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 LSM/YSZ 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.[1]
- 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.[2]
- Performance degradation was markedly higher at lower temperature than at higher temperature, and Mn_3O_4 or Mn_2O_3 was found to be present near the active TPB after studying the LSM/YSZ based SOFC with steam in the cathode for longer operating time.[3]
- 3% moisture in air degraded the LSM/YSZ cathode performance at 750-850°C due to the segregation of SrO/$Sr(OH)_2$ at the LSM surface.[4] La_2O_3 formation on the surface of LSM was also observed by the results of XPS and TEM. Poor electrical conductivity of La_2O_3 may be also related to cell performance degradation.[5]

1. M. Backhaus-Ricoult, K. Adib, T. St.Clair, B. Luerssen, L. Gregoratti, A. Barinov, Solid State Ionics 179 (2008) 891–895.
2. J. Nielsen, A. Hagen, Y.L. Liu, Effect of cathode gas humidification on performance and durability of Solid Oxide Fuel Cells, Solid State Ionics 181 (2010) 517–524
3. Hsiang-Jen Wang, Mark R. De Guire, Zhengliang Xing, Gerry Agnew, Richard Goettler, Zhien Liu, and Arthur H. Heuer, Metallurgical and Materials Transactions E.
4. Effects of humidity on solid oxide fuel cell cathodes, PNNL-24115
5. Seon HyeKim, Toshihiro Ohshima, Yusuke Shiratori, Kohei Itoh and Kazunari Sasaki, Mater. Res. Soc. Symp. Proc. Vol.1041, 1041-R03-10

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

Cells:

- Commercially available MSRI anode supported cells
- Cathode: LSM$[(La_{0.8}Sr_{0.2})_{0.98}MnO_3]$ / LSM-YSZ active layer
- Electrolyte: YSZ
- Anode: Ni-YSZ

Infiltration of nano-materials in LSM/YSZ cells

- Infiltrated nanomaterials: Co, $BaFe_2O_4$, $SrFe_2O_4$, , $Co/BaFe_2O_4$, $Co/SrFe_2O_4$
- Particle size is expected to be 20-50nm
- Solvent: Citric acid solution
- Chemical Precursors: Metal Nitrate (0.125M-0.25M)
- Temperature: 450-850°C
- Time: Repeat infiltration until 2.8mg-3mg infiltration nanomaterial obtained

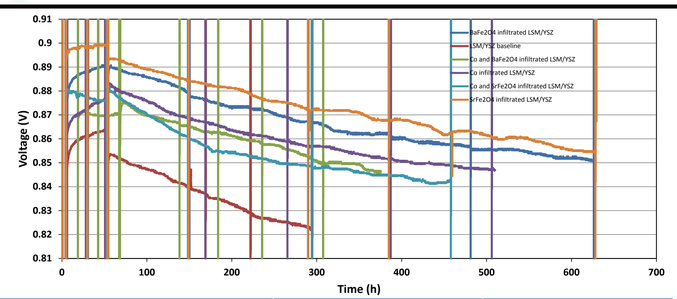
Operating Conditions:

- 800°C, 0.75 A/cm² 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.

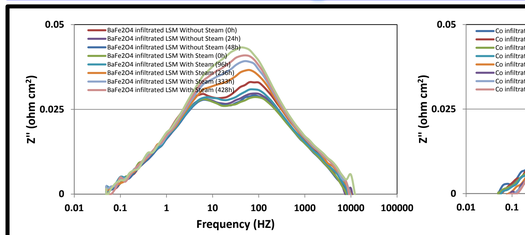
Stability Test of Infiltrated LSM/YSZ Cells @ 20% Steam, 0.75A/cm² and 800°C

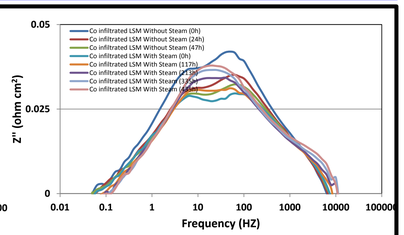


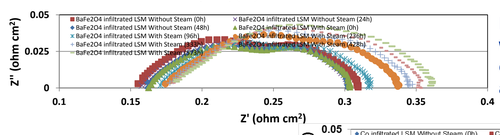
Studied Cells	Degradation Rates (Includes the initial voltage drop after steam)	Degradation Rates (excludes the initial voltage drop after steam)
LSM/YSZ baseline cell	19.86%/1000h	13.58%/1000h
Co infiltrated LSM/YSZ Cell	7.51%/1000h	7.51%/1000h
Co and $BaFe_2O_4$ infiltrated LSM/YSZ Cell	8.73%/1000h	8.7%/1000h
Co and $SrFe_2O_4$ infiltrated LSM/YSZ cell	10.88%/1000h	10.88%/1000h
$BaFe_2O_4$ infiltrated LSM/YSZ cell	7.59%/1000h	7.59%/1000h
$SrFe_2O_4$ infiltrated LSM/YSZ cell	8.65%/1000h	7.42%/1000h

- 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 with steam in cathode.
- All tested cells showed sharp initial voltage drop after steam. $BaFe_2O_4$, Co, $Co/BaFe_2O_4$ and $Co/SrFe_2O_4$ infiltrated LSM/YSZ cells showed voltage recovery in the first 2-3h after steam. Especially the voltage of Co infiltrated cell was increased even higher after steam than before steam, while the baseline cell and $SrFe_2O_4$ infiltrated cell showed sharp initial voltage drop without recovery after steam.
- Co, $BaFe_2O_4$ and $SrFe_2O_4$ 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.

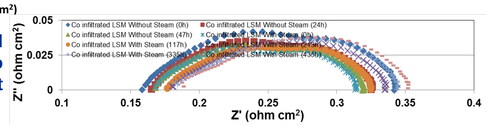
EIS Studies of Representative Infiltrated Cells







Impedance of Co infiltrated cell with frequency related to cathode was decreased in 0h after steam.



Impedance of $BaFe_2O_4$ infiltrated cell with frequency related to cathode did not show significant increase in 0h after steam.

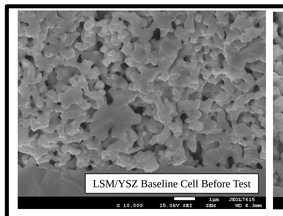
- Impedance with frequency related to cathode for Co and $BaFe_2O_4$ infiltrated cells increased slowly with 20% steam during long term operation.
- Ohmic and total resistance of Co and $BaFe_2O_4$ infiltrated cells both increased during longer term operation with total resistance increasing more than ohmic resistance.
- Electrochemically active Co or $BaFe_2O_4$ may compensate for the active site loss occupied by steam which corresponded to no impedance increase in 0h after steam for both cells.

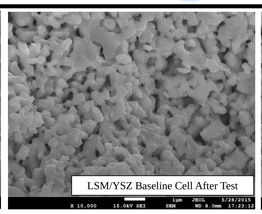
Ohmic/Polar Resistance of Tested Cells

Studied Cells	LSM/YSZ baseline cell		Co infiltrated cell		$BaFe_2O_4$ infiltrated cell		$SrFe_2O_4$ infiltrated cell		$Co/BaFe_2O_4$ infiltrated cell		$Co/SrFe_2O_4$ infiltrated cell	
	Ohmic	Polar	Ohmic	Polar	Ohmic	Polar	Ohmic	Polar	Ohmic	Polar	Ohmic	Polar
0h without steam	0.1665	0.1845	0.1585	0.1836	0.1725	0.1786	0.1534	0.1336	0.1410	0.1572	0.157	0.1356
48h without steam	0.1758	0.1624	0.168	0.1512	0.1839	0.1378	0.157	0.1315	0.1478	0.1541	0.1653	0.1414
0h with steam	0.1745	0.178	0.1681	0.1458	0.1845	0.1405	0.1568	0.1381	0.1495	0.1537	0.1634	0.1424
115-117h with steam	0.184 (115h)	0.189 (115h)	0.1766 (117h)	0.1475 (117h)	0.1999 (115h)	0.1619 (115h)	0.1639 (96h)	0.1433 (96h)	0.1599 (117h)	0.155 (117h)	0.1754 (96h)	0.1478 (96h)
Final hour with steam			0.1876 (435h)	0.1633 (435h)	0.2061 (260h)	0.1768 (260h)	0.1751 (575h)	0.1746 (575h)	0.1655 (241h)	0.1685 (241h)	0.1781 (405h)	0.1711 (405h)

- 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 cm² after initial introduction of steam.
- Polar resistance of the baseline cell was increased the most (about 0.0156 ohm cm²) right after steam among all the test cells followed second by the $SrFe_2O_4$ infiltrated cell (about 0.0066 ohm cm²), 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.

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 $SrFe_2O_4$ 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 $SrFe_2O_4$ infiltrated cell was bigger than that of baseline cell after steam even if the operating duration of the $SrFe_2O_4$ infiltrated cell with steam was 240h 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.

Summary & Conclusion

- All infiltrated cells showed higher performance and lower degradation rate than the baseline cell, which demonstrated appropriate nanomaterial infiltration could improve the performance and mitigate the degradation of SOFC with steam in the cathode.
- Co, $BaFe_2O_4$ and $SrFe_2O_4$ infiltrated cells showed the lowest degradation rates among all the tested cells with 62%, 61% and 56% improvement respectively for degradation rate compared with the baseline cell if including the initial voltage drop after steam.
- EIS tests of all tested cells except the Co infiltrated cell showed increased polarization resistance 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 baseline cell was increased the most (about 0.0156 ohm cm²) right after steam followed second by the $SrFe_2O_4$ infiltrated cell (about 0.0066 ohm cm²), which also corresponded to the most and second most initial voltage drop after steam introduction for the Co infiltrated cell and $SrFe_2O_4$ infiltrated cell.
- The ohmic and polarization resistances of all tested cells were slowly increased during longer operation time with 20% steam.