Abstract

The objectives of this project are to understand the influence of aggressive conditions on performance of solid oxide fuel cells (SOFCs) with cathodes of lanthanum strontium manganite (LSM, (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.8</sub>MnO<sub>1.97</sub>) and to relate the operating conditions and cell performance to the microstructure changes and performance degradation.

LSM-based fuel cells with different levels of excess Mn underwent durability or aging tests under combinations of aggressive versus conventional conditions: 1,000 vs. 900 °C; 760 vs. 380 mA cm<sup>-2</sup>; and reduced partial pressure of oxygen (p<sub>O2</sub> = 0.10, 0.15) versus air (p<sub>O2</sub> = 0.21) on the cathode side. Electrochemical impedance spectroscopy (EIS) was carried out every 24 h during durability testing to study the evolution of cell resistance over time. EIS data were analyzed in two complementary ways:

- Distribution of relaxation times (DRT) analysis, to identify possible electrochemical reactions in certain frequency ranges;
- Equivalent circuit analysis, to track the evolution of frequency-dependent (parallel) and frequency-independent (series) components of the impedance, and to correlate these results with changes in area specific resistance (ASR) during durability testing.

Cells specification; testing procedures

- **Button cells**: • SYSZ electrolyte • NiO-8SYSZ anode
- **Cathodes**: LSM + 8YSZ
  - (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.8</sub>MnO<sub>1.97</sub> (LSM 85-90)
  - (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.8</sub>MnO<sub>1.97</sub> (LSM 80-95)
  - (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.8</sub>MnO<sub>1.97</sub> (LSM 80-98)
- **Test conditions**: Durability and aging tests
  - Conventional or aggressive conditions
  - LSV sweeps + EIS runs (current cycling every 24 h)

**Test fixture**

- A light-weight titanium fixture is used to hold ceramic tubes in position.
- The type K thermocouple was replaced by type R thermocouple to minimize Cr contamination.
- A closed-end tube and gas inlet tube are used to control the partial pressure of O<sub>2</sub>, which enables use of different cathode atmospheres than air.

**Test stand**

1,000-h test in air (21% O<sub>2</sub>): LSM 85-90; 1,000 °C; 0.76 A cm<sup>-2</sup>

- Total test time: 1,008 h (504 h ~ 146 h (OCV) + 358 h)
- Initial ASR: 0.245 Ω cm<sup>2</sup>
- Final ASR: 0.30 Ω cm<sup>2</sup>

Nyquist plots (left) showed a small increase in real and imaginary impedance with time. DRT analysis (right) showed impedance increase in the 3 largest peaks.

- In air: 30 °C < t < 10<sup>5</sup> s; anode: charge transfer (TPB) + 10<sup>5</sup> < t < 10<sup>7</sup> s; oxygen exchange; anode & cathode
- In 10% O<sub>2</sub>: gas diffusion, anode & cathode

With decreasing temperature, Nyquist plots (left) showed normal increases in resistance. DRT analysis (right) at 850 °C, 800 °C, and 800 °C (10% H<sub>2</sub>) showed:
- Increases in all major peaks with increasing t and decreasing T.
- Peak separation in middle frequencies (10<sup>-3</sup> < t < 10<sup>-2</sup> s; 10<sup>-2</sup> < t < 10<sup>-1</sup> s)

500-h aging test in 10% O<sub>2</sub> & air: LSM 80-98, 900 °C

<table>
<thead>
<tr>
<th>temperature [°C]</th>
<th>current density [mA cm&lt;sup&gt;-2&lt;/sup&gt;]</th>
<th>cathode p&lt;sub&gt;O2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>380</td>
<td>0.21</td>
</tr>
<tr>
<td>1000</td>
<td>760</td>
<td>0.1/0.15</td>
</tr>
</tbody>
</table>

OCV, 500 h (left); cathode gas was 90%N<sub>2</sub>/10%O<sub>2</sub> except for 19-187 h (air).

DRT analysis (right) at t=0 h, shows splitting and growth of the low-τ peaks, and growth of the high-τ peaks, as T decreased.

- ASR dropped in Nyquist plots (left, 88 h).
- Peaks shrank and shifted to lower τ in DRT analysis.

Conclusions

- **DRT analysis** was introduced into this project.
  - In a 1,000-h durability test in air at 1,000 °C and 0.760 cm<sup>-2</sup>:
    - All major loss mechanisms (charge transfer, oxygen exchange, and gas transport) steadily increased with time.
    - Brief thermal excursions to 850 and 800 °C showed:
      - Increases in all major loss mechanisms as temperature decreased.
      - Separation of loss mechanisms (peak splitting) in middle frequencies (10<sup>-3</sup> < t < 10<sup>-2</sup> s; 10<sup>-2</sup> < t < 10<sup>-1</sup> s).
      - In low-hydrogen anode atmosphere, charge transfer losses dropped, but gas diffusion losses rose and shifted to longer relaxation times.
  - Equivalent circuit modeling accounts for changes in total cell resistance in terms of changes in series and parallel resistances, in this case during aging in cathode p<sub>O2</sub> = 0.10.
  - Low p<sub>O2</sub> on the cathode side (0.10, 0.15) strongly reduces cell life.

Effects of p<sub>O2</sub> and cathode composition

- LSM 80-98, 1,000 °C; t = 0; 10% O<sub>2</sub> and 15% O<sub>2</sub>: DRT analysis reveals effects of cathode atmosphere, independent of differences in series resistance.
- Peak splits, shifts, and growth with changes in p<sub>O2</sub> will be studied further.

Four cathode compositions, 1,000 °C; t = 0

- LSM 85-90: 11% Mn excess
- LSM 80-95: 5% Mn excess
- LSM 80-98: 2% Mn excess

Differences in series resistance can make interpretation of Nyquist plots difficult.

**DRT analysis**: Facilitates comparisons of mechanisms with distinct relaxation times.
- Peak splits, shifts, and growth with changes in p<sub>O2</sub> will be studied further.

Acknowledgment

This research was based upon work supported by the U. S. Department of Energy, National Energy Technology Laboratory, under the SECA Core Technology Program (award number DE-FE0011189). Disclaimer: This research was based in part upon work supported by an agency of the United States Government, neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.