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

Prabhakar Singh

Department of Materials Science and Engineering
University of Connecticut, CT

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Technical Contributors

**UConn**
- Prabhakar Singh: Professor
- Rampi Ramprasad: Professor
- Steven Suib: Professor
- Boxun Hu: Assistant Research Professor
- Ashish Aphale: Post-doctoral fellow
- Aman Uddin: Post-doctoral fellow
- Sridevi Krishnan: Post-doctoral fellow
- Su Jeong Heo: Graduate Student
- Junkai He: Graduate Student
- Yanliu Dang: Graduate Student
- JunHo Song: Graduate Student
- Justin Webster: Undergraduate Student
- Seraphim Belko: Undergraduate Student

**UAlabama**
- Manoj Mahapatra: Assistant Professor

**Program Manager:** Dr. Patcharin N. Burke, NETL
Problem statement

- One of the largest contributor for electrochemical performance degradation in SOFC is assigned to cathode degradation – associated with increase in the cathode polarization (ohmic/non-ohmic) due to surface poisoning and interface compound formation.
- The long term degradation is mostly irreversible as the chemical and morphological changes in the electrode is largely permanent.
- Identification of cost effective solutions requires understanding of the degradation processes under the “real world” or system operating conditions.

Technical Innovation and impact

- The research provides an understanding of the degradation mechanism and cost-effective approaches for implementation in SOFC system –
  - long-term solution is design agnostic
  - applicable under wide operating conditions.
- Use of low cost, non-noble, non-strategic materials and conventional ceramic processes to fabricate Cr getters.

Existing laboratory capabilities can provide getters for up to 1-2 MWe SOFC’s for near term demonstration
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 and approaches:

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.

d. Develop alloy surface pretreatment conditions to minimize chromium evaporation.

Outcomes

• Proposed approaches successfully developed, validated and implemented.
• Proposed program milestones have been met.
• Conducted materials and technology transfer.
Benefits of Technology to the Program

Potential benefits of this project:

- Mechanistic understanding of the degradation processes in LSM and LSCF (airborne contaminants)
- Development of mitigation process utilizing low cost getters
- Ease of getter synthesis and fabrication
- High Cr capture capacity through tailored high surface area powder and coatings
- Surface pretreatment for BOP application minimizes chromium evaporation
- Supports USDOE Office of Fossil Energy objectives for commercialization of SOFC systems.

Use of conventional low cost materials
Application in 600-950°C range
< 15-20 g of material needed for ~100 kWe SOFC
SOFC Cathode Exposure to “Real World” Air

Composition in air | Concentration
--- | ---
Oxygen | 20.9 v%  
Nitrogen | 78 v%  
Water | 1-3 v%  
Carbon dioxide | 350 ppm  
Sulfur dioxide | ~1 ppm  
Noble gases | <1 v%  
Particles | <50 µg/m³

DOE Target of System Performance Degradation: 0.2%/1,000 hours
Sources of Cr-Vapor

- Chromia forming alloys
- Balance of plant materials
- Presence of H₂O aggravates Cr evaporation

**Impurity capture:**
1. Capture intrinsic impurities at the system inlet
2. Capture extrinsic impurities in BOP or in stack

**Sources of Cr-Vapor**

- Chromium poisoning leading to the long term degradation in SOFC systems
- Permanent performance degradation
- High polarization losses
- Interfacial deposition limits the oxygen access at the triple phase boundary (TPB) sites

**Ambient air constituents**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>20.9 v%</td>
</tr>
<tr>
<td>N₂</td>
<td>78 v%</td>
</tr>
<tr>
<td>H₂O</td>
<td>&lt; 1-3 v%</td>
</tr>
<tr>
<td>CO₂</td>
<td>400 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>75 ppb</td>
</tr>
</tbody>
</table>

**Extrinsic impurities**

- Chromia forming alloys
- Balance of plant materials
- Presence of H₂O aggravates Cr evaporation
Outline

• Accomplishments
• Background
• Experimental
  • Getter synthesis, optimization and stability evaluation
  • Validation of getter performance
  • Fabrication and long term testing of Cr Getter
  • Electrochemical testing – BOP & In-Cell simulation
  • Characterization-SEM-EDX, XRD, and FIB-TEM
  • Alloy surface modification optimization
• Results and Discussion
• Future Work
• Acknowledgements
Chemical Nature of Impurities

Acidic impurities react with basic cathode (Host and dopant)

Cathodic Constituents “BASIC”
- Lanthanide
- Alkaline dopant group

Impurities in the air "ACIDIC"
- Si(OH)$_4$ (g)
- H$_2$O (g)
- CO$_2$ (g)
- H$_2$BO$_3$ (g)
- SO$_2$ (g)
- CrO$_3$ (g)

- 

Thermodynamically Feasible Reaction

Performance Loss
- Secondary compound formation
- Reduction in ORR
- Increased polarization resistance
Prior Work

Cathode in “Real World” Air Exposure Atmospheres

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 La$_2$Zr$_2$O$_7$ and MnO$_x$ at electrode–electrolyte interface.

Presence of CO$_2$ in air:
- Presence of CO$_2$ (up to 3%) in air shows little to no influence on cathode performance degradation (100 hrs. tests).
- La$_2$O$_2$CO$_3$ and SrCO$_3$ form below 800°C but only SrCO$_3$ at 850°C and above.
- Pre-activated electrode shows insignificant degradation even at higher CO$_2$ (~10%CO$_2$) content.

Chromium Poisoning

Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, Synthesis and Stability of Sr\textsubscript{x}Ni\textsubscript{y}O\textsubscript{z} Chromium Getter for Solid Oxide Fuel Cells", ECS, 2018
Different degradation mechanisms exist for LSM and LSCF type cathode materials.

- Gas phase chromium species is largely reduced to $\text{Cr}_2\text{O}_3$ and deposited at the LSM/YSZ interface.
- For MEIC type cathodes, oxygen reduction reaction not only takes place at the TPB (as in the case of LSM) but also at the free exposed surfaces in contact with the gas phase.

Chromium Evaporation

Interconnects and Balance of plant alloys lead to the formation of Cr vapor species during exposure to humidified air.

Vaporization reactions:

1/2 \( \text{Cr}_2\text{O}_3(\text{s}) + \text{H}_2\text{O} (\text{g}) + \frac{3}{4} \text{O}_2 (\text{g}) = \text{CrO}_2(\text{OH})_2 (\text{g}) \)

1/2 \( \text{Cr}_2\text{O}_3(\text{s}) + \frac{1}{2} \text{H}_2\text{O}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{CrO}_2(\text{OH}) (\text{g}) \)

1/2 \( \text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{4} \text{O}_2(\text{g}) = \text{CrO}_3(\text{g}) \)

Cr vapor species have been found to react with cell air / fuel electrode leading to poisoning and performance degradation.
Chromium Getter Development

Significant reduction in the Cr vapor pressure is observed using SrO based getters.

\[
\begin{align*}
\text{SrO} + \text{CrO}_2(\text{OH})_2 (\text{g}) &= \text{SrCrO}_4 + \text{H}_2\text{O} (\text{g}) \\
2\text{SrO} + 2\text{CrO(OH)}_2(\text{g}) + \text{O}_2(\text{g}) &= 2\text{SrCrO}_4 + 2\text{H}_2\text{O} (\text{g}) \\
\text{SrO} + \text{CrO}_3 (\text{g}) &= \text{SrCrO}_4
\end{align*}
\]

Getter Material: \( \text{Sr}_x\text{Ni}_y\text{O}_z \) compound

Materials synthesis: Dip-coating support in aqueous solution of \( \text{Sr(NO}_3\text{)}_2 : \text{Ni(NO}_3\text{)}_2 \) (3:2 mole). Calcined at 600°C for 6 hours.

Substrate: Alumina fiber board

Substrate dimension: 2” (length), 0.8-1” (dia.)

Use of Alkaline earth – Transition-metal elements for Getter
High temperature *in-situ* XRD performed on SrNiOx powder for 40h

- SrNiOx maintains phase stability below sintering temperature of 900°C
- Sintering SrNiOx above 950°C leads to dissociation into separate SrO and NiO phases
- Volume expansion and pulverization is observed above 950°C sintering temperature

**VESTA and COD utilized for crystallographic representation**

XRD analysis after sintering

**Thermal Stability of Cr getters**

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*Ashish Aphale, Aman Uddin, Boxun Hu, Su Jeong Heo, Junsung Hong and Prabhakar Singh, Synthesis and Stability of Sr$_x$Ni$_y$O$_z$ Chromium Getter for Solid Oxide Fuel Cells*, ECS, 2018
Getter Validation: BOP Simulation

**Transpiration**

<table>
<thead>
<tr>
<th>Without getter</th>
<th>With getter</th>
</tr>
</thead>
</table>

**Getter Validation**

- LSM cathode with Cr, no getter
- LSM cathode without Cr, no getter
- LSM cathode with Cr and getter

**Electrochemical**

- Air Flow Rate (SCCM): 50, 100, 200, 500 completed

![Graph showing current density vs. time for different conditions.](image)

**Tests completed/In progress**

In-Cell Chromium Capture

- Half-cell fabrication procedure was maintained for all the half-cell fabrication
- LSM was screen printed and sintered at 1200 °C for 1h
- SNO or LSCF/SNO getter was brush coated and sintered at 850 °C for 20h
- **Config-1:** Getter paste is 5 mm apart from LSM and **Config-2:** Getter paste is in direct contact with LSM

Concept also validated independently by industry
Cr deposition: LSM/YSZ interface

Cross sectional FIB-STEM micrograph and mapping of LSM/YSZ interface after Cr poisoning at 650C

(a) TEM image of region of the chromium deposition taken along [110], (b) The corresponding FFT pattern (c) HRTEM image of the crystalline and (d) the atomic model illustrated.

- FIB-STEM and mapping reveals deposition of chromium at LSM/YSZ interface
- HRTEM results show it is rhombohedral \( \text{Cr}_2\text{O}_3 \) (space group R-3c, no. 167)
Surface Morphology: Pretreatment V/s of Conventional Alloy

- Oxidation of alumina forming alloy leads to formation of mixed oxide scales and alumina subscale.
- Surface pretreatment leads to the formation of exclusive alumina scale only.

Oxidation: Thermodynamics and Scale Growth

Standard Gibbs free energy of formation of oxides as a function of temperature – Ellingham diagram

CO:CO₂ ~10⁴
H₂:H₂O ~10⁴
pO₂ ~ 10⁻²² atm

Temperature (K)

FeO
CoO
NiO
Cr₂O₃
SiO₂
α-Al₂O₃

Formation of an Oxide Scale

O₂
M²⁺ + 2e⁻ + ½O₂ = MO

oxide scale, MO
M²⁺
2e⁻
O²⁻

metallic substrate, M

Scale thickness x is directly related to mass gain due to oxygen pickup: x ∝ Δm
Initial Oxidation – Nucleation and Growth

Necessary and Sufficient Conditions for the formation and growth of surface oxide:

- Surface oxide formation thermodynamically favorable: $\Delta G$ for the reaction is negative
  
  \[ M + \frac{n}{2} O_2 = MO_n, \quad \Delta G = -RT\ln K \]

- Growth of oxide nuclei is determined by bulk anion or cation diffusion process. The oxide thickness is governed by Wagner’s Law:
  
  \[ X^2 = k.t \]

For initial oxidation, it is considered that alloy constituents are accessible to the gas atmosphere and able to react to form respective oxides. Most cations present in the Fe and Ni base alloys (Fe, Ni, Cr, Al, Si, Mn, Ti, RE and others) will oxidize to form their respective oxides.

$\Delta G_{\text{Al}_2\text{O}_3} < \Delta G_{\text{Cr}_2\text{O}_3} < \Delta G_{\text{NiO}} < \Delta G_{\text{FeO}}$
Cr Evaporation Rate Measurement: Alumina Former

- Significant reduction in the Cr evaporation rate is observed after pretreatment of H214 alloy.
- Morphology and chemistry changes - observed after 500 hrs of Cr transpiration from untreated and pretreated H 214 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cr Evaporation Rate (Kgm^2s^{-1})</th>
<th>Cr Partial Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H214</td>
<td>1.82E-10</td>
<td>2.06E-8</td>
</tr>
<tr>
<td>PreTreated-H214</td>
<td>1.24E-11</td>
<td>1.45E-9</td>
</tr>
</tbody>
</table>
Scale chemistry and morphology studies were conducted on post tested alloy samples by FIB/TEM technique.
Mixed oxide scale formation is observed in as received H214 alloy after 500 hrs of Cr transpiration test. Surface pretreatment of the alloy in reducing atmosphere leads to selective oxidation of Al in bulk alloy at the exclusion of the other alloy elements.
• In air atmosphere, all the elements undergo oxidation and form multi-constituent oxides.
• Surface pretreatment in reducing atmosphere leads to selective oxidation of Al

Oxide phase stability at 850C in 3%H₂O air. M_a is unity.
Experimental Results: Evolution of Oxide Scales

High temperature *in-situ* XRD performed on alumina forming alloy 20h at 900C in 3%H₂O air.

- Evolution of oxide scales with time at 900C.
- Early oxide nuclei for Cr, Ni, Al is observed at time (T=0)
- Predominantly alumina sub-scale is formed after 20 hrs of oxidation in air

Transition from mixed oxide scale to passivating alumina scale
Performance comparison

*Alloy performance compared in 3%H₂O air at 850°C, duration 500hrs.*

Minimization of Cr evaporation from is evident from the visual images. Significant minimization of Cr evaporation is observed after 500 hrs. XRD confirms the presence of exclusive alumina scale post 500 hrs of Cr transpiration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Duration (hrs)</th>
<th>Temperature (C)</th>
<th>Atmosphere</th>
<th>Flow rate (SCCM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H214</td>
<td>500</td>
<td>850</td>
<td>3%H₂O-Air</td>
<td>300</td>
</tr>
</tbody>
</table>

![Discoloration of elbow](image1.png)

![No discoloration of elbow](image2.png)
Conclusions

1. Developed cost effective getters for the capture of gaseous Cr vapors.
   - Developed getters can capture gaseous Cr vapors in 600-900°C temperature range
2. Demonstrated excellent blockage of Cr vapor for entering into cathode electrode by electrochemical and transpiration tests
3. Optimized getter coating process, thickness and coating morphologies for large scale testing.
4. Characterized pretest and posttest getters (including getters for our lab, PNNL, and LG Fuel Cell) and cathodes by XRD, SEM-EDS, FIB-STEM and XPS.
5. Investigated the stability of SrNiOx getter as a function of temperature.
6. Scaled up getter powder materials synthesis Laboratory process can meet ~1-2 MWe SOFC system needs.

- Getter design can be tailored to meet various SOFC systems configurations and exposure conditions
- Getter materials can be used for capturing Cr originating from BOP and IC.
- Near term needs can be met by existing laboratory facilities.
Conclusions

- Gas phase acidic airborne impurities react with basic air electrode constituents to form stable reaction products at the free surface and TPB.
- Gr II Alkaline earth and transition metal oxides have been selected as potential getter materials as they offer oxide basicity and ability to capture acidic impurities.
- Thermodynamic calculations based on Gibbs free energy change indicates co-capture of sulfur and chromium impurity in wide temperature range.
- SrMnO based getter has been synthesized and fabricated.
- Getter has been validated electrochemically to demonstrate the successful capture of both Cr and S in gas phase at 850C.
- Posttest results from SEM indicates clean LSM/YSZ interface after 100 hrs of electrochemical test in presence of Cr and SO$_2$ vapor.
- SEM/EDS characterization of SMO getter reveals high concentration of S and Cr at the inlet of the getter and negligible concentrations at the center and the outlet of the getter, indicating complete capture.
Acknowledgements

- Financial support from the US DOE under federal grant DE-FE 0023385
- Dr. Rin Burke for guidance
- UConn for providing laboratory support
Thank you
Evolution of Oxide Scales

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