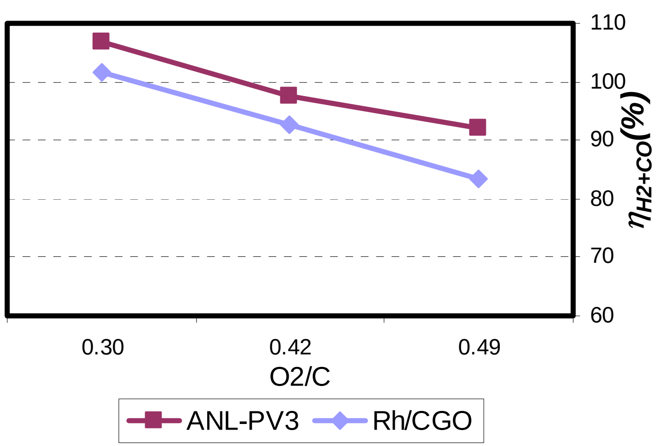


ATR input
$O_2/C = 0.5$
$H_2O/C = 2$

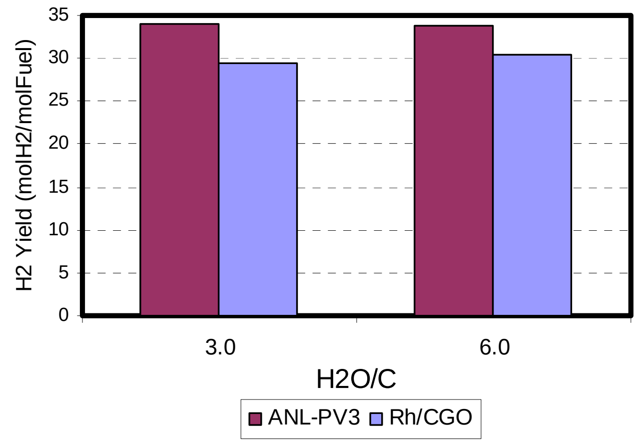
Diesel Reforming Catalyst Development at Argonne – Improving Catalyst Formulation

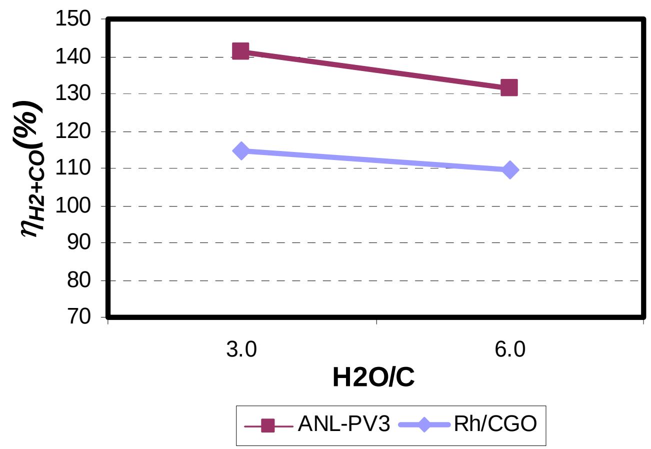
ATR





SR

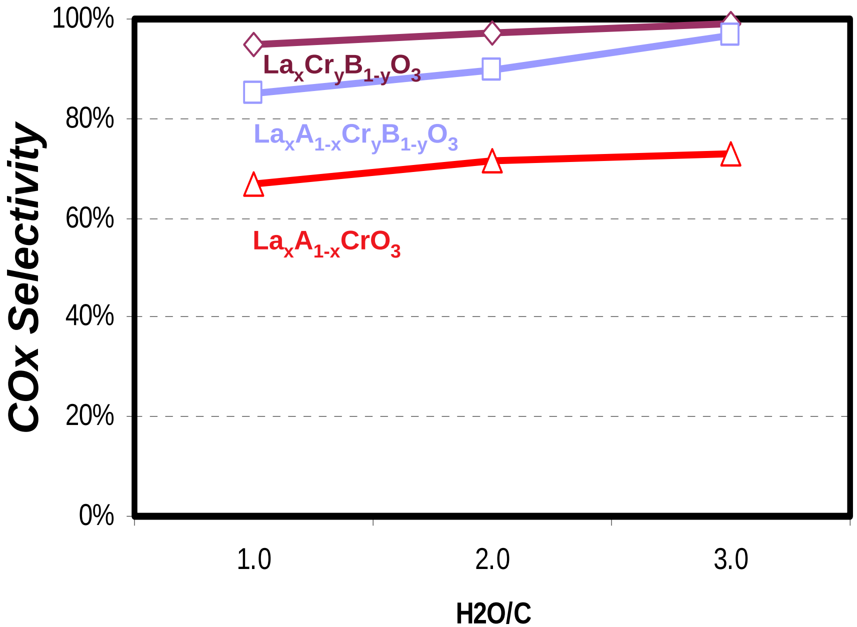




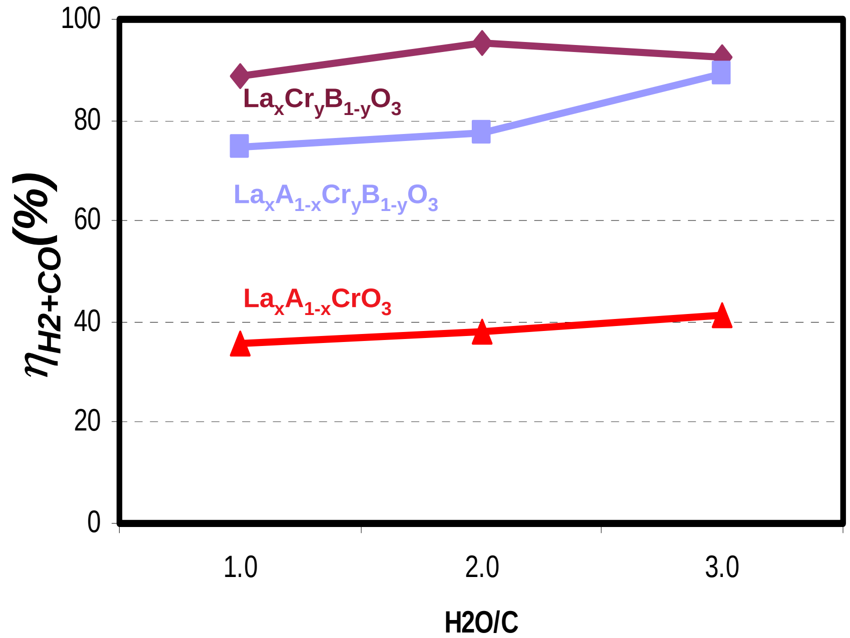
The new ANL catalyst outperforms the benchmark Rh/CGO catalyst

Diesel Reforming Catalyst Development at Argonne – Improving Activity through Site Doping & Vacancy

Selectively doping A & B site results in significant difference in hydrocarbon conversion selectivity…



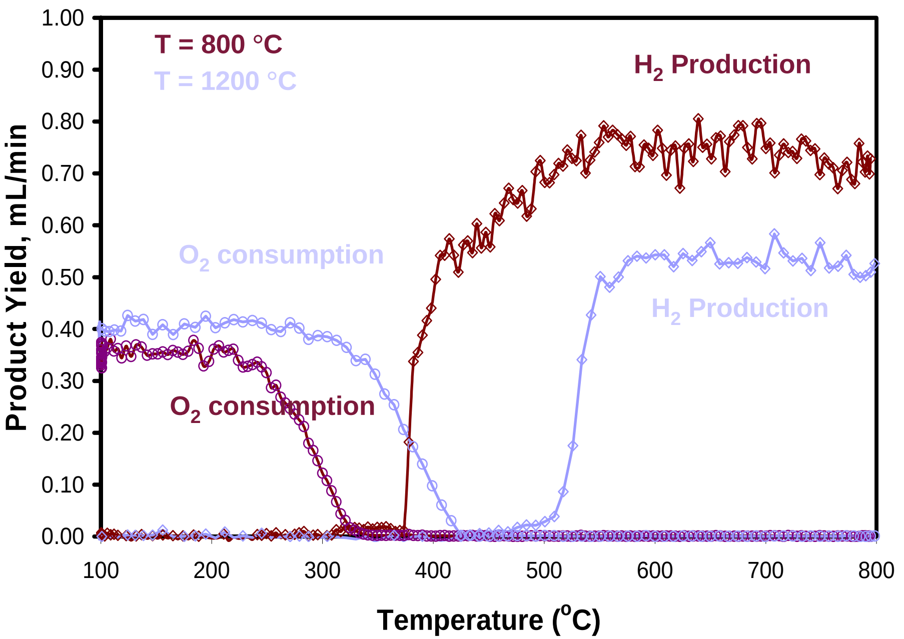
… which also led to drastic change in fuel reforming efficiency.



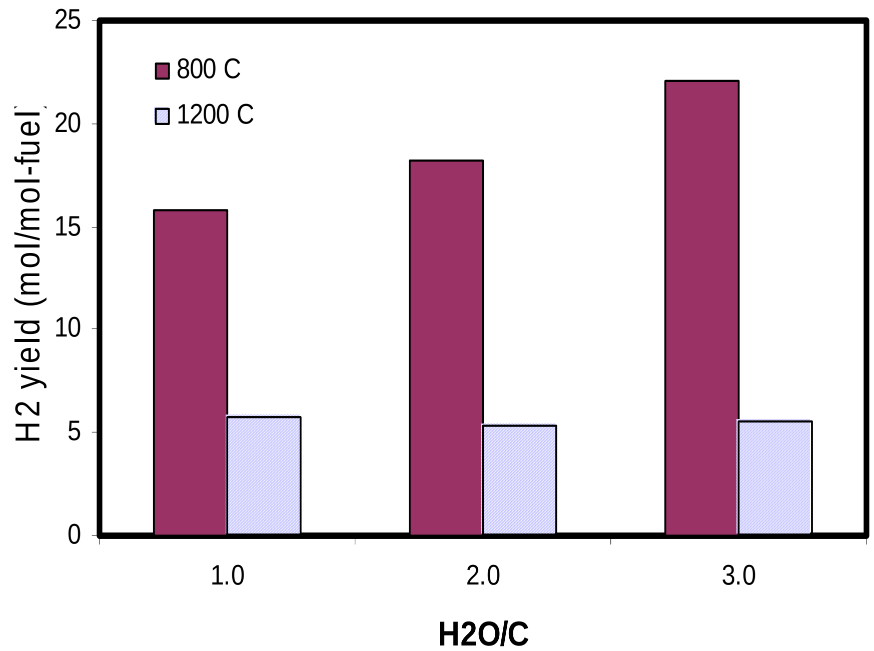
Cationic exchange at *A & B* sites can create lattice vacancy in perovskite structure and a better reforming catalyst

Diesel Reforming Catalyst Development at Argonne – Improving Methods of Catalyst Preparation

Reduced calcination temperature improved H2 lightoff threshold…



… and enhanced hydrogen yield.

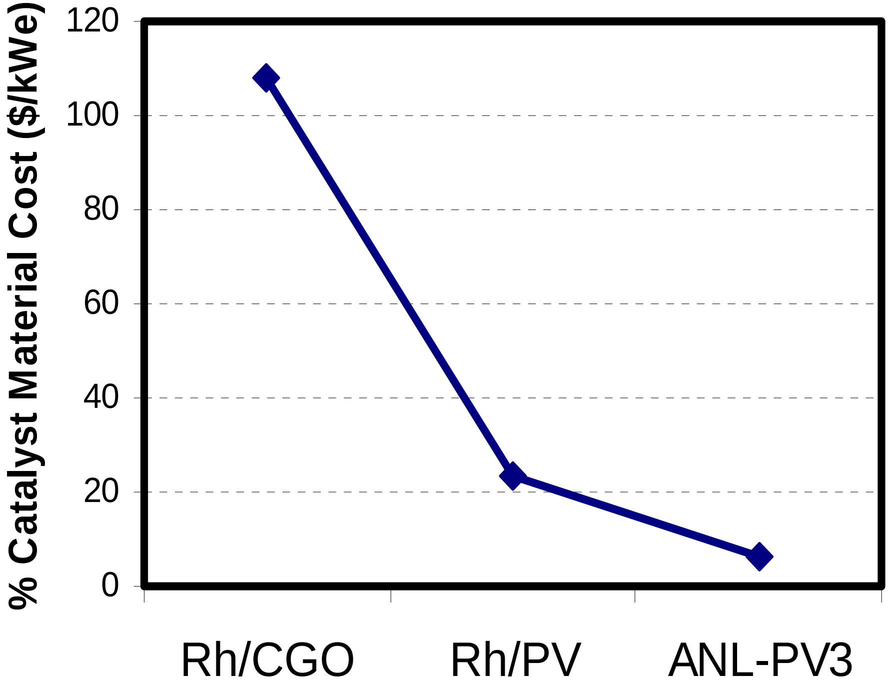


Optimizing calcination temperature resulted in significant activity improvement

Diesel Reforming Catalyst Development at Argonne – Performance & Cost Improvement Summary

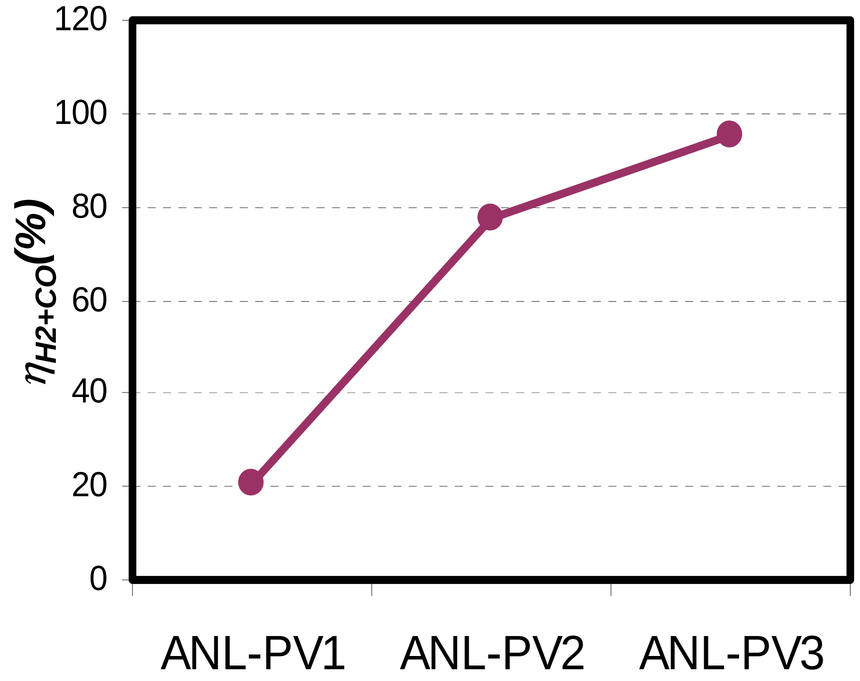
Investigation of new catalyst formulation led to significant decrease of material cost…

Catalyst Cost Reduction vs. Benchmark



…while improved synthesis technique results in increase of reforming efficiency

ATR at O_2/C =0.5 & H_2O/C = 2, GHSV = 55K hr^{-1}



Our diesel ATR catalyst development effort produced new formulations with enhanced performance at lower cost

Future Plans

- Continue to optimize formulation and synthesis method of perovskite based catalyst with improved reforming activity.
- Start to incorporate organic sulfur compounds in surrogate fuel for sulfur tolerance test.
- Explore perovskite catalyst reforming activity with low/no steam usage.
- Start reforming activity test with simulated recycled SOFC emission.
- Long term catalytic aging test.