Self-Cleaning Cathodes for Endurance to Cr Poisoning

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DOE NETL Kickoff Meeting November 29, 2017
Outline

- Background
- Technical Approach
- Project Objectives
- Project Structure
- Project Schedule
- Project Budget
- Project Management Plan and Risk Management
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**Cr-Poisoning in SOFC cathodes**

- Fe-Cr alloy
- Lower cost
- Corrosion resistant
- Conductive Cr$_2$O$_3$ scale

**Background**

\[ \text{CrO}_3 (g, \text{cathode}) + \frac{3}{2} \text{H}_2 (g, \text{anode}) = \frac{1}{2} \text{Cr}_2 \text{O}_3 (s, \text{cathode}) + \frac{3}{2} \text{H}_2 \text{O} (g, \text{anode}) \]

\[ \text{CrO}_2(\text{OH})_2 (g, \text{cathode}) + \frac{3}{2} \text{H}_2 (g, \text{anode}) = \frac{1}{2} \text{Cr}_2 \text{O}_3 (s, \text{cathode}) + \text{H}_2 \text{O} (g, \text{cathode}) + \frac{3}{2} \text{H}_2 \text{O} (g, \text{anode}) \]
Cr-Poisoning in LSM-based Cathodes

- Current-Voltage Measurements with 4 Test Conditions on 4 Identical Cells (800 °C):

<table>
<thead>
<tr>
<th></th>
<th>No Current (OCV)</th>
<th>With Current (0.5 A/cm²)</th>
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<tbody>
<tr>
<td><strong>Dry Air</strong></td>
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<tr>
<td>Cell 1</td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
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<td>Cell 2</td>
<td><img src="image3" alt="Graph" /></td>
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<td><strong>Humidified (10%) Air</strong></td>
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<td>Cell 3</td>
<td><img src="image5" alt="Graph" /></td>
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<td>Cell 4</td>
<td><img src="image7" alt="Graph" /></td>
<td><img src="image8" alt="Graph" /></td>
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</table>

- Cell 1: Dry Air
  - 120 h: Voltage drop from 1.2 V to 0.6 V
  - 0 h: Voltage drop from 1.2 V to 0.6 V

- Cell 2: Dry Air
  - 120 h: Power Density: 0.44 W/cm²
  - 0 h: Power Density: 0.24 W/cm²

- Cell 3: Humidified (10%) Air
  - 120 h: Voltage drop from 1.2 V to 0.6 V
  - 0 h: Voltage drop from 1.2 V to 0.6 V

- Cell 4: Humidified (10%) Air
  - 120 h: Power Density: 0.47 W/cm²
  - 0 h: Power Density: 0.13 W/cm²
SEM images and corresponding EDX spectra of Cr-containing deposits at the cathode/electrolyte interfaces in LSM-based cathode.

Cell 2

Cell 4

Cr Concentration Profile

(LSM+YSZ) (LSM)
Cr-Poisoning Behavior of LSM versus LSF Cathodes

Operating condition (identical):
- Cathode atmosphere: dry air
- Gas velocity: ~4.8 m/s
- Current density: 0.5 A/cm²
- Temperature: 800 °C
- Duration: 150 h
Cr-Poisoning

 Complexity and Impact of Chromium Poisoning Phenomena
  - Cr-poisoning depends on current density, humidity, temperature and type of cathode material
  - Cr-poisoning is one of the major reasons for long-term performance degradation of state-of-the-art SOFCs

 State-of-the-art mitigation strategies
  - Use of Cr diffusion resistant coatings on interconnects
  - Use of cathode materials more tolerant to Cr poisoning
  - Use of materials to getter Cr-vapors
  - Use of alumina forming alloys for balance of plant (BOP) components

 Limitations of the current mitigation strategies
  - Protective coating and the alternate chromium resistant cathode compositions merely postpone the onset of catastrophic degradation due to Cr poisoning.
  - Cr Gettering requires change out of the getter after its capacity is exhausted
  - Not sufficient to ensure stable reliable SOFC performance for 5 years or more
Our Technical Approach

Our approach is to chemically or electrochemically reverse the effects of Cr-poisoning by removing the chromium oxide-containing deposits in the cathode as higher valent oxide and oxy-hydroxide vapor species and restore the cathode to its original state.

The specific advantages of our technique are:
• No modification to any SOFC component from its current state is required and therefore there is no extra capital cost.
• No need to cool down the system, so there is no thermal shock or mechanical damage.
• Relatively quick process.
• No exposure to gas phases that the system does not already see.
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Project Objectives

• Optimize the cell temperature, water vapor content, and gas flowrates for effective chemical cleaning of LSM-based and LSCF-based cathodes.

• Optimize the cell temperature, water vapor content, gas flowrate and bias voltage for effective electrochemical cleaning of LSM-based and LSCF-based cathodes.

• Employ appropriate optimized cleaning technique(s) to demonstrate <0.03% performance degradation in dry air and <0.05% performance degradation in 3% humidified air at 700-800°C after 1000 hours of galvanostatic testing at 0.5-0.75 A/cm²
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Project Structure

Uday Pal (PI)
Project Management
Electrochemical Cell-test Setup
Electrochemical Cleaning of LSM and LSCF Cathodes
(Student 1)

Soumendra Basu (Co-PI)
Coating of Crofer Interconnect
Microstructural Characterization
(Student 1 and 2)

Srikanth Gopalan (Co-PI)
Cell Fabrication
Chemical Cleaning of LSM and LSCF Cathodes
(Student 2)

Weekly Internal Meetings
Quarterly Meetings (BU, LGFC & FCE)
Quarterly and Annual Meetings (DOE-NETL)
Quarterly and Annual Reports
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<table>
<thead>
<tr>
<th>Task/Milestone</th>
<th>Q1</th>
<th>Q2</th>
<th>Q3</th>
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<tbody>
<tr>
<td>Task 1: Project management and planning</td>
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<td>Task 3: Fabrication of EPD spinel coated Crofer mesh</td>
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<td>Task 4: Electrochemical cell test setup and testing</td>
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<td>Task 5: Self-cleaning of electronic and MIEC cathodes under open circuit condition</td>
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<td>Milestone 1: Demonstrate feasibility of chemical cleaning</td>
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<td>Task 6: Self-cleaning of electronic and MIEC cathodes under mild electrolytic conditions</td>
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<td>Milestone 2: Demonstrate feasibility of electrochemical cleaning</td>
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<td>Task 7: Quantitative microstructural characterization</td>
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<td>Milestone 3: Optimize cleaning procedure</td>
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<td>Task 8: Demonstrate at least two cycles of cleaning</td>
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<td>Task 9: Demonstrate cleaning on cells manufactured by commercial vendors</td>
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<td>Milestone 4: Demonstrate 1000 h operation with &lt; 0.03 % degradation in dry air with cleaning</td>
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<td>Milestone 5: Demonstrate 1000 h operation with &lt; 0.05 % degradation in 3% humid air with cleaning</td>
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Legend:
- **Student 1 (Profs. Pal & Basu)**
- **Student 2 (Profs. Basu and Gopalan)**
- **Faculty only**

- **Blue diamond**: Critical milestone
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Project Management Plan (PMP) and Risk Management

The project will be reviewed as we get close to each go/no-go criteria points and adjustments will be made to the project directions and the PMP if necessary.

- Demonstrate feasibility of chemical cleaning of electronic and MIEC based cathodes; - 3/31/18
- Demonstrate feasibility of electrochemical cleaning of electronic and MIEC based cathodes; - 6/30/18
- Optimize cleaning procedure that minimizes time for effective Cr-removal without affecting other cell components for both types of cathodes; - 6/30/19
- Demonstrate less than 0.03% performance degradation after 1000 hours of galvanostatic testing in dry air at 0.5-0.75 A/cm² with intermittent cleaning; - 9/30/19
- Demonstrate less than 0.05% performance degradation after 1000 hours of galvanostatic testing in 3% humidified air at 0.5-0.75 A/cm² with intermittent cleaning; - 9/30/19
- If the above success criteria are met, we will apply for Phase II with our industrial partners, LG Fuel Cell (LGFC) and FuelCell Energy (FCE) to demonstrate self-cleaning on commercial cells and stacks; LGFC cells use LSM-based cathodes and FCE cells use LSCF cathodes.

- **Risk 1 (Description):** The kinetics of chemical cleaning may be slow.

- **Risk 1 (Mitigation strategy):** We will adjust parameters such as cell temperature and water vapor content. If the rate is still too slow, application of a mild electrolytic condition (electrochemical cleaning) will increase the rate and decrease the cleaning time.

- **Risk 2 (Description):** Electrochemical cleaning may affect other components of the stack, including the cathode, electrolyte, anode, interconnect and interconnect coatings.

- **Risk 2 (Mitigation strategy):** We will study the microstructural changes in all the components and adjust parameters such as cell temperature, water vapor content, and bias voltage to ensure that the components are unaffected by the cathode cleaning procedure, while still removing the Cr within an acceptable time.
Thank you!

Questions?