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

Prabhakar Singh

Department of Materials Science and Engineering
Center for Clean Energy Engineering, University of Connecticut, CT

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# Technical Contributors

<table>
<thead>
<tr>
<th>Name</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prabhakar Singh</td>
<td>Professor</td>
</tr>
<tr>
<td>Rampi Ramprasad</td>
<td>Professor</td>
</tr>
<tr>
<td>Steven Suib</td>
<td>Professor</td>
</tr>
<tr>
<td>Boxun Hu</td>
<td>Assistant Research Professor</td>
</tr>
<tr>
<td>Ashish Aphale</td>
<td>Post-doctoral fellow</td>
</tr>
<tr>
<td>Aman Uddin</td>
<td>Post-doctoral fellow</td>
</tr>
<tr>
<td>Sridevi Krishnan</td>
<td>Post-doctoral fellow</td>
</tr>
<tr>
<td>Su Jeong Heo</td>
<td>Graduate Student</td>
</tr>
<tr>
<td>Junkai He</td>
<td>Graduate Student</td>
</tr>
<tr>
<td>Yanliu Dang</td>
<td>Graduate Student</td>
</tr>
<tr>
<td>JunHo Song</td>
<td>Graduate Student</td>
</tr>
<tr>
<td>Justin Webster</td>
<td>Undergraduate Student</td>
</tr>
<tr>
<td>Seraphim Belko</td>
<td>Undergraduate Student</td>
</tr>
<tr>
<td>Manoj Mahapatra</td>
<td>Assistant Professor</td>
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**UConn**

**UAlabama**

**Program Managers:** Drs. Patcharin N. Burke and Jason Lewis, NETL
Outline

• Accomplishments
• Background
• Experimental
  • Getter optimization, process scale up and stability evaluation
  • Evaluation of getter performance
  • Fabrication and long term testing of Cr Getter
  • Electrochemical testing – BOP & In-Cell simulation
  • Characterization-SEM-EDX, XRD, and FIB-TEM
  • High surface area (HSA) getter materials
  • Sensor Development for in-situ Cr monitoring
• Results and Discussion
• Future Work
• Acknowledgements
Long term SOFC Degradation – Role of Cathode

A Universal Degradation Phenomena for HT Electrochemical Systems

Cathode Degradation

- Ohmic losses
- Non-ohmic losses
- Mechanical changes

Gas – Solid Reactions
- Gas phase constituents and contaminants
- Dopant evolution, Compound Formation, Surface Morphology Changes, Interface Diffusion

Solid – Solid Reactions
- Solid state reaction and Inter-diffusion

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>20.9 v%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>78 v%</td>
</tr>
<tr>
<td>Water</td>
<td>&lt;1 to 3 v%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>350 ppm</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>&lt;1 ppm</td>
</tr>
<tr>
<td>Noble gases</td>
<td>&lt;1 v%</td>
</tr>
<tr>
<td>Particulate matter (PM)</td>
<td>&lt;50 µg/m³</td>
</tr>
</tbody>
</table>

Air in fuel cell stack and system may also contain component derived impurities such as Cr (from metals and alloys) Si, B, and alkali (from glass and insulation).
Chromium Evaporation at Low & Intermediate Temperatures

Oxidation and electrochemical poisoning

Gaseous Cr species formation and transport remains a significant issue at lower temperatures similar to high temperature operation conditions. Presence of H₂O in air will lead to high partial pressures of Cr species.

\[
\begin{align*}
\text{Cr}_2\text{O}_3 (s) + 1.5 \text{O}_2(g) + 2 \text{H}_2\text{O} (g) & \rightarrow 2 \text{CrO}_2(\text{OH})_2 (g) \\
\text{Cr}_2\text{O}_3 (s) + \text{H}_2\text{O} (g) + \text{O}_2(g) & \rightarrow 2\text{CrO}_2(\text{OH}) (g) \\
2 \text{Cr}_2\text{O}_3 (s) + 4 \text{H}_2\text{O} (g) + \text{O}_2 (g) & \rightarrow 4 \text{CrO(OH)}_2 (g)
\end{align*}
\]

- Paralinear oxidation
- Electrode poisoning

Air + 3%H₂O atmosphere
P₀₂ = 0.21 atm.
P₇₂O = 0.03 atm.

- Alloy oxidation rate increases.
- Lowering of temperature does not significantly lower the Cr vapor pressure in humidified air as indicated by smaller slope.
- Significant reduction will, however, be obtained in dry air as indicated by larger slope.
Background – Chromium Poisoning of Cathodes

Morphology evolution in the presence of water and chromium vapor

Project Objectives

Develop, Validate and Transfer Technology Related to Materials and Approaches for the Mitigation of SOFC Cathode Degradation in SOFC Power Systems

Long Term Bulk, Interfacial and Surface Stability

Dopants, Electric polarization, Gas phase contaminants (H₂O, CO₂, SO₂, Cr-vapor species, stoichiometry)

Tools: EIS, DC conductivity, XRD, SEM, X-ray absorption spectroscopy, XPS, SIMS, TEM, HTXRD

Compound formation (Solid-solid/solid-gas reactions) dopants exolution and oxides segregation at surface
✓ oxides and compounds at interface
✓ crystal symmetry
✓ microstructure
✓ Micro-cracking and/or delamination

Bulk, Interfaces, Surface Stability

Electrode – Electrolyte / Electrode - IC

Couple/ Symmetric / Full cell/ configurations

Air side contaminants: Water, CO₂, SO₂, Oxide vapors
Other contaminants

In-situ, Ex-situ Bench top tests

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Accomplishments

- Cr capture successfully demonstrated from BOP/In-cell sources
- Cr getter identified, synthesized, tested and characterized
- Synthesis process scaled up to 1kg/batch using lab equipment
- Design studies performed for 40,000 hrs. getter life
- Cr getter provided to PNNL, LG, Cummins, Ceres for testing
- Laboratory findings provided to SOFC industries
- Cathode degradation mechanisms identified
- Getter operation validated at low temperatures
- Alternate HSA getter has been identified and synthesized.

1,2  
TRL  
5,6

Concept validation: Materials, synthesis, testing, characterization

Scale up, testing and validation, technology transfer
Accomplishments-Technical

- Suitable metal oxides have been selected for co-getter materials using thermodynamic calculations.
- Processes have been identified for the synthesis of HSA materials.
- As-synthesized HSA materials have been characterized using SEM, TEM and EDS techniques.
- In-situ electrochemical and ex-situ transpiration tests have been conducted to validate co-getter efficacy for Cr and S capture.
- Getter design is being further optimized by CFD computational analysis.
- New sensor design have been examined to test the sensitivity of Cr.

- Developed chromium getter shows excellent affinity for capturing gaseous Cr\(^{6+}\). Experiments are in progress on validating the capture of Sulfur and Sulfur- chromium species, respectively.
- Pre-formed and “in-situ” getter preparation demonstrated.
- Electrochemical and transpiration tests show excellent blockage of Cr vapor from entering into cathode electrode.
- Getter materials, support structure and HSA getter deposition processes are being developed and optimized.

- Graduate / Undergraduate students being trained - 7
- Post-doctoral fellows - 3
- Outreach: Middle and High School, STEM, International academic institutions
- Publications in peer reviewed journals
## Background: Getter

A list of Cr getter properties against the state of the art Cr poisoning mitigation and getter materials

<table>
<thead>
<tr>
<th>Cr getter critical property</th>
<th>Performance of new Cr getter against baseline state of the art Cr getter</th>
<th>Test conditions (Temp, time, atm)</th>
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<tbody>
<tr>
<td><strong>Phase Stability</strong></td>
<td>Superior: New Cr getter shows no phase changes and interaction with humidity and CO2 present in air.</td>
<td>RT-980C, Ambient air</td>
</tr>
<tr>
<td><strong>Reaction products</strong></td>
<td>As processed getters consist of several oxide phases containing Sr and Ni (Sr9Ni7O21, Sr4Ni3O9 and Sr2Ni4O5).</td>
<td>Powder synthesis process and transpiration, electrochemical testing at 850C for up to 500 hrs in Air -3%H2O</td>
</tr>
<tr>
<td><strong>Microstructures</strong></td>
<td>Stable powder, coating and substrate microstructures obtained. New Cr getter retains its microstructure after high temperature exposures (850C) in humidified air. Literature review does not provide background information on the SOTA.</td>
<td>During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air</td>
</tr>
<tr>
<td><strong>Thermochemistry</strong></td>
<td>Similar or Superior: Based on thermochemical models developed</td>
<td></td>
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<tr>
<td><strong>Physical Properties</strong></td>
<td>Similar or Superior: Based on resistance to ambient air (NAAQS)</td>
<td></td>
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<tr>
<td><strong>Product morphology</strong></td>
<td>Porous powder coating on ceramic substrates</td>
<td>During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air</td>
</tr>
<tr>
<td><strong>Cr Conc. profile</strong></td>
<td>Superior: Capture Cr in the first 1500 - 3000 micron. Reproducible results</td>
<td>During bench top testing at 850C for up to 500 hrs in humid air</td>
</tr>
<tr>
<td><strong>Substrate</strong></td>
<td>Configuration include honeycomb, foam and fibrous structure, Substrate materials include Cordierite, Mullite, zirconia and alumina.</td>
<td></td>
</tr>
<tr>
<td><strong>Ease of fabrication</strong></td>
<td>Conventional powder preparation and coating techniques</td>
<td>pre-formed /In-situ getter formation</td>
</tr>
</tbody>
</table>
Novelty and Innovation

- Design flexibility for integration in wide range of SOFC systems configuration
- Flexibility of operation from 600-900°C
- Use of conventional 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

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.
Getter Chemistry Optimization and Scale up

Validation and testing
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.
Objective: Produce a large batch of SNO for industrial application

Approach: Scale up smaller 20g batches of SNO to produce 1kg batch.

Rationale: Using results from initial 20g and 100g batches, 250g batch is prepared to produce SNO with desired composition. XRD results from assay and temperature comparison of 20g batches were used to optimize 250g batch.

Previous Work: 20g batches were used to optimize powder composition of large batch with respect to initial assay and sinter temperature. Optimal composition and temperature were found to be 49:51 Sr to Ni ratio sintered at 900°C as shown.
# Alternate Synthesis Processes

<table>
<thead>
<tr>
<th>Synthetic Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave</td>
<td>Fast, high surface area</td>
<td>Lack of affinity</td>
</tr>
<tr>
<td>Sol-gel</td>
<td>Simplicity, high surface area</td>
<td>complex</td>
</tr>
<tr>
<td>Impregnation</td>
<td>Doped ions and form secondary coating layer</td>
<td>Need two steps</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>Uniform crystal size</td>
<td>Low surface area, high energy needed</td>
</tr>
<tr>
<td>UCT</td>
<td>Form porous thin layer with HSA</td>
<td>complex</td>
</tr>
</tbody>
</table>
**Process Flowchart**

**Batch**
- Weigh out 347.9g Sr(NO$_3$)$_2$ and 498.0g Ni(NO$_3$)$_2$ separately.

**Dissolve**
- Add Sr(NO$_3$)$_2$ to 500ml of DI water into 2000 ml beaker and begin mixing and heating. Add Ni(NO$_3$)$_2$. Heat @ 80°C until fully dissolved.

**Precipitate**
- Titrate 300 ml of NH$_4$OH into solution or enough to bring pH above 8.75.

**Dry**
- Heat at 80°C while maintaining pH above 8.75 through titration.

**Sinter**
- Finish drying in oven set at 80°C for 72 hours. After 72 hours remove from oven and crush into small particles using mortar and pestel.

**Analyze**
- Place powder in furnace. Begin calcination process. Ramp oven to 500°C @ 3°C/min. Hold for four hours. Ramp oven to 900°C @ 3°C/min. Hold for 48 hours. Quench to Room Temperature.

**This work: thermal effects**

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Synthesis Methods for High Surface Area Getter

MO\textsubscript{x} nanofibers

Microwave Method

Impregnation Method

Hydrothermal method
Honeycomb/ Foam Substrate Getters

Schemes of Cr getter with honeycomb structure surface-coated with SrNiO$_x$

High surface area and porous SrNiOx coating (10-30 $\mu$m)
Coating Optimization: Slurry coating of honeycomb

- After 3rd coating, coating thickness: 40-60 µm.
- Coating is porous.

<table>
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<tr>
<th>Coating</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNO</td>
<td>10g</td>
</tr>
<tr>
<td>Durban</td>
<td>1.2ml</td>
</tr>
<tr>
<td>PVP</td>
<td>3g</td>
</tr>
<tr>
<td>Cement</td>
<td>1g</td>
</tr>
<tr>
<td>Solvent</td>
<td>50%/50%</td>
</tr>
<tr>
<td>Water/Ethanol</td>
<td>50ml</td>
</tr>
</tbody>
</table>

After RT drying

- After 900°C heat treatment for 5 hour
- After 850°C heat treatment for 5 hour
- After 900°C heat treatment for 5 hour

Coating #5

SNO 10g
Durban 1.2ml
PVP 3g
Cement 1g
Solvent 50ml
Water/Ethanol 50%/50%

EDS Quantitative Results

Element Wt% At%
AlK 13.84 30.57
NiK 32.35 32.84
SrK 53.81 36.60

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Coating Optimization: Slurry coating of honeycomb

Cross section

SEM images of the cross-section of the Cr getter and elemental analysis by EDS.

Pores in the substrate (cordierite) contain Sr and Ni
It is suggested that the SrNiOH penetrated into the holes cause strong adhesion between the coated layer and the substrate.
The SrNiO layer is ~10 – 15 µm in thickness.
Stability of Getter Materials

Before sintering

850°C (20h)

After sintering

1000°C (20h)

- Sintering at 850°C for 20h: No change in color and shape of the pellet
- Sintering at 1000°C for 20h: Pellets became brown and the shape was intact immediately after removal from furnace at room temperature, but after 24h the pellets were pulverized completely.

Evaluate the stability of SrNiOx
Validate in-cell getter to capture Cr from IC source

- No/ negligible changes in morphology was observed for SNO sintered at 850°C for 20h
- Particles agglomeration was observed for SNO sintered at 1000°C for 20h
Thermal stability

- No change in color and shape of the pellet after sintering at 850°C for 20h.
- Sintering at 1000°C for 20h leads to pulverization of SNO powders. Initially, the pellets turn brown in color immediately after taking out of the furnace, changing to green and completely pulverized after 24h left in lab atmosphere.
The XRD pattern of 850 °C sintered SNO indicates presence of only $\text{Sr}_x\text{Ni}_y\text{O}_z$ phase with presence of minor $\text{SrCO}_3$ phase.

In contrast, XRD patterns of pulverized powder (1000°C) shows the presence of $\text{Sr(OH)}_2\cdot\text{H}_2\text{O}$ phase along with the strong peaks of $\text{SrCO}_3$.

Strong peaks of NiO phase appear with absence of SrO phase in XRD patterns of the pulverized samples.
Phase Stability has been studied by high temperature *in-situ* XRD performed on SrNiOx powder for up to 40h.

- SrNiOx demonstrated phase stability sintered at 850°C and 900°C.
- SrNiOx sintered at 950°C and 1000°C dissociates into SrO and NiO phases.
Endothermic peaks at 105 and 489°C indicating release of H2O from SNO powder samples sintered at (a) 850°C and (b) 1000°C (20Hrs)
In Stack Cr Capture

- Ni coarse and sulfide compound formation
- Cr poisoning & Sealing

Diagram showing fuel, anode, electrolyte, cathode, and air flow with interconnects and cell repeat units.
Half-cell configuration

- Config-1: Getter paste is 5 mm apart from LSM and Config-2: Getter paste is in direct contact with LSM.

Conditions
- Temperature: 850°C
- Flowrate: 150 sccm
- Cr Source: Cr₂O₃
- Cr Getter: SNO/ LSCF-SNO composite
- Bias: -500 mV

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.

- Half-cell configuration
  - Anode Air
  - Pt
  - YSZ
  - LSM
  - 5 mm
  - (Ni-supported) Getter Paste
  - Cathode Air

- Cathode Air
- Getter Paste
- Config-2
- Anode Air
- Pt
- YSZ
- LSM
Electrical Conductivity of LSM is approximately 120 S/cm at 850°C
Electrical conductivity of SNO is approximately 1.2 S/cm at 850°C
Addition of SNO in LSM lowers the conductivity of LSM-SNO composites
Electrical conductivity of LSCF is more than 800 S/cm at 850°C
LSCF-SNO composites display higher conductivity compared to LSM-SNO composites.

I-t data shows stable performance for 100h in all the half-cell configurations. Config-1 shows higher performance because of no direct contact of getter with the LSM cathode. 75LSCF-50SNO getter shows higher current density (~1100 mA/cm²) as compared to 50LSCF-50SNO getter (~700 mA/cm²).
Electrochemical Evaluation

Posttest characterization (SEM)

75LSCF-50SNO (Screen printed) Cross-section

- Higher Cr concentration observed at the surface
- Cathode/ electrolyte interface remained free from Cr
Electrochemical Evaluation

Posttest characterization (SEM)

- All Cr are mostly captured at the surface of the cathode with faceted particle formation.
- No Cr or product was found inside cathode or cathode-YSZ interface.
Getter reaction and Cr capture

\[ \text{Air +3\%H}_2\text{O+Cr}_v \]

\[ \text{SrNiO}_x \]

Product layer
\[ \text{SrCrO}_4(s) \]

\[ \text{SrNiO}_x \]

Cr(g)

Product layer
\[ \text{SrCrO}_4 \]

Cr(g)

Solid-Gas interface

\[ \text{CrO}_3 (g) + \text{Sr}_x\text{Ni}_y\text{O}_z = \text{SrCrO}_4 + \text{NiO} + \text{O}_2 (g) \]

\[ \text{CrO}_2(\text{OH})_2 (g) + \text{Sr}_x\text{Ni}_y\text{O}_z + \text{O}_2 (g) = \text{SrCrO}_4 + \text{NiO} + \text{H}_2\text{O} (g) \]
In-Situ 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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Thermodynamic Analysis
Thermodynamic Analysis

Cr poisoning in SOFC cathodes

- Cr poisoning effects in SOFC cathodes
  - \((\text{La}, \text{Sr})\text{MnO}_3\)
  - \((\text{La}, \text{Sr})(\text{Co})\text{O}_3\)
- Ab-initio thermodynamic with a linear programming approach
- Reaction Energetics of the SOFC cathodes with \(\text{CrO}_3\)

* The structure of the LSCO and LSMO at different Sr concentration have been studied.
* We have identified the minimum energy structures in each of the compositions and they agree well with experiments.
* Reaction energetics of \(\text{CrO}_3\) with the compounds \(\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3\) and \(\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3\) were studied.
* We find that while LSCO results in reactive products for the experimental window, the LSMO remains unreactive.
Based on the reaction energetics, the formation of these products: LaCoO$_3$, Co$_3$O$_4$, SrCrO$_4$, and O$_2$ are energetically favored in the experimental window.
Based on the reaction energetics, the formation of Cr deposition products are not energetically favored in the experimental window.
Background – Chromium Poisoning of Cathodes

Morphology evolution in the presence of water and chromium vapor

Sr-Ni-O, Sr-Mn-O, Sr-Fe-O perovskite type compounds with relatively high electrical conductivity are the potential coating materials for getter application.

CaO and MgO are considered.

The oxidation of both Cr vapor and SO$_2$ occurs the most by SrO getter material over a wide temperature range.

Co-stability calculated based on Gibbs free energy and equilibrium constant.
Thermodynamic Calculations of $p_{\text{Cr}}$ and $p_{\text{SO}_2}$ vapors at High Temperatures

- SrO is better than CaO, and MgO as a getter material for Cr and S capture.
- SrO is capable of forming SrCrO$_4$ and SrSO$_4$ compounds at extremely low concentrations of Cr and SO$_2$ vapors, even below 1 ppb.
Design and fabrication

- Sensor design:
  - Planar sensor design to monitor the presence of chromium within the getter

SensorFabrication

- LSM sintered at 1200 °C in air and Pt sintered at 850 °C in air with the ramp rate of 3C/min for 1h
- LSM and Pt ink was brush coated on the YSZ disk as sensing (SE) and reference electrode (RE)
Validation

- S1 is inserted within the getter at about 2 mm from inlet
- S2 is inserted about 8 mm from inlet of the getter
- Observe the changes in polarization resistance and ohmic resistances to determine extent of Cr related degradation
**Governing Equations, Boundary Conditions, and Parameters**

Mass conservation equation:
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0
\]

Momentum conservation equation:
\[
\frac{\partial (\rho \mathbf{u})}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot (\mu^{\text{eff}} \nabla \mathbf{u}) + \rho \mathbf{g}
\]

Species conservation equation:
\[
\frac{\partial (C^{Cr})}{\partial t} + \nabla \cdot (\mathbf{u} C^{Cr}) = \nabla \cdot (D \nabla C^{Cr}) + S_{Cr}
\]
\[S_{Cr}: \text{sink term for Cr.}\]

**Boundary Conditions**

\[u, C^{\text{Cr}}_{\text{inlet}}\]

**Numerical Procedure**

- Set of equations is discretized using a finite-volume method.
- Discretized equations are solved within the commercially available CFD software, Fluent, by customizing via user-defined functions.
- The software utilizes the well-known SIMPLE algorithm.

**Modeling Parameters**

- Modeling Geometry: 50 mm long and 1 mm width
- Temperature: 850°C
- Cr partial pressure 0.1 Pa and 0.001 Pa
- Air density: 0.3139 kg/m³ at 850°C
- Gas phase Cr diffusivity: 1.08775e-4 m²/s
- Solid phase Cr diffusivity: 1e-19 m²/s
- Solid phase Sr diffusivity: 1e-17 m²/s

- Getter material: SrNiOₓ
- SrNiOₓ density: 5406 kg/m³
- SrNiOₓ molecular weight: 1.53542 kg/mol
Electrode poisoning at low temperatures

In cell validation
The LSM/YSZ/Pt half-cell exposed to 3% H₂O/air in the presence of Cr vapor shows a rapid drop in the current within the first few hours while the I-t curves from the standard cell (No Cr vapor) and the cell exposure to Cr and followed a chromium getter show similar curve with stable electrochemical performance.
Changes in EIS with/without Cr and Cr/getter

**Exposure to Cr vapor**
- Rp increases with time when cell was exposure to Cr while Rp keeps stable if no Cr species present.

**No Cr vapor**
- Time Increased

**Exposure to Cr with getter**
- Time Increased
Cr deposition in the cell

Observations: $\text{Cr}_2\text{O}_3$ deposits at the LSM/YSZ interface at 650°C when cell was exposed to Cr vapor.
Summary

• Cr capture has been successfully demonstrated from BOP/ In-cell sources
• Cr getter materials have been identified and synthesis process have been developed and scaled up.
• Synthesis process scaled up to 1kg/batch using lab equipment
• Design studies have been performed to obtain 40,000 hrs. getter life
• Fabricated Cr getter samples and materials have been provided to PNNL, LG, Cummins, Ceres and others for testing
• Laboratory findings have been provided to SOFC industries
• Cathode degradation mechanisms have been identified and published.
• Getter operation has been validated at low (650C) temperature
• Alternate HSA getter has been identified and synthesized.

Getters can be provided to SOFC industries and research institutions for independent testing and validation
Acknowledgements

• Drs. Rin Burke, Jason Lewis and Shailesh Vora for guidance and encouragement
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• Drs. Yu Zhong (FIU), Yoed Tsur(Technion) for thermochemical model
• UConn for providing laboratory facility and support
Thank you
**Getter Materials Optimization**

**Electrical conductivity measurement: In-cell getter**

Composite with LSM – LSCF with SNO

- LSM/ LSCF pellets were sintered at 1200°C
- LSM/LSCF-SNO composite pellets were sintered at 950°C for 1h
- Pt electrodes were attached using Pt paste and sintered at 850°C
- Pellet: Dia: ~12.70mm, Thickness: ~2.07mm, ~Wt: 0.9655g
- 4-probe measurement method applied
## Background: Getter

A list of Cr getter properties against the state of the art Cr poisoning mitigation and getter materials

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<td>Superior: New Cr getter shows no phase changes and interaction with humidity and CO2 present in air.</td>
<td>RT-980C, Ambient air</td>
</tr>
<tr>
<td><strong>Reaction products</strong></td>
<td>As processed getters consist of several oxide phases containing Sr and Ni (Sr9Ni7O21, Sr4Ni3O9 and Sr2Ni4O5).</td>
<td>Powder synthesis process and transpiration, electrochemical testing at 850C for up to 500 hrs in Air -3%H2O</td>
</tr>
<tr>
<td><strong>Microstructures</strong></td>
<td>Stable powder, coating and substrate microstructures obtained. New Cr getter retains its microstructure after high temperature exposures (850C) in humidified air. Literature review does not provide background information on the SOTA.</td>
<td>During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air</td>
</tr>
<tr>
<td><strong>Thermochemistry</strong></td>
<td>Similar or Superior: Based on thermochemical models developed</td>
<td></td>
</tr>
<tr>
<td><strong>Physical Properties</strong></td>
<td>Similar or Superior: Based on resistance to ambient air (NAAQS)</td>
<td></td>
</tr>
<tr>
<td><strong>Product morphology</strong></td>
<td>Porous powder coating on ceramic substrates</td>
<td>During processing up to 980C in air During bench top testing at 850C for up to 500 hrs in humid air</td>
</tr>
<tr>
<td><strong>Cr Conc. profile</strong></td>
<td>Superior: Capture Cr in the first 1500 - 3000 micron. Reproducible results</td>
<td>During bench top testing at 850C for up to 500 hrs in humid air</td>
</tr>
<tr>
<td><strong>Substrate</strong></td>
<td>Configuration include honeycomb, foam and fibrous structure, Substrate materials include Cordierite, Mullite, zirconia and alumina.</td>
<td></td>
</tr>
<tr>
<td><strong>Ease of fabrication</strong></td>
<td>Conventional powder preparation and coating techniques</td>
<td>pre-formed /In-situ getter formation</td>
</tr>
</tbody>
</table>
Cr getter

Appearance

1. Fabrication Process (coating x2)
   : Coating with SrNi(OH)\(_x\) → sintering at 850 2C for 1 h → Coating with SrNi(OH)\(_x\) → sintering at 650 2C for 1 h

2. Expectation from the appearance
   (1) Black color in all positions → Uniformly coated
   (2) No clogging → Uniform and ideal
   (3) No powder dust detached from the getter → Strong adhesion

Figure Cr getter coated with SrNiO (3 cm in diameter, 2 inch in length)
High temperature *in-situ* XRD performed on 75LSCF-25SNO powder for up to 40h at 850 C

- SNO does not dissociate into SrO or NiO - indicating phase stability.
- LSCF remains stable throughout the 40h sintering process
- After 40h sintering strontium iron oxide (SFeO) and lanthanum cobalt iron oxide (LCoFeO) appeared in smaller quantity.
Figure 6. XRD patterns of SNO sintered at 850 °C showing stability and showing the formation of Sr(OH)$_2$ and SrCO$_3$ compounds in the pulverized samples sintered at 1000 °C for 20h.
SNO getter (Config-1) half-cell shows least ohmic resistance and polarization and remained stable throughout.

75LSCF-25SNO and 50LSCF-50SNO getter with (Config-2) half-cell demonstrated decrease in the ohmic resistance as well as polarization resistance during first 20h and later remained stable.

100 SNO getter (Config-2) based half-cell has consistent ohmic resistance as well as polarization resistances, 0.6 and 1.5 ohms respectively.
Future Work

• Complete validation of 1 kg/ batch getter powder synthesis process
• Use the above getter powder for coating getter support (foam, honeycomb)
• Complete getter design
• Test coated getters under SOFC system conditions
• Test getters in the cell
• Provide powder and fabricated getters to SOFC industry under DOE guidelines
• Assist DOE in technology transfer
I-t performance

- Performance of S1 decreases continuously and S2 performance stabilizes after 5h
Changes in Rp and Rnp

- Polarization resistance (Rp) of S1 continuously increases and within 30h, it increased by more than 60%.
- Increase in Rp of S2 is relatively stable over time.
- No significant changes in Rnp for both sensors.
- Continue to monitor the performance over longer time.
Design and Optimization of Chromium Getter through Computational Modeling
Design and Optimization of Chromium Getter through Computational Modeling

Aman Uddin
Collaboration with PNNL
Objectives

The overall objective is to design and optimize chromium getter to capture the chromium species originating from the metallic stack and BOP components. The objectives include:

- Parametric study of getter to predict the effects of the key parameters such as geometric surface area, porosity, thickness of coating materials, etc. when:
  - Surface reaction is rate limiting
  - Solid state diffusion is rate limiting
  - Diffusion through porous product layer is rate limiting
- Optimize design for higher utilization and low pressure drop requirement.
- Fabricate and test getter according to the proposed model and validate

- A transient, two dimensional model of chromium getter is developed to predict the utilization of getter with various rate limiting cases.
- In this model, cordierite substrate with 400 cpsi (cells per square inch) is considered as the getter support material for 1 kW SOFC system (4 SLPM flow rate), and the model is solved for high Cr partial pressure (1e-6 atm).
- In solid state diffusion case, Chromium front moves forward before reaching to maximum capacity because porosity of getter decreases due to product layer formation with time and diffusion is rate limiting.
- Chromium front moves faster in solid state diffusion case compared to reaction rate limited case.
- Current efforts are underway to optimize design for higher utilization and low pressure drop requirement.
Background

- Cr poisoning is one of the major causes of cathode degradation in high temperature electrochemical systems such as SOFC.
- A novel approach called Cr getter is developed to mitigate the Cr poisoning.
- Cr getter contains SrNiOx getter material supported by various structure.
- Support materials: cordierite, porous alumina.
- Successfully captured Cr within 2-3mm of getter.

![Image of samples and graph](image.png)

*Hu et al. J. Power Source, 2016, submitted*

Graph showing the intensity percentage of chromium at different distances from the inlet, with different getters showing varying efficiency. Air flow rate comparisons are also shown:

- Air flow rate of 50 sccm for 100hr at 850°C.
- Air flow rate of 300 sccm for 500hr at 850°C.
Rate Limiting Step: Solid state diffusion

Assumption:
- 10µm thick coating with 50% porosity
- Product layer reduces porosity of getter
- Solid State Diffusion

\[
S_{Cr} = D_e \frac{C_{Sr}}{\delta(t)} \frac{A}{V}
\]

Where, \(C_{Sr}\) = concentration of Strontium, \(D_e\) = Diffusion coefficient; \(\delta(t)\) = thickness product layer, \(A/V\) = area to volume ratio

Chromium profile at 4 SLPM flow rate with 0.1 Pa Cr pressure

Porosity of getter

Comparison (after 56hr)

- Chromium front moves forward before reaching to maximum capacity because porosity of getter decreases and diffusion is rate limiting.
- Chromium front moves faster in solid state diffusion case compared to reaction rate limited case.
Electrochemical Performance (Baseline- No Cr-No Getter)

- Results from 100 h I-t data shows stable performance
- Polarization resistance remained stable at \( (R_p) \sim 60 \Omega \)
- Ohmic resistance also remains constant at \( (R_{np}) \sim 80 \Omega \)
Electrochemical Performance (Cr- No Getter)

- LSM degrades rapidly after the exposure to Cr vapor
- Nyquist plot indicate continuous increase in the polarization resistance due to Cr degradation
Acknowledgements

• Helpful technical feasibility discussions with Dr. Rin Burke
• Systems and applications related discussion
  ➢ Drs. Goettler, Ghezel-Ayagh, Aligner, Mukherjee
  ➢ Provided experimental data to LGFC, FCE, GE, Ceres Power
  ➢ Discussed scale-up issues
  ➢ Discussed system constraints and experimental parameters
• Cell and stack related discussion with Dr. Stevenson
  ➢ Provided getter materials and performance data
  ➢ Discussed approaches for application in cells