Multi-Constituent Airborne Contaminants Capture and Mitigation of Cathode Poisoning in Solid Oxide Fuel Cell

Kevin Lee, Pawan Dubey, Michael Reisert, Junsung Hong, Ashish Aphale, Seraphim Belko, Prabhakar Singh
University of Connecticut, Storrs, CT

US DOE Program: DE-FE-0031647

Program Manager: Dr. Patcharin Burke
Email: Patcharin.Burke@NETL.DOE.GOV

October 25-27, 2022

23rd ANNUAL SOLID OXIDE FUEL CELL (SOFC) PROJECT REVIEW MEETING
Pittsburgh Airport Marriott Hotel
Presentation Outline

• Program Objective
• Broader Impact
• Technical Accomplishments
• Approach, Results and Discussion
• Summary and Conclusions
• Acknowledgements

✓ Low cost
✓ Conventional materials and processes
✓ Wide range of applications

Identification

Validation

Mitigation

Implementation
Program Objectives

- Identify the origin, formation processes and the nature of gas phase airborne contaminants (intrinsic and extrinsic) present in the air stream entering elevated temperature electrochemical systems.

- Develop mechanistic understanding of contaminant interactions (chemical, electrochemical and structural) with conventional air electrode materials.

- Identify cost effective getter materials and processing techniques to capture trace contaminants. Synthesize and validate getter performance and efficacy.

- Design and fabricate getters for stack and BOP applications. Validate the above under system conditions. Transfer technology to industrial partners.
Accomplishments

- Intrinsic and extrinsic trace gaseous contaminants present in ambient air stream, entering the elevated temperature electrochemical systems, have been identified.
- Formation, transport and interactions of contaminants with the air electrode has been examined. Role of alloy surface scale chemistry, pre-treatment conditions, formation of point and 3D-defects in the scale and molecular transport have been studied.
- Pretreatment of alloys under controlled exposure conditions modify the scale chemistry and morphology influencing the formation and transport of trace extrinsic contaminants.
- Getters have been fabricated for the capture of trace S (intrinsic) and Cr, Si, B (extrinsic) gaseous contaminants.
- Getter materials can be provided for test validation with DOE permission.
- Technical approach offers pathway for the capture of trace gaseous contaminants present in high temperature fuel cells, electrolyzers and chemical reactor systems.

Large range of contaminants  large volume of reactants  longer operating times
Select publications: Cr evaporation and capture (my group)

2. Junsung Hong, Su Jeong Heo, Prabhakar Singh “Combined Cr and S poisoning behaviors of La1-xSrxMnO3δ+ε and La1-xSrxCoy1-yFe2O3-x cathodes in solid oxide fuel cells” Applied Surface Science, Volume 530, 15 November 2020, 147253
7. Boxun Hu, Srideti Krishnan, Chiyung Liang, Su Jeong Heo, Ashish N.Aphale, Rampi Ramprasad, Prabhakar Singh “Experimental and thermodynamic evaluation of La1-xSr0.9Mn0.1O3 cathodes and La1-xSr0.9Co0.1Fe2O3-x cathodes in Cr-containing humidified air” International Journal of Hydrogen Energy, Volume 42, Issue 15, 13 April 2017, Pages 10208-10216

October 25-27, 2022
Background: Contaminant Types, Transport and Interactions

- Intrinsic and extrinsic
  - originating from or on the outside
    - acidic: SOx, NOx, H2S, HCl, HBO3, P2O5, SiOHx, CrOHx
    - basic: Ammonia, Alkali hydroxides, Alkali halides
- Types and levels
  - ppm/ppb
- Influence on SOFC systems life and performance
  - Enhanced corrosion
  - Surface deposition
  - Reaction products formation
  - Performance/Life reduction

Breadth and complexity of the topic pertaining to trace contaminant, interactions and removal has been examined. The influence of contaminants on the performance and life can be further examined based on operational flexibility.
Options: Long term degradation mitigation

- Reduce contaminant formation and its transport – new materials?
- Use contaminant tolerant cell components - new materials?
- Consume contaminants at the component surface – additional reactions!
- Capture contaminants on low-cost getters – clean surface/ interface?
Background: Trace Contaminants

Presence of trace gaseous contaminants are part of oxidant and fuel streams entering high temperature electrochemical systems (Fuel cells, electrolyzer etc.). There remains a need for the reduction/elimination of contaminants from the gaseous streams during long term operation to minimize performance degradation due to its accumulation / continued reaction in the electrodes.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Impurities</th>
<th>Impact</th>
<th>Implication</th>
</tr>
</thead>
<tbody>
<tr>
<td>State of the art</td>
<td>Intrinsic</td>
<td>Electrode poisoning +</td>
<td>Degradation</td>
</tr>
<tr>
<td></td>
<td>Extrinsic</td>
<td>Structural changes</td>
<td></td>
</tr>
<tr>
<td>Materials modification</td>
<td>Intrinsic</td>
<td>Reduced poisoning +</td>
<td>Lower degradation</td>
</tr>
<tr>
<td></td>
<td>Reduced extrinsic</td>
<td>Structural changes</td>
<td></td>
</tr>
<tr>
<td>Impurity capture</td>
<td>Reduced Intrinsic</td>
<td>Reduced poisoning +</td>
<td>Lower degradation</td>
</tr>
<tr>
<td></td>
<td>Reduced extrinsic</td>
<td>&gt;&gt; Extended life</td>
<td></td>
</tr>
</tbody>
</table>

Large input of air volume entering the electrochemical systems over its lifetime (000’s of hrs.) can lead to accumulation of appreciable amounts of contaminants (100’s of grams to kilo grams) in the electrodes.
### Criteria Pollutants – National Ambient Air Quality Standards

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Primary/Secondary</th>
<th>Averaging Time</th>
<th>Level</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon Monoxide (CO)</strong></td>
<td>primary</td>
<td>8 hours</td>
<td>9 ppm</td>
<td>Not to be exceeded more than once per year</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 hour</td>
<td>35 ppm</td>
<td></td>
</tr>
<tr>
<td><strong>Lead (Pb)</strong></td>
<td>primary and secondary</td>
<td>Rolling 3 month average</td>
<td>0.15 μg/m$^3$ (1)</td>
<td>Not to be exceeded</td>
</tr>
<tr>
<td><strong>Nitrogen Dioxide (NO$_2$)</strong></td>
<td>primary</td>
<td>1 hour</td>
<td>100 ppb</td>
<td>98th percentile of 1-hour daily maximum concentrations, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td>primary and secondary</td>
<td>1 year</td>
<td>53 ppb (2)</td>
<td>Annual Mean</td>
</tr>
<tr>
<td><strong>Ozone (O$_3$)</strong></td>
<td>primary and secondary</td>
<td>8 hours</td>
<td>0.070 ppm (3)</td>
<td>Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years</td>
</tr>
<tr>
<td><strong>Particle Pollution (PM)</strong></td>
<td>primary</td>
<td>1 year</td>
<td>12.0 μg/m$^3$</td>
<td>annual mean, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td>secondary</td>
<td>1 year</td>
<td>15.0 μg/m$^3$</td>
<td>annual mean, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td>primary and secondary</td>
<td>24 hours</td>
<td>35 μg/m$^3$</td>
<td>98th percentile, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td><strong>PM$_{10}$</strong></td>
<td>primary and secondary</td>
<td>24 hours</td>
<td>150 μg/m$^3$</td>
</tr>
<tr>
<td><strong>Sulfur Dioxide (SO$_2$)</strong></td>
<td>primary</td>
<td>1 hour</td>
<td>75 ppb (4)</td>
<td>99th percentile of 1-hour daily maximum concentrations, averaged over 3 years</td>
</tr>
<tr>
<td></td>
<td>secondary</td>
<td>3 hours</td>
<td>0.5 ppm</td>
<td>Not to be exceeded more than once per year</td>
</tr>
</tbody>
</table>

There is a need to understand the role of VOC, NH$_3$, PM’s, alkali, salt etc. on the long term accumulation in the porous electrodes.
Airborne Contaminants and Cathode Degradation in SOFC Systems

- Air electrode (predominantly basic, Lanthanide group) remain prone to degradation due to interactions with acidic contaminants.
- Degradation leads to dopant exsolution, compound formation, and surface/interface morphology changes.

Cathode Degradation

- Gaseous contaminants
- Airborne intrinsic impurities
- Evaporation of extrinsic impurities

Solid-Gas

Solid-Solid

- Solid state reaction and interdiffusion
- Cathode/electrolyte
- Cathode/interconnect

Ohmic losses, Non-ohmic losses, Mechanical changes

Electrocatalytic Deactivation
Compound Formation
Surface adsorption

Acidic gaseous species
Basic AE Surface

Trace contaminants accumulate with time in the electrode. Valance change, dopant exsolution, compound formation and electrode decomposition can occur during long term exposure to air.
Extrinsic contaminants formation in SOFC system

- Surface reaction – Exposed surfaces on cell and BOP components
- Defects and second phases present in the surface oxides
- Spallation of oxides and exposure of internal reactive oxides
- Steam induced corrosion and transport of contaminants

- Formation of gaseous oxides are considered to be due to interactions between the gas phase (H2O) and surface oxides. Cr, Si, B, Bi present in the surface oxide can form their respective hydrated oxides.
- Transport of gaseous Si, Cr, B, Bi etc. in the form of oxides (Mog) is ruled out since their formation would not depend on the availability of water.
- Pretreatment of the surface to modify oxide chemistry benign to gaseous oxide formation
- Large cracks and open porosity in the scale can promote gaseous oxide formation from sub surface oxides.

Evaporation and gas phase transport

- Defects present in the surface oxides can lead to evaporation faster than through dense oxide / coatings (gaseous transport/redox).
- Reaction layers at underlying oxide interfaces can accelerate Cr, Si, B evaporation.
- Pretreatment of surface to modify oxide chemistry can reduce gaseous product formation.
- Formation of micro cracks with exposure time can promote evaporation.

Examine molecular transport of reactants and products through defective surface oxides
Surface treatment and oxide scale chemistry

Exposed metal surfaces lead to alloying additive oxide nuclei formation and growth at the surface.

In air, all reactive constituents form oxide nuclei.

In controlled atmosphere, only select alloying additive oxidize to form oxide nuclei.

A modified surface oxide with Cr or other additives can be formed by controlling exposure atmosphere PO2.

FIB cross-section (a) and high-resolution TEM image (b) of ZMG232G10® after 10 h pre-treatment in air at 900 °C. Elemental analysis is included for Figure (b).

FIB cross-section (a) and high-resolution TEM image (b) of ZMG232G10® after 10 h pre-treatment in H2-3%H2O atmosphere at 900 °C. Elemental analysis is shown for Figure (b).

Reisert et al., “Controlled thermal pre-treatment of ZMG232G10® for corrosion mitigation under simulated SOFC interconnect exposure conditions” Accepted for publication, IJHE 2022
Surface treatment and oxide scale chemistry

- Changes in the surface oxide chemistry and morphology is observed with changes in PO2.
- Formation of protective Mn-Cr oxide scale under controlled conditions lowers Cr evaporation rate due to lower Cr2O3 activity and blockage of underlying scale.
- Lower PO2 exposure minimizes Fe contamination in the outer scale leading to the prevention of iron oxide rich nodules.

Schematic of scale formation and Mn^{2+} diffusion during (a) air and (b) H2-3%H2O pre-treatment. Fe^{3+} diffusion pathways and iron oxide rich scale formation during pretreatments in (c) air and (d) H2-3%H2O.

Reisert et al., “Controlled thermal pre-treatment of ZMG232G10® for corrosion mitigation under simulated SOFC interconnect exposure conditions” Accepted for publication, IJHE 2022
Experimental Arrangement

Design Philosophy

Design Parameters:
Input:
- Residence time, Space velocity
- Cr2O3 activity (Scale)
- Humidity level, temperature
- Coating SA, uniformity

Response:
- Product stability, $\Delta G_R$
- Getter utilization, PB ratio
- Thermal cyclability and adherence

Humid Air Flow

Chromium Source

Chromium Getter

Cr2O3
Getter on Honeycomb support
Furnace (750-950°C)

% Cr
End of Life, t+40,000 Hrs.

Background Cr Level

Air Flow

Cr + Air Flow

t+ x,000 Hrs.
Getter Processing

Cordierite honey comb
Alumina foam
Getter – SMO (sol-gel)
Heat treated in air

Collaboration with Professor Scott Misture, Alfred U.
Getter Processing: Fracture surface
Getter Processing: Fracture surface
Getter Processing: Surface morphology

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>26.50</td>
<td>61.20</td>
</tr>
<tr>
<td>Sr L</td>
<td>42.40</td>
<td>17.90</td>
</tr>
<tr>
<td>Mn K</td>
<td>31.10</td>
<td>20.90</td>
</tr>
</tbody>
</table>
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.
Gaseous Silica Contaminant formation and cell component interaction

Gas phase silica transport in both oxidizing and reducing atmospheres of electrochemical cells can take place during operation. Humidity in air or its increased concentration with the addition of steam can lead to increased evaporation and degradation of air and fuel electrodes.

- **Ambient air**
  - Oxygen ion conducting electrolyte
  - SiOHx transport and interactions with perovskite

- **Ambient air + water (Increased humidity)**
  - Proton conducting electrolyte

- **Hydrocarbon fuels + water (Reforming)**
  - Catalytic poisoning of anode
  - SiOHx transport, deposition on anode, carbon formation

**Sources of Si contaminant** – Raw materials, Corrosion products, cell/ system component materials, PM, Water
Surface morphology of LSCF: Exposure to Air-H2O-SiO2

LSCF exposed to humidified air (over SiO2 source) at 800°C for 50 hrs.

Glassy surface deposit observed

(a) Pretest
(b) Pretest
(e) Posttest
(f) Posttest
Surface Deposit Morphology: LSCF Substrate
Conclusions

- Intrinsic and extrinsic trace gaseous contaminants, present in ambient air stream entering the elevated temperature electrochemical systems, have been identified.
- Formation, transport and interactions of contaminants with perovskite air electrode has been examined.
- Role of surface scale chemistry, pre-treatment conditions, formation of defects in the scale and molecular transport have been studied.
- Pretreatment of alloys under controlled exposure conditions modify the scale chemistry and morphology influencing the formation and transport of trace extrinsic contaminants.
- Getters have been fabricated for the capture of trace S (intrinsic) and Cr, Si, B (extrinsic) gaseous contaminants.
- Technical approach offers pathway for the capture of trace gaseous contaminants present in high temperature fuel cells, electrolyzers and chemical reactor systems.
  - Cell to cell interconnect shows accelerated corrosion and spallation of scale. Cr evaporation under accelerated corrosion condition will be experimentally evaluated.
  - Approaches for the mitigation of scale spallation and Cr evaporation have been examined.
Acknowledgements

- Dr. Rin Burke for technical and programmatic discussion
- Drs. Nilesh Dale, AbdulJabbar Hussain, Takeshi Shiomi (Nissan Motors) for technical discussion
- Dr. Toshio Suzuki (PCI) for technical discussion
- Professor Scott Misture for collaboration and getter coating
- UConn for providing test facility
Thank you