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 MnO_x formation at the LSM/YSZ interface [1, 2]. Mn_3O_4 was present near the active TPB when the cell was operated at 925°C, while both Mn_3O_4 and Mn_2O_3 were present in the cell operated at 800°C [1] .
- Studies also found steam in the cathode may enhance the removal of Mn^{2+} 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 segregation of $SrO/Sr(OH)_2$ at the LSM surface. $La_2Zr_2O_7$ and MnO_x formation at the LSM-YSZ interface was also observed. La_2O_3 formation on the surface of LSM was also observed by XPS and TEM, poor electrical conductivity of La_2O_3 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 the increasing cathode polarization, while the manganese concentration on the electrolyte surface was increased with increased cathode bias. It was also found [5] that manganese spreading from 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 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 degrade the performance during long term operation.

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Purpose of the Study

- Evaluate the impact of Sr-Fe-O infiltration on LSM/YSZ cathode stability in steam-containing environments in comparison with uninfiltrated 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.
- Gauge what improved performance and performance stability of Sr-Fe-O infiltrated cells.

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

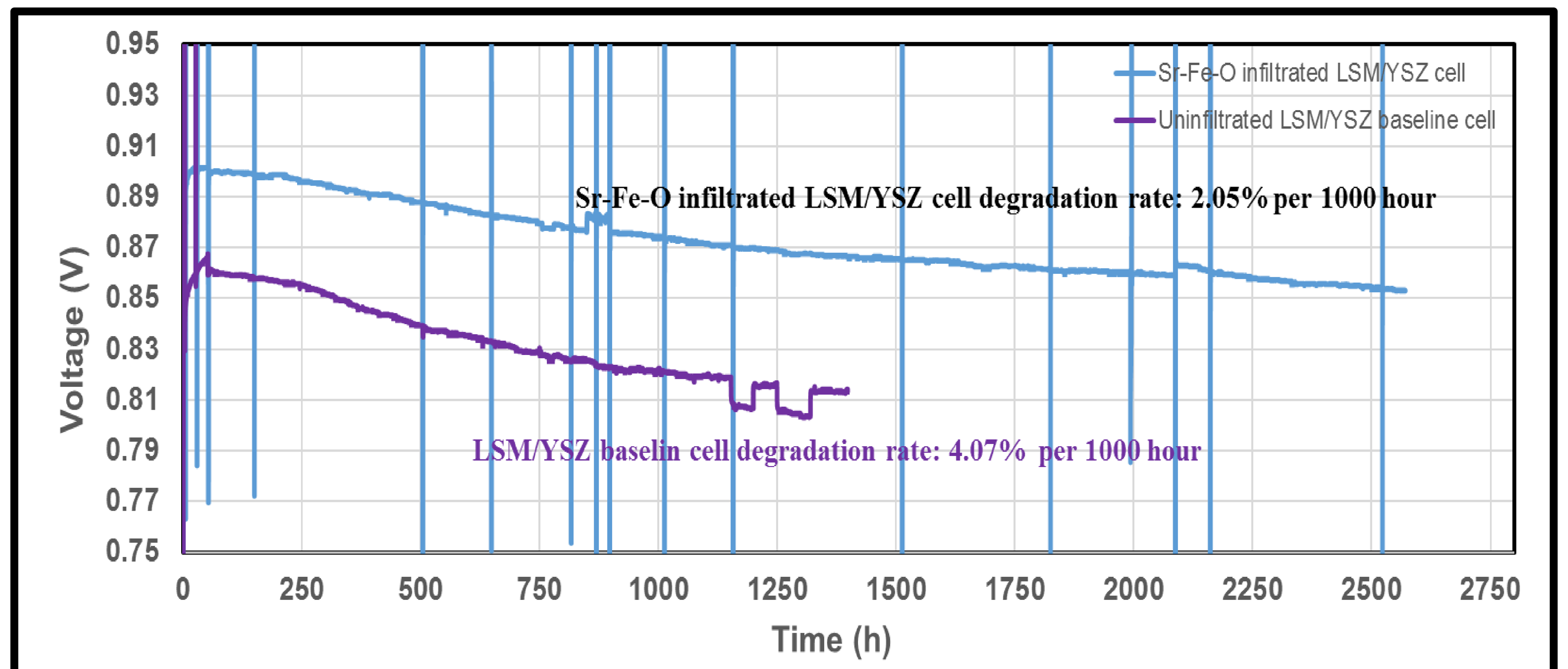
Operating Conditions:

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

TEM/HRTEM and EDS studies and analysis:

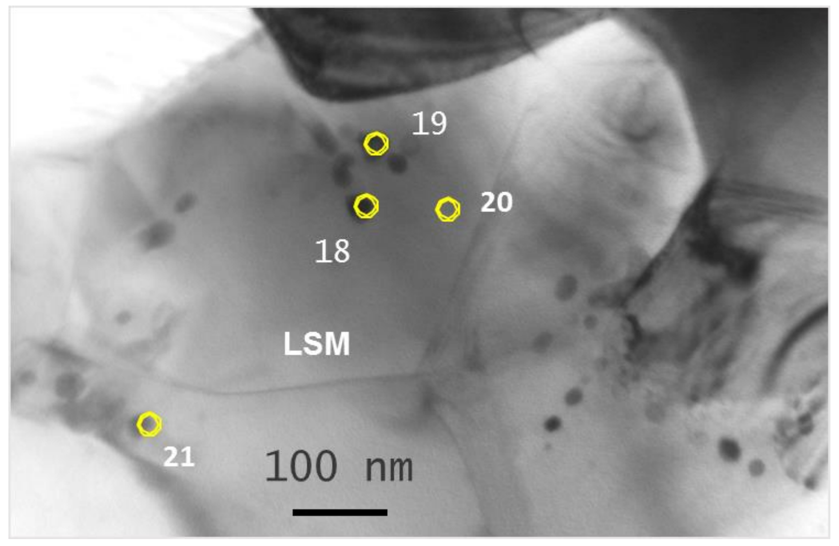
- Nanostructure changes of Sr-Fe-O infiltrated cell before and after long term test by TEM/HRTEM observation
- EDS studies for chemistry changes before and after long term tests.

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

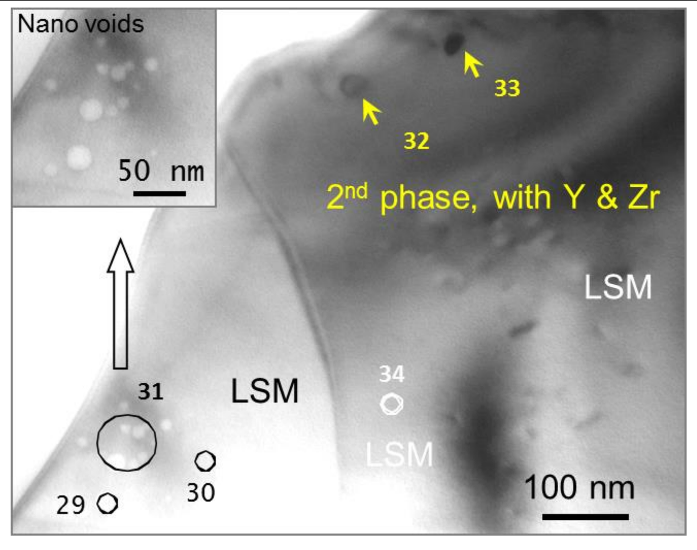


- Uninfiltrated LSM/YSZ baseline cell showed initial sharp voltage drop after steam. Sr-Fe-O infiltrated LSM/YSZ cell showed less voltage drop and recovered in the first 3-4h after steam.
- Degradation rate of uninfiltrated baseline cell is 4.52% per 1000h including initial voltage drop after steam (4.07% 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.

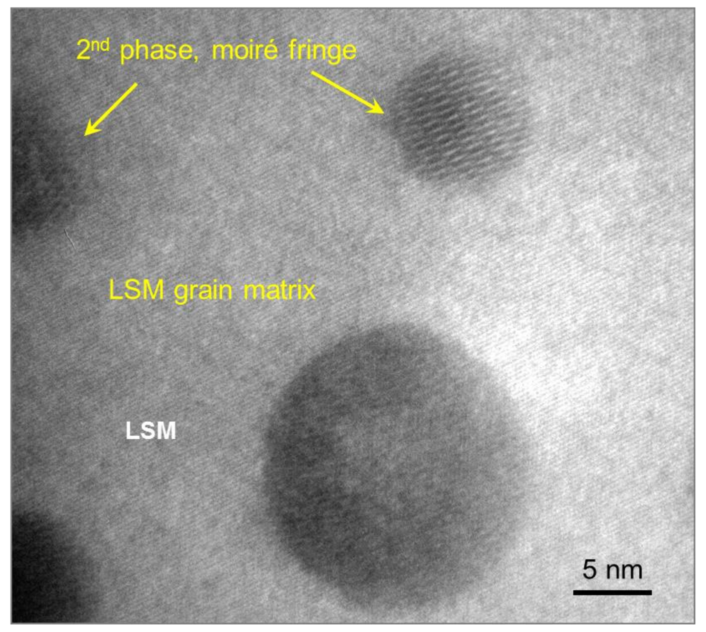
TEM/EDS Studies of Uninfiltrated LSM/YSZ Cell Operated @ 800°C, 10% Steam and 0.75A/cm² for 1325 h



at %	O	Mn	La	Sr	Zr	Y
18	63.72	16.42	11.91	3.18	3.95	0.82
19	63.23	18.54	12.84	3.54	1.54	0.33
20	60.6	20.52	14.06	4.26	0.56	
21	66.53	15.96	10.57	2.89	3.3	0.76

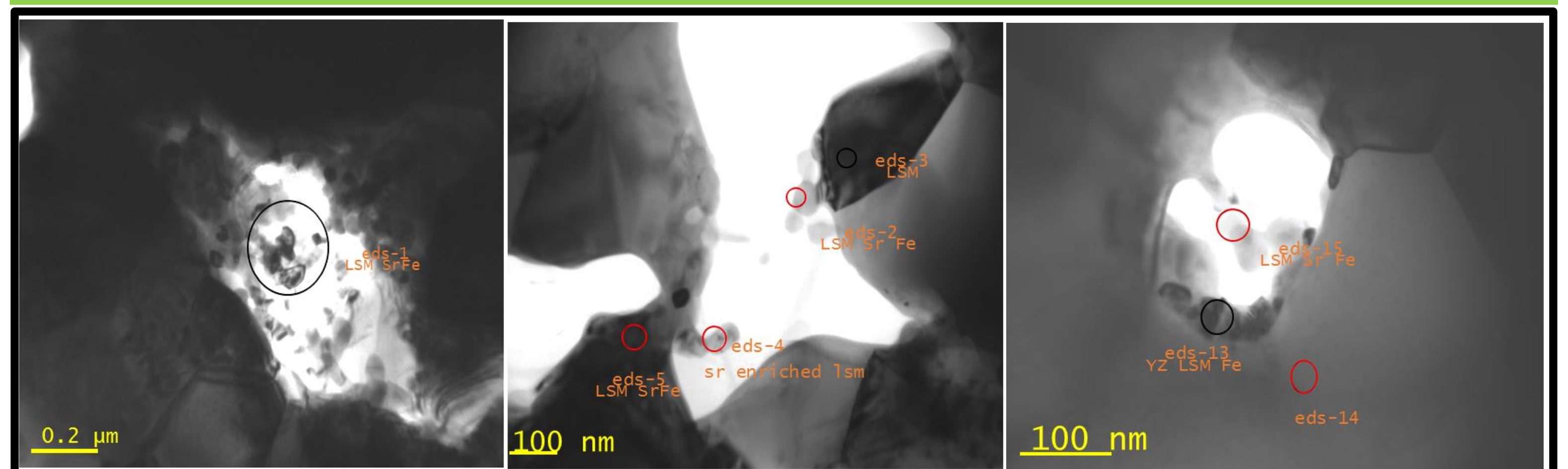


%	O	Mn	La	Sr	Zr	Y
29	74.49	13.38	9.53	2.6		
30	73.39	13.63	10.13	2.85		
31	74.41	13.32	9.55	2.72		
32	62.94	18.75	12.28	3.97	2.06	
33	65.04	14.41	9.96	2.57	6.58	1.43
34	67.66	17.25	11.58	3.52		



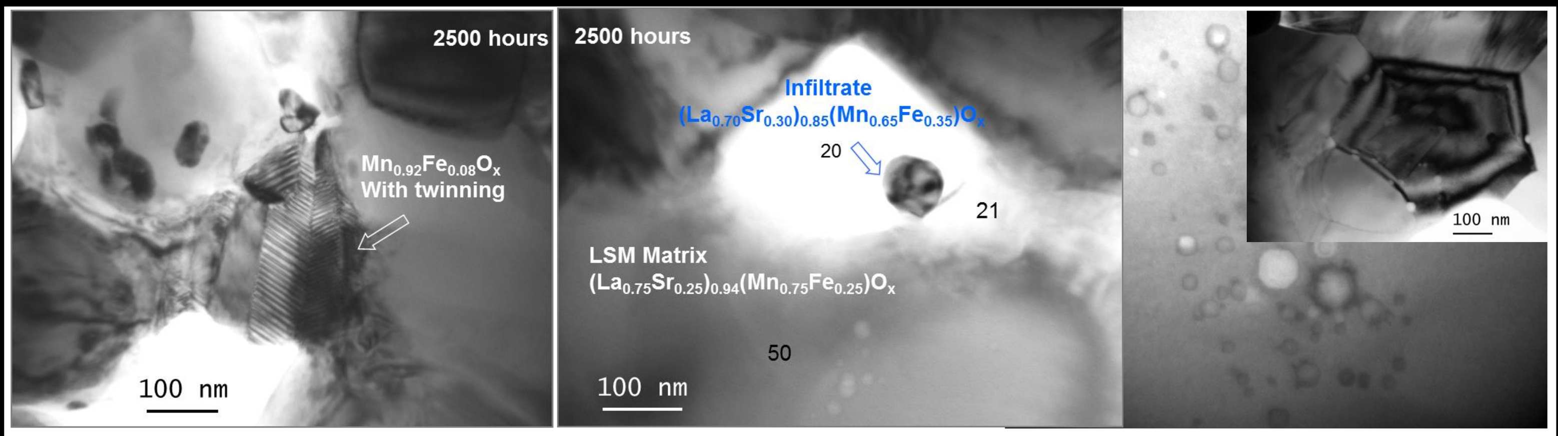
- ~10-20 nm spherical shaped 2nd phase crystals containing Y and Zr exhibited crystal feature with moire fringe which different form nano-voids randomly distributed on/in LSM grain from the active layer.
- Nano-voids do not have additional elements and no additional fringe in the images.
- Formation of Mn enriched & Mn-La-Sr-Y doped ZrO2 secondary phase nanoparticles accompanied by the additional holes/voids at LSM/YSZ interface may cause the degradation of cell.

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



- Infiltrate with the size of 20-200nm penetrate into the original pore of cathode active layer.
- The desired composition of $SrFe_2O_4$ 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 $(La_{0.70}Sr_{0.30})_{0.85}(Mn_{0.65}Fe_{0.35})O_x$.
- Fe from the infiltrate also diffused into the LSM backbone, with a typical surface composition of the LSM backbone of $(La_{0.75}Sr_{0.25})_{0.94}(Mn_{0.75}Fe_{0.25})O_x$.
- 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.

(MnFe)Ox particles: Infiltrated Fe was doped into those MnOx precipitated from LSM backbone and formed (MnFe)Ox which the ratio of Mn: Fe= 11.5:1
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.
Nanovoid: Nano-void was observed on LSM backbone and LSM interior. Nano-void may cause the performance degradation of fuel cell.

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 $SrFe_2O_4$ was not observed in the cathode for both before and after tests.
- The newly formed Fe-substituted LSM 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 observed on LSM backbone and LSM interior may cause the performance degradation of fuel cell.

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