Chromium Poisoning and Diesel Reforming

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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$_3$
Approach to Determining Reactivity of Chromia Scale and Cathode

• Coupon samples of metal interconnect are coated with cathode material and held at 700-800°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 800°C and 700°C (using SEM/EDS) after 400 hours in 25% Humid Air

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

E-Brite chromia scale at 800°C is 10 Micron vs. 1 micron at 700°C
Cr content of cathode layers on 430 SS Coupons at 800°C and 700°C (using SEM/EDS)

430 SS has a 1 micron chromia scale at 800°C and Cr depletion at 700°C, 10 micron Fe layer.

430 SS has an incomplete chromia scale at 800°C and Cr depletion at 700°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 $Cr(OH)O_2 (g)$

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

Cross-section of SOFC Test Cell (6 cm²)
SOFC #17 at 700 °C exhibits ongoing performance decline, LSM with 430 SS and 2% Humidity
SOFC Performance at 800°C (#16) and 700°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°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 = 2.8x10^{-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.

![Graph showing reforming efficiency of selected catalyst samples](image-url)
Diesel Reforming Catalyst Development at Argonne – Improving Catalyst Formulation

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

Catalyst Cost Reduction vs. Benchmark

% Catalyst Material Cost ($/kWe)

Rh/CGO  Rh/PV  ANL-PV3

0  20  40  60  80  100  120

Rh/PV ANL-PV3

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

…while improved synthesis technique results in increase of reforming efficiency

ATR at O₂/C = 0.5 & H₂O/C = 2, GHSV = 55K hr⁻¹

η₇H₂+CO₂(%) 0  20  40  60  80  100  120

ANL-PV1 ANL-PV2 ANL-PV3
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.