Study of the Durability of Doped Lanthanum Manganite Cathode Materials under “Real World” Air Exposure Atmospheres

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Outline

- Accomplishments
- Background
- Experimental
  - Role of Humidity and CO2
  - Contribution of IC- AE interface
  - Phase stability study using in-situ XRD
- Results and Discussion
- Future work
- Acknowledgements
Accomplishments

- Electrochemical testing of LSM/YSZ/LSM symmetric cell in humidified air and CO2/air has been conducted for up to 100 h and post-test analytical study (XRD, SEM-EDS, XPS, FTIR) has been performed.
  - SrO/Sr(OH)2 has not been detected in the cells tested in dry air regardless of testing conditions.
  - SrO/Sr(OH)2 has been detected in the cells in presence of humidity in air.
  - Nucleation and growth of SrO increases with cathodic bias, increase in humidity content, temperature, and test duration.
  - LSM degradation mechanism in humidified air has been developed and proposed.
  - Formation of (Sr/La) carbonates have been identifies when the cell is tested in Air-10%CO2

- Ohmic contribution of AISI 441 interconnect on the performance of anode supported single cell (Ni-YSZ/YSZ/LSM-YSZ) has been measured and quantified.

- In-situ XRD investigation has been conducted to identify structural change of YSZ and compound formation/phase evolution due to interaction with manganese, LSM, and LSCF.

- XRD approach has been developed to detect tetragonal form of YSZ.
  - Manganese dissolution into YSZ destabilizes the cubic symmetry to tetragonal symmetry.
  - No reaction compound has been detected due to interaction of 20% LSM/LSCF with YSZ/GDC at 1400°C in air for <24h.
Impact and Technical Significance

- Observations and mechanistic understanding of chemical and morphological changes, derived from long term experiments, have helped SECA industry teams in optimizing air electrode.
- Studies provide insight into long term interfacial porosity formation and delamination (AE/Elec.)
- Studies provide insight into destabilization of YSZ
- Accelerated tests in steam and CO2 containing atmospheres show air electrode decomposition.
Project Objectives

Mechanistic understanding of lanthanum manganite and lanthanum cobaltite cathode degradation in ‘real world’ air exposure during SOFC operation

Long Term Bulk, Interfacial and Surface Stability

Dopants, Electric polarization, Gas phase contaminants (H$_2$O, CO$_2$, Cr-vapor species, stoichiometry)

Compounds 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

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

Bulk, Interfaces, Surface Stability

Electrode – Electrolyte / Electrode - IC

Air side contaminants: Water, CO$_2$, Oxide vapors Other contaminants

In-situ, Ex-situ Bench top tests

Couple/ Symmetric / Full cell/ configurations
Background

- Cathode electrode maintain intimate contact with electrolyte and interconnect and exposed to air which contains H₂O, CO₂, H₂S/SO₂ etc.
- Bulk and interfacial stability of cathode due to solid-solid and solid-gas interactions significantly contributes to performance losses and degradation in SOFC stacks. Two key factors:
  - Polarization losses at cathode/electrolyte interface
  - Ohmic and contact losses at cathode/interconnect interface, especially with metallic interconnect
- Poor contact (reduced contact area) between ceramic cells and metallic interconnects (even with use of contact paste) results in higher Ohmic loss. Contributing factors for poor contact include:
  - Operating characteristics (temperature distribution, thermal expansion mismatch)
  - Interfacial compound formation and morphology change
- Solid-solid and solid-gas interactions lead to undesirable compound formation at the cathode/electrolyte and cathode/interconnect interface, as well as well as at the surface.
Background

Cathode contributions: SOFC performance degradation

Fabrication  →  SOFC  →  Operation

- Temperature
- Impurities
  - Intrinsic
  - Extrinsic

Electrical potential

Cathode

- Decomposition
- Oxygen stoichiometry
- Microstructure (morphology, oxide segregation, porosity)
- Solid-solid reaction
- Solid-gas reaction

Changes in thermo-physical properties, active sites, gas flows

- Interaction with electrolyte/interconnect (interfacial compounds/segregation)
- Change in interface microstructure

SOFC performance degradation
Examples of Elemental Migration

Stack Cathode Side

Cr Profile

Sr Profile

Region under channel

Region under rib
Background: Gas phase contamination and interaction

Background:

- Gas phase contamination and interaction

![Graph showing vapor pressure vs. temperature for various compounds](image)

- Chromia
- AISI 310S
- Nimonic 602 HT
- Alnico YHF
- AFA OC-4

![Graph showing atomic percentage vs. cycles](image)

- 850°C for 1 min in Wet Air (3%H2O) (1200 grit polished)
Background: CE/MI Interface Evolution

- METALLIC INTERCONNECT
- OXYGEN ELECTRODE
- CONTACT PORE
- RESISTIVE PHASE
- CONTACT AREA CHANGE
- INTERFACE

TIME
Role of H$_2$O/Air and CO$_2$/Air on LSM Cathode Degradation
Experiments Conducted

Interfacial, Surface and Bulk Interactions

Analytical study for as fabricated cells (HTXRD, HRSEM, EDS)

Electrochemical testing

Input parameters
- Temperature (750 - 850°C)
- Atmosphere (air containing 0 - 50% H₂O, up to 10% CO₂)
- Time (up to 100 h)
- Electrical bias (0-0.5V)

Post-test analysis: Bulk, interface, and surface XRD, SEM, XPS, and FTIR

Note: Dry air indicates the in-house compressed air flowing through molecular sieve column.

SOFC in an alumina test enclosure

Integrated SOFC test system
Electrical Performance in Humidified Air

800°C, 0.5 V

- Ohmic and non-ohmic resistance increases with increase in H₂O content
- The resistances decrease if the PO₂ is maintained at 0.21 atm in H₂O containing air

850°C, 0.5 V  Non-Ohmic resistance

Oxygen added to maintain PO₂ = 0.21 atm
**LSM Morphology: Without Applied Bias**

- **Oxide segregation at the cathode surface in humidified air**
- **Extent of oxide segregation increases with $\text{H}_2\text{O}$ content**

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**As-fabricated (1200°C, 2h) cell**

- **1 µm**

**850°C, 10% $\text{H}_2\text{O}$/Air**

- **500 nm**

**850°C, 50% $\text{H}_2\text{O}$/air**

- **300 nm**
Morphology of LSM Cathode: 0.5 V Bias, 850°C, 100 h

- No oxide segregation in dry air
- Oxide segregation increases with H₂O content
- Oxide segregation also decreases if PO₂ is maintained at 0.21 atm
Post-test Characterization - XRD

- SrO and Mn$_2$O$_3$ segregates on the LSM surface
- Sr(OH)$_2$ forms during cooling since it is favorable in lower temperature
- La$_2$Zr$_2$O$_7$ (LZ) forms at the LSM-YSZ interface
- Unidentified peaks are of Pt (from Pt-paste)
- H$_2$O content favors oxide segregation as well as interfacial compound formation
- Formation of La$_2$Zr$_2$O$_7$ ($\Delta G = -146.2 \pm 5.0$ kJ/mol at 1200K) is favorable than SrZrO$_3$ ($\Delta G = -92.01$ kJ/mol at 1200K)

**Free Energy Calculation for Hydroxide Formation on LSM**

<table>
<thead>
<tr>
<th>SrO (s) + H$_2$O(g) = Sr(OH)$_2$ (s)</th>
<th>La$_2$O$_3$ (s) + 3H$_2$O(g) = 2La(OH)$_3$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Delta G</td>
</tr>
<tr>
<td>C</td>
<td>kJ</td>
</tr>
<tr>
<td>500</td>
<td>-23.7</td>
</tr>
<tr>
<td>600</td>
<td>-13.4</td>
</tr>
<tr>
<td>700</td>
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<tr>
<td>800</td>
<td>4.5</td>
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<tr>
<td>900</td>
<td>12.6</td>
</tr>
<tr>
<td>1000</td>
<td>20.1</td>
</tr>
</tbody>
</table>
Elemental Analysis: LSM Cathode Surfaces

0.5 V, 850°C, 100 h

<table>
<thead>
<tr>
<th></th>
<th>XPS</th>
<th>SEM-EDAX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sr/La</td>
<td>Sr/(Mn+La)</td>
</tr>
<tr>
<td></td>
<td>Molar ratio</td>
<td>Molar ratio</td>
</tr>
<tr>
<td>As-fabricated</td>
<td>0.23±0.01</td>
<td>0.13±0.01</td>
</tr>
<tr>
<td>Air-10% H₂O</td>
<td>0.34±0.02</td>
<td>0.21±0.01</td>
</tr>
<tr>
<td>Air-20% H₂O</td>
<td>0.58±0.04</td>
<td>0.24±0.01</td>
</tr>
<tr>
<td>Air-50% H₂O</td>
<td>1.89±0.09</td>
<td>0.76±0.04</td>
</tr>
</tbody>
</table>

- Sr-enriched LSM surface
- Sr-enrichment increases with increase in H₂O content

**LSM Degradation: Hypothesis**

\[ O_2 + 4e^- \rightarrow 2O^2- \]
\[ 2H_2O + O_2 + 4e^- \rightarrow 4OH^- \]

**Dry air with bias:**
\[ V_{La}'''' + SrO + 3Mn_{Mn} + e' \leftrightarrow Sr_{La}' + 0.5O_2 + 3Mn_{Mn}^x \]

**Wet air with no bias:**
\[ Sr_{La}' + 2OH^- \rightarrow SrO + H_2O + V_{La}''' \]
\[ H_2O + Sr_{La}' + 2O_0 \rightarrow SrO + V_{La}'''' + 2OH_0^- \]

**Wet air with bias:**
\[ H_2O + Sr_{La}' + 2O_0 \rightarrow SrO + V_{La}'''' + 2OH_0^- \]
\[ Sr_{La}' + 0.5O_2 + 2e' \rightarrow SrO + V_{La}' \]

Electrolyte-air electrode interface showing the air electrode contact area and formation of La$_2$Zr$_2$O$_7$ at the periphery.

Formation of La$_2$Zr$_2$O$_7$ ($\Delta G = -146.2 \pm 5.0$ kJ/mol at 1200K) is favorable than SrZrO$_3$ ($\Delta G = -92.01$ kJ/mol at 1200K)

$$2\text{LaMnO}_3(s) + 2\text{ZrO}_2(s) \rightarrow \text{La}_2\text{Zr}_2\text{O}_7(s) + \text{Mn}_2\text{O}_3(s)$$
**Microstructure Evolution - SEM**

- Undulated surface
- Extent of undulation increases with increasing temperature
- EDS analysis shows the presence of ~ 10 at% Mn in YSZ

Dissolution of Mn in the YSZ lattice leads to structural destabilization leading to interface separation and increase in ASR.

SOFC Stability in CO$_2$/air

- Ambient air contains 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide, and small amounts of other gases.
- Higher carbon dioxide contents are used for accelerated degradation.

- Role of CO2 may vary with temperature.
- Polarization resistances increases with cell operating time.
FT-ATR Spectra of LSM Exposed to 10% CO₂/Air at 750 °C

- Sr- rich carbonates have formed at LSM surface (Free energy of La₂(CO₃)₃ formation is not found.
- More carbonates formed on working LSM electrodes than the LSM without a bias.

Investigation of AE/IC Contacts
Experimental Approaches

- Experiments with single cells and single cells combined with metallic interconnects to determine contribution of CE/MI contact resistances to performance losses
  - Techniques: I/V measurements, AC impedance
- Experiments with cells and symmetrical samples to investigate and correlate contact resistance changes and microstructural and chemical/phase composition evolution
  - Techniques: AC impedance, van der Pauw, 4 point DC, SEM, EDAX and others
Single Cell Testing

- Button cells (anode supported): YSZ electrolyte, Ni/YSZ anode, LSM/YSZ cathode
- Ag current collectors and pastes
- Test conditions:
  - Fuel: Hydrogen-3% H₂O, Oxidant: Air
  - Temperature: 750°C, 800°C, 850°C
- I-V curves after cell conditioning
Single Cell Performance

Fuel: H₂ – 3% H₂O
Oxidant: Air

Endurance Cell Testing

ASR (750°C): 0.47 ohm-cm²
ASR (800°C): 0.41 ohm-cm²
ASR (850°C): 0.31 ohm-cm²

800°C, 0.425A/cm²
Single Cell Stack Setup

Gas Manifolds
Performance of Single Cell Stack

Temperature: 800°C
Fuel: Hydrogen-3%H₂O
Oxidant: Air

Ohmic Contribution in Single Cell Stack

Ohmic contribution of interconnect in stack performance is significant
Bulk and Interfacial Stability: In-situ XRD Studies
Mechanics of XRD: De-stabilization of the YSZ is invisible except under carefully optimized conditions

- Optimized XRD approach: Grazing incidence at 2, 4, and 6 degrees vs. coupled measurements – coupled measurements provide better peak shapes and more reliable quantification.
- Optimized fitting approach: Full-pattern Rietveld with very high 2θ data, fixed cubic YSZ initial lattice parameter, introduce T-ZrO$_2$, and then freely refine all variables.

Peak width analysis shows small TYSZ crystallite size, suggests core-shell, diffusion-controlled reaction.

XRD Approach to Detect Tetragonal form of YSZ
Mn Interaction with YSZ

Can be observed using in-situ XRD with 1400°C hold, 12 hours, with MnO₂ admixed at 50 wt.%. 

![Graph showing Mn Interaction with YSZ](image-url)
Mn Interaction with YSZ

Data are offset in x and y for clarity

- Lower MnO₂ concentrations make detection more difficult, as this is a diffusion-controlled reaction
- The reaction was NOT observed under <20wt.% added LSM and LSCF with YSZ
- No reaction of LSM with GDC noted in 12h at 1400°C (data not shown)
CTE for LSM in Different Atmospheres

Track unit cell size/volume with high accuracy and cell distortion (alpha angle for trigonal LSM)

Chemical expansion noted under reduced pO$_2$, as expected

RT values before and after cooling differ because of oxygen nonstoichiometry equilibration (chemical expansion)
Summary

- LSM/YSZ/LSM symmetric cells have been tested in humidified air and CO2/air for up to 100hrs.
  - SrO/Sr(OH)2 has not been detected in the cells tested in dry air regardless of testing conditions.
  - SrO/Sr(OH)2 has been detected in the cells in presence of humidity in air.
  - Formation of (Sr/La) carbonates have been detected when the cell is tested in Air-10%CO2

- LSM degradation mechanism in humidified air has been developed.

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Future Work

- Post-test analytical study of cells operated in Air-10%CO2 and development of degradation mechanisms
- AFM analysis of the post-test cathodes
- Electrochemical testing in Air/3% CO2, Air-CO2-H2O atmospheres
- Evaluation of the role of air contaminants on the ohmic contribution from metallic interconnect in a single cell stack test approach
- Post test analytical study to find the source of ohmic contribution and related mechanisms
- In situ XRD study to precisely detect the phase evolution and structural changes of various cathodes and electrolytes resulting from solid-solid and solid-gas interaction
- Development of mechanistic understanding of cathode performance degradation
  Development of mitigation approaches for cathode degradation
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