Effects of Humidity on Degradation of Sr-Fe-O 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. For practical use of SOFC it is important to acquire knowledge about the impact on performance and durability of operation with ambient air.
- Recent studies showed that humidity in the cathode gas had significant impact on the performance and durability of LSM/YSZ composite cathode based SOFC[1-3].
- 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, Zhengdong 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-20115
5. Seon HyeKim, Toshihiro Ohshima, Yusuke Shiratori, Kohei Ito and Kazunari Sasaki. Mater. Res. Soc. Symp. Proc. Vol.1041 1041-R03-10

Purpose of the Study

- Evaluate the effects of humidity on stability of Sr-Fe-O infiltrated LSM/YSZ SOFC compared with uninfiltrated baseline cell.
- Evaluate the effects of current density and steam concentration on stability of Sr-Fe-O infiltrated LSM/YSZ SOFC
- Improve long term stability of SOFC by infiltration.

Experimental Methods

Cells:

- Commercially available MSRI anode supported LSM/YSZ SOFC 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: Sr-Fe-O
- Particle size is expected to be 50-100nm
- Solvent: Aqueous 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

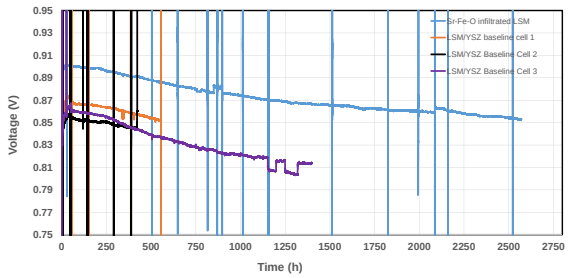
Operating Conditions:

- 800°C, 0.25-0.75 A/cm² current load, 10-20% steam balanced in air

Performance tests:

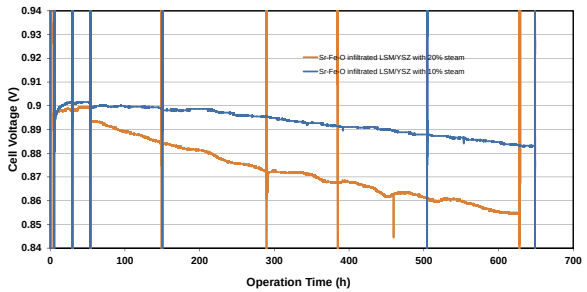
- Electrochemical Impedance spectroscopy tests to evaluate the performance degradation of Sr-Fe-O infiltrated cells under different current density and different steam concentration.
- Characterization by TEM/HRTEM observation

Stability Test of Sr-Fe-O Infiltrated LSM/YSZ Cells @ 10% Steam, 0.75A/cm² and 800°C



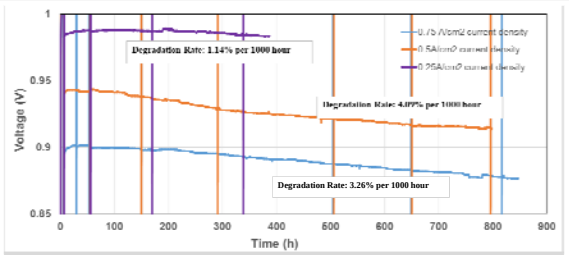
- Uninfiltrated baseline cells showed initial sharp voltage drop after steam. Sr-Fe-O infiltrated LSM/YSZ cells showed less voltage drop and recovered in the first 3-4h after steam.
- Degradation rated of uninfiltrated LSM/YSZ cell 1 and 2 is about 5.98% per 1000h including initial voltage drop after steam (3.986% per 1000h excluding voltage initial drop after steam).
- Degradation rate of uninfiltrated baseline cell 3 is 4.52% per 1000h including initial voltage drop after steam (4.07% per 1000h excluding initial voltage drop after steam)
- Degradation rate of Sr-Fe-O infiltrated LSM/YSZ cell is 2.05% per 1000h.
- Sr-Fe-O infiltrated cells showed higher performance and lower degradation rate than uninfiltrated baseline cells, which demonstrated that appropriate nanomaterial infiltration could improve the performance and mitigate the degradation of SOFC with steam in cathode.

Effect of Steam Concentration on Degradation of Sr-Fe-O infiltrated LSM/YSZ Cells @ 800°C and 0.75A/cm²



- Degradation rate of Sr-Fe-O infiltrated cell operated under 20% steam is 8.65% per 1000h including initial voltage drop after steam, and 7.42% per 1000h excluding initial voltage drop after steam.
- Degradation rate of Sr-Fe-O infiltrated cell operated under 10% steam is 3.39% per 1000h including initial voltage drop after steam, and 3.08% per 1000h excluding initial voltage drop after steam.
- Therefore performance degradation was accelerated at higher steam concentration due to deactivation of surface near three phase boundary by more adsorption of steam under higher steam concentration.

Effect of Current Density on Degradation of Sr-Fe-O infiltrated LSM/YSZ Cells @ 800°C and 10% Steam



- Performance degradation rate of Sr-Fe-O infiltrated LSM/YSZ cell operated under 0.25A/cm² was about 1.14% per 1000 hour; Performance degradation rate of Sr-Fe-O infiltrated cell operated under 0.75A/cm² was about 4.09% per 1000 hour.
- Therefore performance degradation of Sr-Fe-O infiltrated LSM/YSZ cell operated under 10% steam and 800°C was more pronounced at higher current density.

TEM Images

- TEM showed no Sr-Fe-O infiltrated nanoparticles expected to be found in the cathode from cell before test.
- EDS showed La-Sr-Mn-Fe-O nanoparticles formed in the pore due to reaction between infiltrated Sr and Fe and LSM/YSZ backbone before steam test.
- EDS also showed significant reaction between infiltrated nanoparticle and LSM/YSZ backbone for infiltrated cell tested under steam for 2500h as the following:
  - (MnFe)Ox particles: these particles were with size of ~100nm.
  - YSZ backbone: Fe doped LSM particles with size of 10-50nm were found on YSZ grain surface.
  - LSM backbone: Fe-doped LSM particles were also identified on the surface of LSM grain, and also Fe diffusion into LSM grain was observed by TEM. There is nano-void like morphology shown in LSM grain interior.

Summary & Conclusion

- Sr-Fe-O infiltrated cells showed higher performance and lower degradation rate than uninfiltrated baseline cells, which demonstrated that appropriate nanomaterial infiltration could improve the performance and mitigate the degradation of SOFC.
- Uninfiltrated baseline cells showed sharp voltage drop after steam. Sr-Fe-O infiltrated LSM/YSZ cells showed less voltage drop and recovered in the first 3-4h after steam.
- Degradation rate was accelerated at high steam concentration due to deactivation of surface area near TPB by more adsorption of steam under high steam concentration.
- Performance degradation of Sr-Fe-O infiltrated LSM/YSZ cell operated under 10% steam and 800°C was more pronounced at higher current density.
- TEM showed no Sr-Fe-O infiltrated nanoparticles expected to be found in the cathode from cell before test; EDS showed La-Sr-Mn-Fe-O nanoparticles formed in the pore due to reaction between infiltrated Sr and Fe and LSM/YSZ backbone before steam test.
- EDS also showed significant reaction between infiltrated nanoparticle and LSM/YSZ backbone for infiltrated cell tested for 2500h under 10% steam, 800°C and 0.75A/cm².