Improved Performance Stability of Solid Oxide Fuel Cells Achieved Through Sr-Fe-O Infiltration of LSM/YSZ Cathode

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Introduction

- Solid oxide fuel cells (SOFC) are operated with fuel in the anode and ambient air in the cathode which contains about 3% moisture. For practical use of SOFC it is important to acquire knowledge about the impact of steam in cathode on performance and durability of SOFC.
- Several studies found inter-diffusion of Mn may be enhanced by moisture due to OH- and MnO2 formation at the LSM/YSZ interface [1, 2]. MnO2 was present near the active TPB when the cell was operated at 925°C, while both MnO and Mn2O3 were present in the cell operated at 800°C [1].
- Studies also found steam in the cathode may enhance the removal of Mn from the TPB reaction zone and cause a decomposition of LSM at the LSM/YSZ interface [3].
- It was also found [2] that 3% moisture in air degraded LSM/YSZ cathode performance at 750-850°C due to the degradation of SrO/SrOH2 at the surface. La2O3 and MnO2 formation at the LSM/YSZ interface was also observed. La2O3 formation on the surface of LSM was also observed by XPS and TEM, poor electrical conductivity of La2O3, may be also related to the cell performance degradation [4].

In-situ study of LSM/YSZ cathode under polarization by photoelectron microscopy [5] found that manganese surface oxidation state was changed by cathode polarization, the manganese concentration on the LSM surface decreased with increasing cathode polarization, while the manganese concentration on the electrolyte surface increased with increased cathode bias. It was also found [5] that manganese spreading from TPB over the electrolyte surface was observed to slow down when the cathode bias was reduced, and the spreading of manganese over the electrolyte was reversible and could be repeated for several times, the spreading became more sluggish and required larger bias activation with an increased number of repetitions. Therefore, long term current loading on the LSM/YSZ cell could cause manganese precipitation from LSM which degrades the performance during long term operation.

Purpose of the Study

- Evaluate the impact of Sr-Fe-O infiltration on LSM/YSZ cathode stability in steam-containing environments in comparison with uninfiltred LSM/YSZ baseline cell.
- Evaluate nanostructure and chemistry changes of Sr-Fe-O infiltrated cells before and after long term test through TEM/HRTEM and EDS studies and analysis.

Experimental Methods

- **Cells**: Commercially available MSRI anode supported LSM/YSZ SOFC cells
- **Cathode**: LSM/[La0.7Sr0.3]0.75Mn0.25O4 / LSM-YSZ active layer
- **Electrolyte**: YSZ
- **Anode**: Ni-YSZ
- **Infiltration of nano-materials in LSM/YSZ cells**
  - Infiltrated nano-materials: 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 nano-material obtained

**Operating Conditions**
- **800°C**, 0.75 Acn current load, 10% steam balanced in air

**TEM/HRTEM and EDS studies and analyses**
- Nanostructure changes of Sr-Fe-O infiltrated before and after long term test by TEM/HRTEM observation
- EDS studies for chemistry changes before and after long term tests.

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

- Uninfiltrated LSM/YSZ baseline cell showed initial sharp voltage drop after steam, Sr-Fe-O infiltrated LSM/YSZ cell showed less voltage drop and recovered in the first 3-4h after steam.
- Degradation rate of uninfiltred baseline cell 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 cell showed improved performance and lower degradation rate than uninfiltrated baseline cell, which demonstrated that appropriate nanomaterial infiltration could improve the performance and mitigate the degradation of SOFC with steam in cathode.

**Summary & Conclusion**

- Sr-Fe-O infiltrated cell showed improved performance and lower degradation rate than uninfiltrated baseline cell, which demonstrated that appropriate nanomaterial infiltration could improve the performance and mitigate the degradation of SOFC with steam in cathode.
- EDS showed significant reaction between infiltrated nanoparticle and LSM/YSZ backbone for infiltrated cell before and after tests. The desired composition of SrFeO4 was not observed in the cathode for both before and after tests.
- The newly formed Fe-substituted LSM nano-grains on the YSZ grain surface are expected to add additional new TPBs for the electrochemical reactions.
- The cathode performance enhancement can also be partially attributed to the Fe doping of the original LSM backbone.

**TEM/EDS Studies of Sr-Fe-O infiltrated LSM/YSZ Cell Before Steam Test**

- Infiltrate with the size of 20-30nm penetrate into the original pore of cathode active layer.
- The desired composition of SrFeO4 was not observed in the cathode.
- The Sr and Fe infiltrates strongly interact with LSM/YSZ backbone and formed Fe-substituted LSM.
- The newly formed Fe-substituted LSM particles are distributed on the internal surface of both LSM and YSZ backbone grains.

**TEM/EDS Studies of Sr-Fe-O infiltrated LSM/YSZ Cell Operated @ 800°C, 10% Steam and 0.75A/cm² for 2500h**

- After 2500 hours operation in steam, the typical chemistry of the infiltrate is [(La0.7Sr0.3)0.75(Mn0.25Fe0.75)O4]
- Fe from the infiltrate also diffused into the LSM backbone, with a typical surface composition of the LSM backbone of [(La0.7Sr0.3)0.75(Mn0.25Fe0.75)O4]
- The newly formed Fe-substituted LSM nano-grains on the YSZ grain surface are expected to add additional new TPBs for the electrochemical reactions.
- The cathode performance enhancement can also be partially attributed to the Fe doping of the original LSM backbone.

**Nano-void** Nano-void was observed on LSM backbone and LSM interior. Nano-void may cause the performance degradation of fuel cell.