

**Effects of Steam on Long Term Performance of Metal Ferrite Infiltrated Solid Oxide Fuel Cells**

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### Introduction

- Solid oxide fuel cells (SOFC) are operated with fuel in the anode and with ambient air in the cathode which contains about 3% moisture. It is critical to study the impact of moisture on the performance and stability of SOFC.
- In-situ study of LSMYSZ cathodes under polarization by photoelectron microscopy found that the manganese concentration on the LSM surface decreased with increasing cathode polarization, while the manganese concentration on the electrolyte surface was increased with increased cathode bias. Manganese spreading from three phase boundary (TPB) over the electrolyte surface was observed to retreat slowly when the cathode bias was released, and the spreading of manganese over the electrolyte was reversible and could be repeated several times, though the spreading became more sluggish and required larger bias activation with an increased number of repetitions.
- It has been observed that there is no significant effect on the impedance as a function of the degree of air humidification at open circuit voltage (OCV), indicating that the humidification effect on the cathode of LSM/YSZ is not a catalysis poisoning effect with a blocking of active sites.

### Purpose of the Study

- Evaluate the effects of high steam on performance and stability of infiltrated LSM/YSZ based SOFC cathode comparing with baseline cell.
- Improve performance and long term stability of SOFC by infiltration.

### Experimental Methods

- Commercially available MSRI anode supported cells
- Cathode: LSM/(La\(_x\)Sr\(_y\)Fe\(_{1-x}\)O\(_{3-δ}\))\(_x\)MnO\(_y\) \(x\) \(y\)
- Electrolyte: YSZ
- Anode: Ni-YSZ
- Infiltration of nano-materials in LSM/YSZ cells
  - Infiltrated nanomaterials: Co, BaFe\(_2\)O\(_4\), SrFe\(_2\)O\(_4\), Co/BaFe\(_2\)O\(_4\), Co/SrFe\(_2\)O\(_4\)
  - Particle size is expected to be 20-50nm
- Solvent: Citric acid solution
- Chemical Precurser: Metal Nitrate (0.125M-0.25M)
- Temperature: 450-450\(^\circ\)C
- Time: Repeat infiltration until 2.8mg-3mg infiltration nanomaterial obtained

#### Operating Conditions:

- 800\(^\circ\)C, 0.75 A/cm\(^2\) current load, 20% steam balanced in air

#### Performance tests:

- Electrochemical impedance spectroscopy (EIS) tests to evaluate the performance degradation of the infiltrated cells compared with baseline cells operated at high current and high steam.

#### Stability Test of Infiltrated LSM/YSZ Cells

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Time (h)</th>
<th>Voltage Change (mV)</th>
<th>Impedance Increase (ohm cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co infiltrated cell</td>
<td>24h</td>
<td>0.91</td>
<td>0.025</td>
</tr>
<tr>
<td>SrFe(_2)O(_4) infiltrated cell</td>
<td>24h</td>
<td>0.91</td>
<td>0.030</td>
</tr>
<tr>
<td>Co and SrFe(_2)O(_4) infiltrated cell</td>
<td>24h</td>
<td>0.91</td>
<td>0.035</td>
</tr>
</tbody>
</table>

#### Impedance of Co infiltrated cell

- Impedance with frequency related to cathode was decreased in 0h after steam.

#### Impedance of BaFe\(_2\)O\(_4\) infiltrated cell

- Impedance with frequency related to cathode was increased in 0h after steam.

### Summary & Conclusion

- All infiltrated cells showed higher performance and lower degradation rate than baseline cells, which demonstrated that appropriate nanomaterial infiltration could improve the performance and mitigate the degradation of SOFC under steam.
- All tested cells showed increased performance and improved degradation rate compared with baseline cell if including the initial voltage drop after steam.
- Co, BaFe\(_2\)O\(_4\) and SrFe\(_2\)O\(_4\) infiltrated cells showed the lowest degradation rates among all tested cells with 62%, 61% and 56% improvement for degradation rate respectively compared with the baseline cell if including the initial voltage drop after steam.

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**Ohmic/Polar Resistance of Tested Cells**

- All tested cells except the Co infiltrated cell showed increased polarization resistance right after steam due to sudden occupation of steam on the active TPB.
- It was worth to notice that the polar resistance of the Co infiltrated cell was decreased about 0.0054 ohm cm\(^2\) after initial introduction of steam.
- Polar resistance of the baseline cell was increased the most (about 0.0156 ohm cm\(^2\)) right after steam among all the test cells followed second by the SrFe\(_2\)O\(_4\) infiltrated cell (about 0.0066 ohm cm\(^2\)) which also corresponded to the most and second most initial voltage drop after steam addition.
- Ohmic and polarization resistances of all tested cells were increased during longer operation time with 20% steam.

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**SEM Images**

- Grain particles of the baseline cell operated for 335h with 20% steam in the cathode showed some degree of breakdown compared with before test.
- Grain particles of SrFe\(_2\)O\(_4\) infiltrated cell operated with 20% steam in cathode for 575h also showed some degree of breakdown compared with baseline cell without test.
- However, grain size of the SrFe\(_2\)O\(_4\) infiltrated cell was bigger than that of baseline cell after steam even if the operating duration of the SrFe\(_2\)O\(_4\) infiltrated cell with steam was 24h longer than the baseline cell.
- Infiltration may prevent the breakdown of LSM grain particles for long term testing with high steam which may relate to less performance degradation for infiltrated cell.

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**EIS Studies of Representative Infiltrated Cells**

- Impedance of Co infiltrated cell with frequency related to cathode was decreased in 0h after steam.
- Impedance of BaFe\(_2\)O\(_4\) infiltrated cell with frequency related to cathode did not show significant increase in 0h after steam.

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**Grain of SrFe\(_2\)O\(_4\) infiltrated cell operated with 20% steam for 575h**

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**Calculated Results:**

- Calculated ohmic and total resistance of Co and BaFe\(_2\)O\(_4\) infiltrated cells both increased during longer operation time with 20% steam.
- Polarization resistance of the baseline cell was the most (about 0.0156 ohm cm\(^2\)) right after steam due to the sudden occupation of steam on the active electro-catalytic sites of the triple phase boundary.
- Polarization resistance of the infiltrated cell was the most (about 0.0054 ohm cm\(^2\)) right after steam following second by the SrFe\(_2\)O\(_4\) infiltrated cell (about 0.0066 ohm cm\(^2\)) which also corresponded to the most and second most initial voltage drop after steam introduction for the Co infiltrated cell and SrFe\(_2\)O\(_4\) infiltrated cell.
- The ohmic and polarization resistances of all tested cells were increased during longer operation time with 20% steam.