Materials and Approaches for the Mitigation of SOFC Cathode Degradation in SOFC Power Systems

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Program Manager: Dr. Patcharin N. Burke, National Energy Technology Laboratory
Presentation Outline

- Project Objectives
- Benefits of technology to the Program
- Accomplishments
- Background
- Experimental
  - Fabrication and testing of Cr Getter
  - Electrochemical Testing
  - Characterization-SEM-EDX, XRD, XPS, FIB-TEM
- Results and Discussion
- Future Work
- Acknowledgements
The overall objective of the proposed research program is to develop cost effective materials, modifications of the material chemistry and the exposure environments that inhibit long term solid-gas and solid-solid interactions to minimize/mitigate the degradation of SOFC cathode. The objectives include:

a. Develop and demonstrate the viability of the application of cost effective ‘chromium getter’ to capture the chromium species originating from the metallic stack and BOP components,
b. Develop modified cathode compositions to control and prevent oxide segregation and compound formation at the surface and interfaces during exposure to “Real world” air exposure,
c. Develop cathode contact layer and modification to avoid chromium poisoning originating from metallic current collector/interconnect.

Simple and complex oxides ranging from pure and doped oxide (AOₓ), spinel (AB₂O₄), perovskites (ABO₃), and double-perovskites (A₂BO₄) will be examined as efficient and stable chromium getter capable of forming thermodynamically stable chromites and chromates to further reduce the emanating gaseous Cr species by 3 to 4 orders of magnitude. Architectures utilizing high surface area nano and micro-sized getter particles in the contact layer as well as supported on highly porous ceramic backbone will be developed and experimentally tested and validated in the laboratory. Computational and experimental tools will be employed to rationally design materials to mitigate the adverse effects of the contaminants on the surface segregation, and compound formation. In-depth understanding of the cathode degradation in ‘real world’ atmosphere (work performed in our laboratory under the ongoing research projects) and existing laboratory capabilities will be leveraged for materials development. The proposed technology development program will transfer the technology and processing knowhow to materials suppliers and the SOFC industry to accelerate the demonstration and deployment.
Benefits of Technology to the Program

Potential benefits of this project will lead to:

- Mitigation the LSM and LSCF degradation arising from the presence of moisture and chromium species in the real-world cathode environment.
- Significantly increase the performance stability and long-term reliability of SOFCs, thus accelerating the demonstration and deployment of the technology.
- Design flexibility for the integration in wide range of SOFC systems configuration
- Flexibility of operation from 600-1000C
- Use of non-strategic and non-noble low cost metal oxides for getter synthesis
- Ease of getter synthesis and fabrication
- High Cr capture capacity through tailored high surface area powder and coatings
- Replaceable unit with getter health monitoring and sensing
- Scalable design for application in distributed and centralized power generation

The innovation will also find application in related high temperature electrochemical systems such as OTM and SOEC for the prevention of Cr assisted performance degradation. The proposed approach for Cr capture can also be applied to oxycombustion and other advanced combustion techniques for the reduction of Cr vapor in the exhaust gas stream.
Accomplishments

- Mechanisms for cathode degradation in “Real world Air Atmosphere” due to dopant exolusion, structural changes and interfacial compound formation has been developed and documented.
- Concept of capturing gas phase chromium vapor species, originating from SOFC sub-systems (e.g. HX) and cell components (e.g. IC), have been developed utilizing fundamental thermochemical principles and solid-gas interaction mechanisms.
- Getter materials selection basis has been developed based on reaction product morphology, substrate structure and reaction processes.
- In-situ electrochemical and ex-situ transpiration tests have been conducted for periods up to 500 hrs to assess the Cr capture tendency of fabricated getters.
- Getter and test cells have been characterized using EIS, SEM, EDS, FIB, TEM, and ICP techniques to examine the Cr capture trend.

- Chromium getter shows excellent affinity for capturing gaseous Cr species. Cr species are captured close to the air inlet.
- Electrochemical and transpiration tests show excellent blockage of Cr vapor for entering into cathode electrode.
- Scale up of getter materials, support structure and HSA getter deposition processes are being developed and optimized.

- Getter design can be tailored to meet various SOFC systems configurations.
- Getter materials can be used for capturing Cr originating from BOP and IC.
- Approaches for scale up (higher TRL) have been developed.
Accomplishments - Program Outcome

- Graduate / Undergraduate students being trained - 3
- Post-doctoral fellow: 2
- Patent disclosure: 1
- Technical Publications in progress - 3
- Outreach: Middle and High School, Davinci Program, STEM

Peer reviewed publications
- B Hu, MK Mahapatra, P Singh “Performance regeneration in lanthanum strontium manganite cathode during exposure to H2O and CO2 containing ambient air atmospheres” Journal of the Ceramic Society of Japan 123 (4), 199-204 2015
- B Hu, MK Mahapatra, V Sharma, R Ramprasad, N Minh, S Misture, “Durability of lanthanum strontium cobalt ferrite ((La0.60Sr0.40)0.95(Co0.20Fe0.80)O3-x) cathodes in CO2 and H2O containing air” Proceedings of the 39th International Conference on Advanced Ceramics 2015
- V Sharma, MK Mahapatra, P Singh, R Ramprasad “Cationic surface segregation in doped LaMnO3” J Mater Sci 50 (8), 3051- 3056, 2015

Technical Report, Book Chapters and News release
- P Singh “Developing chromium capture technology prevents poisoning of solid oxide fuel cell” American Ceramic Society Bulletin 95 (2), 16-17VJ 2016

Technical Presentations
- Sharma, S Krishnan, B Hu, MK Mahapatra, P Singh, R Ramprasad “Cationic surface segregation in doped LaMnO3: A first principles thermodynamics study” NETL SOFC Meeting, Pittsburgh 2015
- S Krishnan, V Sharma, MK Mahapatra, P Singh, “Probing for cationic dopants in lanthanum manganite for solid oxide fuel cell applications” The American Physical Society 2015
- Chiying Liang, Boxun Hu, Sridevi Krishnan, Manoj Mahapatra, Rampi Ram Prasad and Prabhakar Singh “Mitigation of Chromium Poisoning in SOFC” International Conference and Exposition on Advanced Ceramics and Composites, American Ceramic Society 2016

US Patent Application
- U.S. Patent Application No.: 14/821,677 “High temperature electrochemical systems and related methods”
Accomplishments - Program Outcome

**Industrial/ National Laboratory Network**
- LG Fuel Cells Fuel Cell Energy
- Praxair Saint Gobain
- ITN General Electric
- InnoSense Accumenics
- Cummins Power Pacific Northwest National Laboratory
- Naval Undersea Warfare Center

**Technical publications in preparation**
- In-operando validation of the mitigation of Cr assisted cathode poisoning
- Evaluation of Cr getter by transpiration technique
- Book chapter – Cathode poisoning
- Cr assisted poisoning and morphological changes in LSM and LSCF

**Enabled adjacency areas (selected):**
- S. Gupta and P. Singh “Nickel and Titanium Doubly Doped Lanthanum Strontium Chromite for High Temperature Electrochemical Devices” Journal of Power Sources 2015 Accepted
- Sapna Gupta, Joseph Adams, Jamie Wilson, Eric Eddings, Manoj Mahapatra, Prabhakar Singh “Performance and post-test characterization of an OTM system in an experimental coal gasifier” Applied Energy Accepted
- N Li, A Verma, P Singh, JH Kim, “Characterization of La 0.58 Sr 0.4 Co 0.2 Fe 0.8 O 3− δ−Ce 0.8 Gd 0.2 O 2 composite cathode for intermediate temperature solid oxide fuel cells” Ceramics International 39 (1), 529-538, 7, L Ge, A Verma, R Goettler, D Lovett, RKS Raman, P Singh, “ Oxide scale morphology and chromium evaporation characteristics of alloys for balance of plant applications in solid oxide fuel cells” Metallurgical and Materials Transactions A 44 (1), 193-206
Background

Durability of Cathode Materials under “Real World” Air Exposure Atmospheres

- **Issue:** Presence of impurities (H₂O/CO₂/Cr-vapor) in air degrades cathode and long-term SOFC performance.
- **Approach:** Experimentally measure performance degradation and characterize chemical and morphological changes; Develop degradation mechanisms and optimize materials chemistry utilizing computational modeling

**Presence of moisture in air:**
- Presence of moisture in air degrades electrochemical performance and the degradation increases with moisture content, exposure temperature, and cathodic bias. Both ohmic and non-ohmic resistances increase with increase in moisture content.
- Electrode surface shows SrO/Sr(OH)₂ segregation (nM particles) and formation of La₂Zr₂O₇ and MnOₓ at electrode–electrolyte interface.

**Presence of CO₂ in air:**
- Presence of CO₂ (up to 3%) in air shows little to no influence on cathode performance degradation (100 hrs. tests).
- La₂O₂CO₃ and SrCO₃ form below 800°C but only SrCO₃ at 850°C and above.
- Pre-activated electrode shows insignificant degradation even at higher CO₂ (~10%CO₂) content.


**Morphological evolution in the presence of CO₂**

**Electrode performance stability in air containing H₂O and CO₂**

**Cr deposit on the elbow from SS**

**No visual change in color**

**Significant reduction in Cr evaporation has been achieved by alloy, atmosphere and materials chemistry modifications.**
Background

- SOFC cathode are prone to poisoning and degradation arising from (a) impurities present in the incoming air (intrinsic and extrinsic impurities) and (b) interactions with the electrolyte.
  - Intrinsic gas phase impurities – H2O, CO2, ...
  - Extrinsic gas phase impurities – CrOx, CrO(OH)x...
- Degradation due to solid–gas and solid–solid interactions
- Exolution and compound formation
- Surface coverage and resistance to oxygen reduction

- BOP components and cell interconnections contribute to Cr evaporation and poisoning of the cathode.
- Poisoning is due to coverage of active surface and TPB, compound formation and deposition of chromia.

At three phase boundary:

\[
2(\text{CrO}_2 + \text{Cr}_2\text{O}_3(\text{OH}))_2(g) + 6e^- = 2\text{CrO}_3 + (30^{2-} + 30^{2-} + H_2O)
\]

\[
2M^{3+}_{\text{LSM}} + O^{2+}_{\text{LSM}} + V_{O(YSZ)} = 2M^{3+}_{\text{LSM}} + O^{2+}_{\text{LSM}} + V_{O(YSZ)} + 2P_{\text{LSM}}
\]

\[
\text{CrO}_2(\text{OH})_{2(\text{gas})} + M^{3+}_{\text{LSM}} = \text{Cr} - M - O_{\text{polar}}, CrO_2(\text{OH})_{2(\text{gas})} + Cr - M - O_{\text{polar}} = 2\text{CrO}_3 + CrO_2(\text{OH})_{2(\text{gas})} + H_2O_{(\text{gas})}
\]

At three phase boundary,

\[
\text{O}_2(g) + 4e^- = 2O^{2-}
\]

At two phase boundary,

\[
\text{La}_{1-x}\text{Sr}_x\text{MnO}_3 + x(\text{CrO}_2, \text{Cr}_2\text{O}_3(\text{OH}))_2(g) = (1-x)\text{LaMnO}_3 + [x\text{SrCrO}_4 + x\text{SrCrO}_4 + H_2O(g)]
\]

SEM micrographs of the YSZ electrolyte surface in contact with a LSM electrode coating in the presence of a FeCr alloy at 900 C after cathodic polarization for (a) 5 min, (b) 15 min, (c) 30 min, (d) 4 h,
There is limited/little literature on capturing chromium vapor before reaching active cathode.

Approaches for mitigation of chromium poisoning include minimization of chromium evaporation from exposed metallic surfaces – alloy chemistry modification and surface coating.

Calculated partial pressure of \( \text{CrO}_3 \) over \( \text{Cr}_2\text{O}_3 \) and \( \text{MnCr}_2\text{O}_4 \).

**AFA Oxidation and Passivation – 850C, 500 hrs.**

**Protective Ceramic Coatings**
Solid Oxide Fuel Cell (SOFC) Balance-of-Plant Components (InnoSense LLC (SBIR Phase 1))

<table>
<thead>
<tr>
<th>No. of Alloy</th>
<th>Conventional Nickel-Base Alloys (Cr(_2)O(_3) formers)</th>
<th>New Alloy (Iron-Based Al(_2)O(_3) former)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome</td>
<td>AFA 110</td>
<td>110</td>
</tr>
<tr>
<td>Humidity 90%</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Reduced</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Reduced</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

Lighter discoloration with coating

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Background

**Literature – Air Products ITM Report**

- Coated alloy samples reduced Cr contamination
- Performance of coated alloy sample was only slightly better
- Cr deposits formed on the active ITM surface led to reduction in oxygen flux

- Use of MgO based getter is speculated based on report.
- References: Chapter 6, Chapter 14, Chapter 16
- Limited data on the use of cathode (LSCF) powder for capturing Cr from IC exists. Long term performance remains unknown
**State of the Art**

- **Cr evaporation**
- **Air, H2O, CO2...**
- **SOFC components**
  - Stack hardware, interconnects, BOP hardware

Reduce Cr flux to minimize cathode poisoning by surface coating, alloy metallurgy modification.

**Proposed Approach**

- **Cr evaporation**
- **Air, H2O, CO2...**
- **Cathode**

Capture Cr before reaching cathode by employing stable and active getter - complex oxides.

Getters containing complex oxides where all cations are capable of reacting and forming stable Cr compounds.
Cr Getter: Materials, Structure and Reaction Mechanisms

Selection Matrix → Test Validation → Manufacturing

Cr Gettering from BOP and IC
Materials selection, synthesis and test validation
Scale up and validation in large SOFC systems

Getters have been extensively used in chemical, electronics, metal manufacturing and nuclear industries for the removal of trace gas phase impurities.
Getter Materials, support and Fabrication

- **Thermodynamic requirement:**
  - \( \Delta G (\text{CrO}_x/\text{MO}, \text{Cr}_2\text{O}_3) < \Delta G (\text{CrO}_x/\text{Cr}_2\text{O}_3) \)
  - \( \sum P_{\text{CrO}_x, \text{CrO(OH)}_x (\text{Air}/\text{Cr}_2\text{O}_3)} << \sum P_{\text{CrO}_x, \text{CrO(OH)}_x (\text{MO} / \text{Cr}_2\text{O}_3)} \)

- **Physical requirement:**
  - Structural / chemical stability of MO in ambient air
  - Gas Phase and substrate interactions

- **Morphological requirement:**
  - \( (\text{Porosity, Vol})_{\text{Reaction Product}} < (\text{Porosity, Vol})_{\text{Reactant}} \)

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**Utilization of Getter**

Dense Surface product Layer
Complete Surface coverage

Porous Surface product Layer
Continued interaction with Getter

Support Substrate
Getter Materials, support and Fabrication

• **Materials selection**
  ✓ Thermochemistry - Chemical stability and free energy minimization
  ✓ Physical properties - Resistance to hydrolysis, support reaction
  ✓ Product morphology - Porous product layer with access to substrate

• **Support selection**
  ✓ High surface area - Support HSA porous getter materials coating
  ✓ Chemical stability - Resistant to interaction with coating
  ✓ Structure - Porous, low dP, allows diffusion through coating
  ✓ Form - Cartridge, conformable overlay, bond coat

• **Fabrication Processes**
  ✓ Porous coating - Precursor solution, sol-gel, slurry
  ✓ Heat treatment - Adherence and HSA
  ✓ Tailored porosity - Scaffolding

Two different approaches for mitigating Cr poisoning arising from BOP and IC have been considered.
Oxide solid solutions and mixtures from Alkaline earth and Transition metal group are preferred and considered over single phases due to chemical stability and resistance to interactions with gas phase impurities.
Chromium vapors: Gr-II MO Interactions

Cr2O3 + 1.5O2(g) = 2CrO3(g)
2Cr2O3 + O2(g) + 4H2O(g) = 4CrO(OH)2(g)
Cr2O3 + 1.5O2(g) + 2H2O(g) = 2CrO2(OH)2(g)

CrO3(g) + SrO = SrCrO4
CrO2(OH)2(g) + SrO = SrCrO4 + H2O(g)
2CrO(OH)2(g) + 2SrO + O2(g) = 2SrCrO4 + 2H2O(g)

2CrO3(g) + 4SrO = 2Sr2CrO4 + O2(g)
2CrO2(OH)2(g) + 4SrO = 2Sr2CrO4 + O2(g) + 2H2O(g)
CrO(OH)2(g) + 2SrO = Sr2CrO4 + H2O(g)

2CrO3(g) + 3SrO = Sr3Cr2O4 + 2.5O2(g)
2CrO2(OH)2(g) + 3SrO = Sr3Cr2O4 + 2.5O2(g) + 2H2O(g)
2CrO(OH)2(g) + 3SrO = Sr3Cr2O4 + 2H2O(g) + 1.5O2(g)

4CrO3(g) + 6SrO = 2Sr3Cr2O8 + O2(g)
4CrO2(OH)2(g) + 6SrO = 2Sr3Cr2O8 + O2(g) + 4H2O(g)
4CrO(OH)2(g) + 6SrO + O2(g) = 2Sr3Cr2O8 + 4H2O(g)

HSC Database is used to calculate the phase co-stability and eqlbm. CrOx {CrO3, CrO(OH)2 and CrO2(OH)2}pressure using pure solid phases formation.

CrO3(g) + CaO = CaCrO4
CrO2(OH)2(g) + CaO = CaCrO4 + H2O(g)
2CrO(OH)2(g) + 2CaO + O2(g) = 2CaCrO4 + 2H2O(g)

CrO3(g) + BaO = BaCrO4
CrO2(OH)2(g) + BaO = BaCrO4 + H2O(g)
2CrO(OH)2(g) + 2BaO + O2(g) = 2BaCrO4 + 2H2O(g)

CrO3(g) + MgO = MgCrO4
CrO2(OH)2(g) + MgO = MgCrO4 + H2O(g)
2CrO(OH)2(g) + 2MgO + O2(g) = 2MgCrO4 + 2H2O(g)

2CrO3(g) + MgO = MgCr2O4 + 1.5O2(g)
4CrO(OH)2(g) + 2MgO = 2MgCr2O4 + 4H2O(g) + O2(g)
2CrO2(OH)2(g) + MgO = MgCr2O4 + 1.5O2(g) + 2H2O(g)

2CrO3(g) + MgO = MgCr2O3 + 2O2(g)
2CrO(OH)2(g) + MgO = MgCr2O3 + 2H2O(g) + O2(g)
2CrO2(OH)2(g) + MgO = MgCr2O3 + 2O2(g) + 2H2O(g)
Interactions with CaO, BaO, SrO & MgO

Thermochemistry: Co-stability of reaction products

**CaO- CaCrO4**

**BaO- BaCrO4**

**SrO-SrCrO4**

**MgO-MgCr2O4**

\[ P_{BaO/CrOx(OH)x} < P_{SrO/CrOx(OH)x} < P_{MgO/CrOx(OH)x} < P_{CaO/CrOx(OH)x} \]
# Thermochemistry – Eqlbm. Cr Pressure

<table>
<thead>
<tr>
<th>Gr II Oxides reactants</th>
<th>Products</th>
<th>Log $P(\text{CrO}_3)$</th>
<th>Log $P(\text{CrO(OH)}_2)$</th>
<th>Log $P(\text{CrO}_2(\text{OH})_2)$</th>
<th>$P(\text{H}_2\text{O})$</th>
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</thead>
<tbody>
<tr>
<td>MgO</td>
<td>MgCrO$_4$</td>
<td>-7.35E+00</td>
<td>-9.670788145</td>
<td>-5.89049607</td>
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<td></td>
<td>MgCr$_2$O$_4$</td>
<td>-10.52454137</td>
<td>-12.84742013</td>
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<td></td>
<td>MgCr$_2$O$_3$</td>
<td>-13.58297699</td>
<td>-15.90585574</td>
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<tr>
<td>BaO</td>
<td>BaCrO$_4$</td>
<td>-19.3711882</td>
<td>-21.69406695</td>
<td>-17.91377487</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>CaCrO$_4$</td>
<td>-8.776154142</td>
<td>-11.09903289</td>
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<tr>
<td>SrO</td>
<td>SrCrO$_4$</td>
<td>-1.64E+01</td>
<td>-17.21788015</td>
<td>-13.43758807</td>
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<tr>
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<td>Sr$_2$CrO$_4$</td>
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<td>-17.61298936</td>
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<tr>
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<td>Sr$_3$CrO$_4$</td>
<td>-23.10338349</td>
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<td>Sr$_3$Cr$_2$O$_8$</td>
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<td>-18.71867804</td>
<td>-14.93838597</td>
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<tr>
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<td>-9.954834771</td>
<td>-10.75483478</td>
<td>-6.974542703</td>
<td></td>
</tr>
</tbody>
</table>

Conditions: 850°C, Air-3% H$_2$O, All solid phases are pure
Reaction Energetics of LSM & LSC with CrO₃

- Thermodynamically favorable reaction pathways explored using first principles thermodynamics.
- Energetics of the reaction between (La, Sr)MnO₃ and (La, Sr)CoO₃ with the CrO₃ is studied.
- List of possible products included in the product pool:
  - Elemental metals, binary oxides & ternary oxides
  - Other products like MnₓCr₃₋ₓO₄, SrCrO₄, LaCrO₃, CoCr₂O₄

- No reaction in the experimental (P₃O₃, T) range was observed for LSM without oxygen vacancy.
- For LSM with oxygen vacancy, the spinel compounds MnCr₂O₄ and SrCrO₄ coexist as favorable reaction products.
  - The mole fraction of SrCrO₄ is ~2 orders of magnitude less than that of MnCr₂O₄
- For LSCO without oxygen vacancy, SrCrO₄ is found as favorable reaction product, whereas the CoCr₂O₄ is not favored as products in line with experimental observations.
Results and Discussion
A wide variety of support materials and configurations are available for application in SOFC system. Selection will be based on:
- Materials stability in SOFC atmosphere
- Materials interaction with applied coatings
- Design flexibility

Flexible Fibrous Support in Al2O3, ZrO2, Mullite and other oxides
- HSA support
- High permeability
- Favorable contact and mixing
3D Representation

3D imaging shows alumina structure thickness to be on the order of 700 – 850 µm with pore sizes around 4.0 mm. Surface of alumina matrix appears to have roughness.

Tomography’s performed on porous alumina samples:
- 4ppi and 60ppi samples

3D Visualizations able to resolve the alumina structure:
- Coarse alumina sample appears to have a rough surface texture
- Fine alumina sample may have same surface roughness, but further imaging at 10X did not provide contrast between air and alumina.

After 3 imaging sessions where sample was exposed to 60kV X-ray beam, fine alumina sample began to discolor (appear to have a yellowish tint) where exposed to X-rays.

Additional coloring is available in Xradia’s 3D Viewer software. Color provides no additional information & is purely aesthetic.
Porous Al$_2$O$_3$ Getter

- Getter properties:
- Material: Al$_2$O$_3$
- Porosity: 85%
- Dimension: diameter-21 mm, length-37 mm
- Through hole diameter: 1 mm

![Pressure drop measurement setup](image)

![Getter](image)
Experimental Setup

- Chromium source: Cr/2O3
- Cr. Getter: ABOx over cordierite
- Temperature: 850°C
- Time: 500 hrs.
- Exposure atmosphere: Air - 3% H2O

No discoloration of the quartz elbow
Elbow pictures at outlet

Reactor elbow discoloration due to Cr-vapors

Without getter  With getter
Higher Cr intensity (analysis performed using EDS technique) is observed near the air inlet (~1200 micron). Flat Cr profile is observed over the entire length after ~1500 micron indicating little/no Cr.

<table>
<thead>
<tr>
<th>Getter</th>
<th>Treatment of cordierite substrate</th>
<th>Chemistry</th>
<th>Coatings</th>
<th>Chromium evaporation test</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>Solution: aqueous solution of 0.6 M of Sr(NO₂)₂ and 0.4 M of Ni(NO₃)₂·6H₂O</td>
<td>Heat treatment at 950°C for 2 h</td>
<td>None</td>
<td>850°C</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>Heat treatment at 1000°C for 2 h</td>
<td>Heat treatment at 850°C for 10 h</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Boil in 20wt% of nitric acid for 3 hours; sonic cleaning in 0.1 M of hydrochloric acid and DI water</td>
<td>Heat treatment at 950°C for 2 h</td>
<td>Heat treatment at 850°C for 10 h</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIB X-Sectional Evaluation

Lower magnification

Higher magnification
In-Operando Electrochemical Characterization

Test assembly: Half cell configuration

Temperature: 850°C
Cathode atmosphere: 3% H2O/air (balance), flow rate: 50 - 500 sccm
Anode atmosphere: dry air, flow rate: 150 sccm
Cathodic Bias vs reference: 0.5 V
Getter: cordierite/alumina fiber supported SrNiOx

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## Overall Cell Performance Comparisons

### LSM Cathodes with a Getter and without a Getter under Exposure of Cr Vapor

#### Operating Conditions

<table>
<thead>
<tr>
<th></th>
<th>Blank test (no Cr, no getter)</th>
<th>Control test (with Cr, no getter)</th>
<th>Getter test (with Cr and getter)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature</strong></td>
<td>850°C</td>
<td>850°C</td>
<td>850°C</td>
</tr>
<tr>
<td><strong>Cathode Atmosphere</strong></td>
<td>3% H2O/air, Cr vapor</td>
<td>3% H2O/air, Cr vapor</td>
<td>3% H2O/air, Cr vapor</td>
</tr>
<tr>
<td><strong>Anode Atmosphere</strong></td>
<td>Dry air</td>
<td>Dry air</td>
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<td><strong>Cathodic Bias</strong></td>
<td>0.5 V</td>
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<td><strong>Getter</strong></td>
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<td><strong>Test time with EIS</strong></td>
<td>1-100 h</td>
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**Air Flow Rate (SCCM)**: 50, 100, 200, 500 and 1000

Tests completed/ In progress
Half cell tests – Base line; With Cr source; With Cr source & getter

Morphologies comparisons of the LSM cathode with no Cr, no getter (A), with Cr, no getter (B), and with Cr, with getter (C).
XRD and XPS Analysis: Presence of Cr₂O₃ in tested cell

**XRD**

- Pretest LSM-YSZ
- Posttest 1 LSM-YSZ with Cr at 850°C
- Posttest 2 LSM-YSZ with Cr at 850°C

**XPS Elemental Analysis of LSM Cathodes**

- La 3d
- Mn 2p
- O 1s
- C 1s
- Sr 3p
- Cr 2p
- Mn 2p
- La 3d
- LSM with getter and Cr

**XPS**

- LSM as fabricated at 1200°C

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Overall Cell Performance Comparison

Humidified air flow rates varying from 50-500sccm showed little/no effect on the symmetric cell performance degradation indicating the effectiveness of getter at higher flow rates.

Symmetric cell performance with air flow rate

Chromium intensity with distance from inlet

EDAX measurement by using probe area of 277μm*277μm
Half Cell with Cr and Getter

Posttest Getter Morphology

- **Getter inlet**: Cr atom%: 1.07%
- **Getter middle**: Cr atom%: 0.1%
- **Getter outlet**: Cr atom%: 0%

Decrease of Cr concentration

Cr species were captured mostly at the inlet of the SrNiOx coated getter
 Getter Morphology

200 sccm

Inlet

Cr dominating particles at inlet

Outlet ~ 35mm

100 sccm

200 sccm

3mm

100 sccm

Outlet ~ 35mm

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FIB-STEM Element Mapping of Posttest Getters

FIB X Section and elemental analysis

Interaction of strontium with chromium results in the formation of strontium chromate on the getter surface. Exolved NiO precipitates and serves as marker at the reaction interface.
In-Cell Simulation

Air-3%H₂O, 850°C, LSM, 0.5 V bias

Further testing to simulate contact paste – In progress
Project Schedule/Milestones

<table>
<thead>
<tr>
<th>Milestone Number and Task</th>
<th>Milestone Title</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Development of Chromium Getter for BOP components by ‘top-down’ approach</td>
<td>Q6</td>
<td>Q6</td>
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<tr>
<td>2</td>
<td>Modification of cathode chemistry to tolerate moisture and chromium poisoning by ‘top-down’ approach</td>
<td>Q10</td>
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<td>3</td>
<td>Evaluation of the feasibility of the chromium getter and the modified cathodes</td>
<td>Q12</td>
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<td>Modification of cathode contact layer to reduce chromium poisoning</td>
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<td>5</td>
<td>Development of conductive coating to mitigate chromium evaporation from metallic interconnects</td>
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<td>6</td>
<td>Documentation, Reporting, and Publication</td>
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<td>7</td>
<td>Intellectual property and technology transfer</td>
<td>Q12</td>
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</tbody>
</table>

- Complete thermochemical assessment of Cr gettering (T, PH2O, PO2) Q6
- Examine oxide systems and characterize surface reaction products Q6-Q8
- Evaluate NiO, MnO and other additives and develop Cr capture profile Q6-Q8
  - Transpiration experiments – f(PH2O, T, t, Q)
  - Getter coating and utilization
- Design and conduct long term tests under systems operating conditions Q8-Q12
  - Fiber / fiber-foam composites / blanket configuration
- Develop fabrication processes for large samples Q8-Q12
- Qualify getters application in cell/stack for in the cell Q8-Q10
- Work with industry in validating getters in the large systems Q11-Q12

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### Project Schedule/Milestones

<table>
<thead>
<tr>
<th>Milestone/ Tasks</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
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**Project Summary**

**Key technical accomplishments include:**
- Laboratory experiments show that the getters successfully capture gas phase chromium and prevent cathode poisoning.
- Electrically tested cells with Cr show preferential deposition of Cr at the cathode – electrolyte interface. Presence of getter mitigated Cr deposition in the cathode.
- Getter materials and support configurations have been identified.
- Getter powder has been synthesized and characterized.

**Lessons Learned:**
- Alkaline earth and transition metal group oxides (solid solutions and compounds) show excellent tendency for the capture of Cr. Repeated experiments validate the observation.
- Ceramic honeycomb, foam and fibrous structures have been examined for getter support.
- Getter powder synthesis and getter fabrication and test techniques have been developed.

**Outstanding issues:**
- Getter design for optimum Cr capture / getter utilization
- Getter design to meet system requirements
- Long term test validation under simulated system conditions
- Support design and vendor

**Plans for remaining key technical challenges:**
- Initiate tests under SOFC system conditions
- Initiate scale up of getter fabrication
- Initiate in depth characterization of getter surface
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Thank You

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