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

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Outline

- Program Objective-Vision and Strategy
- Technical and Broader Impact
- Accomplishments
- Technical approach
- Results and Discussion
- Summary and Conclusions
- Acknowledgements

- Novel approach for the capture of trace impurities present in air stream
- Concept applicable to IT-HT SOFC, SOEC, and OTM systems
Program Objectives

- Develop a comprehensive understanding of the origin, formation processes and the nature of gas phase airborne contaminants present in the air stream entering elevated temperature electrochemical systems.

- Identify trace airborne gas phase contaminants (intrinsic and extrinsic) and develop mechanistic understanding of 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 at stack/system level. Transfer technology to industrial partners.
Broader Impact: High Temperature Electrochemistry

- Airborne contaminants
- Surface-interface processes
- Electrode poisoning

High Temperature Electrochemical Systems

- Ions
- Protons
- Electrons

Trace contaminants and accumulation in electrodes

Thermally assisted chemo/electro/mechano degradation

- Power Generation
- Energy Storage
- Gas Separation
- Fuel Production
Broader Impact

- Graduate / Undergraduate students being trained - 7
- Post-doctoral fellows: 3
- Outreach: Middle and High School, Davinci Program, STEM
- Undergraduate Internship: 4

Training and Placement

Mr. Michael Reisert  
Bloom Energy

Dr. Ashish Aphale  
Asst. Professor, Kennesaw University

Mr. Justin Webster  
Collins Aerospace (Pratt & Whitney)

Dr. Su Jeong Heo  
Post-doctoral Fellow, NREL

Dr. Boxun Hu  
Scientist, LBNL

Dr. Junsung Hong  
Post-doctoral Fellow, Northwestern University

Dr. Sapna Gupta  
Intel Corporation

Dr. Amman Uddin  
Assistant Professor, BUET, Bangladesh

This project develops basic scientific and engineering understanding of electrode degradation processes arising due to the presence of intrinsic and extrinsic gaseous impurities present in air stream. Research efforts also provide pathways for the mitigation of the cathode degradation. Low cost getters, identified and fabricated, will be used in the stack and system to offer long term resistance to electrode poisoning.
Broader Impact: Electrode poisoning in IT/HT Electrochemical Systems

- Intrinsic and extrinsic trace gas phase contaminants
  - Originating from BOP, Stack and cell components
  - Ingested through water

- Vapors of Cr, B, Bi etc. from alloys/seals
- Vapor of Si from water
Broader Impact: Electrode Poisoning and SiO$_2$ Deposition

Water containing SiOHx have tendency to deposit on catalytically active Ni surface. Surface coverage by SiO2 can promote carbon deposition, pulverization and electrode poisoning.

- Reduction in P$_{H_2O}$ leads to silica deposit formation
- Silica deposition in the anode is dictated by H$_2$O concentration profile
- Electrolysis mode may be more prone to SiO$_2$ deposition at FE-Elec interface


\[
\begin{align*}
CH_x, H_2O, Si(OH)x & \rightarrow H_2, CO \\
\rightarrow SiO_2 + 2H_2O & \rightarrow Si(OH)4(g) \\
\rightarrow Si(OH)4(g) & \rightarrow SiO_2(s) + 2H_2O \\
\rightarrow CH_4 + H_2O & \rightarrow CO + 3H_2 \\
\rightarrow Si(OH)4(g) & \rightarrow CO, H_2, CH_4, H_2O
\end{align*}
\]
Electrode poisoning: Role of water and air borne contaminants

Water chemistry monitoring and control remains important for long term stable operation of electrolyzers. Electrode can poison leading to increased polarization during long term.

\[
\text{Silica dissolution at site 1: (solid-Liquid)} \quad [\text{SiO}_2] + (H_2O) = \{\text{Si(OH)}_4\} \quad (1)
\]

\[
\text{Silica evaporation at site 2: (Solid-Gas)} \quad [\text{SiO}_2] + (H_2O) = \{\text{Si(OH)}_4\} \quad (2)
\]

\[
\text{Silica deposition at site 3: (Gas-solid)} \quad \{\text{Si(OH)}_4\} = [\text{SiO}_2] + (H_2O) \quad (3)
\]
SrO and BaO interactions with Si vapor

BaO (s) + Si(OH)4 (g) = BaSiO3 (s) + 2H2O(g); ΔG = -489.486 kJ/mole
SrO(s) + Si(OH)4 (G) = SrSiO3 (s) + 2H2O(g); ΔG = -458.953 kJ/mole

Sample calculation for BaSiO3 (FactSage):
ΔG = G_{product} − G_{reactant}
= (G_{BaSiO3} + 2G_{H2O}) − (G_{BaO} + G_{Si(OH)4})
= (-1788366-2*448571) –(-646130-1549892)
= - 489.486 kJ/mole

Thermocalc shows chemical interaction between cations and Si(OH)4

SrO and BaO interactions with Cr vapor

The calculations confirm the thermodynamic feasibility of stable CoCr$_2$O$_4$, BaCrO$_4$ and SrCrO$_4$ formation in the presence of Cr$_2$O$_3$ or Cr vapor exposure.
Getter selection for multi-contaminant systems

Capture of gas phase impurities by ‘Getters’ based on Gibbs free energy and equilibrium constant k. Unit solid phase activity assumed.

- Calculated ratio of partial pressures of various gas phase impurities over their partial pressure in presence of getters at 850 and 550°C.
- SrO getter can lower the partial pressure of all gas phase impurities in 550-950°C.
- Intrinsic impurities can be captured before entering stacks
- Large amount (~200g) of getter powders have been provided to Alfred Univ. for developing optimized coating processes.

Response parameters:
- Contaminants vapor pressure
- Getter validations
- Posttest getter morphology and chemistry
- Cathode performance: surface and cross section
Combined Degradation

Localized metal loss, Scale spallation, High resistance

Continued Cr evaporation due to spallation, higher Cr loss

Metal-Hydrogen Interaction Pathways

\[ H_2(g) \text{Atm} = H_2(g) GB \]
\[ H_2(g) = 2(H)_{\text{Metal}} \]
\[ (H)_A + (H)_{B} = (H)_{A+B} \]
\[ (H)_{M} + (O)_{MO} = (M)_{MO} + (H_2O)_{g} \]

T ~ 600-800 °C

Atm

Grain boundary Transport
Sievert’s Law
Bulk transport
Heterogeneous Nucleation
Dissolved species interaction
Metal oxide Reduction
**Metal-Hydrogen Interaction Pathways**

\[
\begin{align*}
H_2(g)^{\text{Atm}} & = H_2(g)_{\text{GB}} \\
H_2(g) & = 2(H)_{\text{Metal}} \\
(H)_M A & = (H)_M B \\
(H)^A & = (H_2)g^A \\
(H)_M + (O)_M & = (H_2O)g \\
(H)_M + MO & = (M) + (H_2O)g
\end{align*}
\]

- (Grain boundary Transport)
- (Sievert’s Law)
- (Bulk transport)
- (Heterogeneous Nucleation)
- (Dissolved species interaction)
- (Metal oxide Reduction)
Corrosion behavior of FSS in dual atmosphere

1) Corrosion behavior of FSS in dual atmosphere

2) Oxidation occurs via O2 dissociation and H2O dissociation at surface

3) Monatomic hydrogen may diffuse into MO scale and become interstitial proton

4) Charge imbalance from proton would induce more negative charge (metal ion vacancies)

5) Leads to outward FeOx growth, porous scale, thicker CrOx below which is exposed upon scale spalling
Dual Atmosphere Exposure: Test Validation

1. STF1200 furnace
2. Dual atmosphere reaction chamber
3. Si stopper
4. Thermocouple probe
5. Temperature feedback
6. H₂O bubbler.
Cr Transpiration and Dual Atmosphere Test
Getter Fabrication

Optical Images and Dimensions of samples

Work performed by prof. Scott Misture, Alfred University
Evaporation Studies: B and Si evaporation form glasses

Schematic of SMO getter performance test.

Na$_2$CO$_3$ coated Al$_2$O$_3$ foam
Evaporation Studies: B and Si evaporation form glasses

SEM morphology and EDS analysis of posttest SMO getter at inlet and outlet after test in humidified air for 300h at 700C

Si and B gas phase contaminants are captured by alkali carbonates.

Comparison of the amount of boron and silicon concentration in the presence and in the absence of SMO getter

**Sample Details**

<table>
<thead>
<tr>
<th></th>
<th>Boron concentration</th>
<th>Silicon concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Na₂CO₃ aqueous solution): without SMO getter</td>
<td>10680 µg/L</td>
<td>21570 µg/L</td>
</tr>
<tr>
<td>B (Na₂CO₃ aqueous solution): With SMO getter</td>
<td>6500 µg/L</td>
<td>8027 µg/L</td>
</tr>
<tr>
<td>(Concentration in A / Concentration in B) X 100</td>
<td>60.9 %</td>
<td>37.2 %</td>
</tr>
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B and Si concentrations in Na₂CO₃ (determined by inductively coupled plasma (ICP))
Conclusions

- Sources of airborne impurities have been identified. Trace (ppm to ppb) levels of impurities can exist in the gas phase.
- Gas phase impurities remain predominantly acidic in nature and have affinity to react with basic constituents of the air electrode resulting in the formation of thermodynamically stable and electrochemically inactive reaction products.
- Cell to cell interconnect shows accelerated corrosion and spallation of scale. Cr evaporation under accelerated corrosion condition will be experimentally evaluated.
- Approaches for mitigation of scale spallation and Cr evaporation will be examined based on thermochemical models.
Acknowledgements

- Dr. Rin Burke for technical and programmatic discussion
- Dr. Nilesh Dale for technical discussion
- Professor Scott Misture for getter fabrication
- UConn for providing test facility
Thank you
Electrode Poisoning

Schematic diagram of the sulfur poisoning and recovery process of the LSCF and LSM electrodes under the presence and absence of SO2.g/ : (A) SO2 absorption at SrO present on the LSCF particle surface, (B) SrSO4 formation and Co-Fe exsolution over LSCF, (C) SO2 desorption and partial dissolution of SrSO4 and (Co,Fe)Ox onto LSCF under SO2-free air flow, (D) SO2 absorption on the Sr-terminated LSM particle surface, (E) SrSO4 island formation on the LSM surface leaving a Sr-deficient LSM, and (F) SO2 desorption and partial dissolution of SrSO4 onto LSM under SO2-free air flow.