Electrochemical Impedance Spectroscopy Study of Metal Ferrite Infiltrated LSM/YSZ Solid Oxide Fuel Cells

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Introduction

Infiltration Technology:

- Infiltration has been proved to be the most effective way to develop highly active and advanced nanoscale engineering of electrode structures for SOFCs. Opens a new horizon in the advanced electrode development.
- Infiltrated nanomaterials not only substantially increase the three phase boundaries for the reaction but also play important catalytic roles in the enhancement of the fuel cell reactions.

Metal Ferrite Infiltration Technology:

- Metal ferrites with the general molecular formula $M^{2+}Fe_2^{3+}O_4$ such as MFe_2O_4 (M=Co, Cu, Mn, Ni) have a spinel-type structure similar to that of the mineral $MgAl_2O_4$.
- The lattice of metal ferrites consists of 32 divalent oxygen ions, which are in direct contact with one another forming a closed-pack face-centered cubic arrangement with 64 tetrahedral interstitial sites (A sites) and 32 octahedral interstitial sites (B sites). Out of these, eight tetrahedral (A sites) and 16 octahedral (B sites) sites are occupied by the divalent and trivalent cations. Thus, the large fraction of empty interstitial sites makes its crystal structure a very open structure that is conducive to cation migration [1].
- Therefore, a whole range of distribution of cations is possible in spinel ferrites which can contribute to their remarkable magnetic, catalytic, optical, and electrical properties [2].
- $BaFe_2O_4$ and $SrFe_2O_4$ does not crystallize in a spinel structure, but in an complicated orthorhombic structure since the size of Ba^{2+} and Sr^{2+} is too large to be accommodated in the octahedral sites [3], which will contribute to better electrochemical reaction due to the loose O^{2-} in $BaFe_2O_4$ and $SrFe_2O_4$.

1. Kumar, L.; Kumar, P.; Narayan, A.; Kar, M. Int. Nano Lett. 2013, 3, 8.
2. Carta, D.; Casula, M.; Falqui, A.; Loche, D.; Mountjoy, G.; Sangregorio, C.; Corrias, A. J. Phys. Chem. C 2009, 113, 8606−8615.
3. Kahlenberg, V.; Fischer, R. Solid State Sci. 2001, 3, 433−439.

Experimental Methods

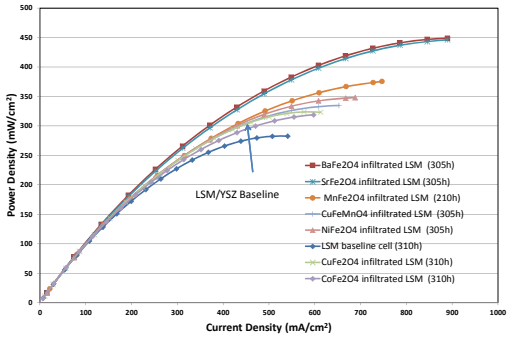
Infiltration of Metal Ferrite Nanomaterials in LSM/YSZ Cells

- Metal Ferrite infiltrated nanomaterials: MFe_2O_4 (M = Ba, Sr, Cu, Co, Mn, Ni) and $CuFeMnO_4$
- Particle size is expected to be 20-50nm
- Solvent: Aqueous solution with citric acid
- Chemical Precursors: Metal Nitrate (0.125M-0.25M)
- Calcination Temperature: 850°C
- Time: Repeat infiltration until 7.0 - 7.5 wt% infiltrated nanomaterial obtained

Metal Ferrite Nanomaterial Characterization

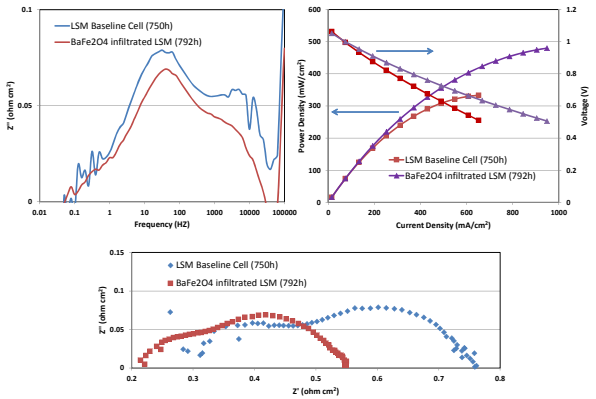
- Electrochemical Impedance spectroscopy (EIS) test in MCA (Multi Cell Array) system to identify the promising metal ferrite infiltrated LSM Cells.
- Stability test of the promising metal ferrite infiltrated LSM cell in Single Cell Test Stand (SCTS).

MCA Test of Metal Ferrite Infiltrated LSM



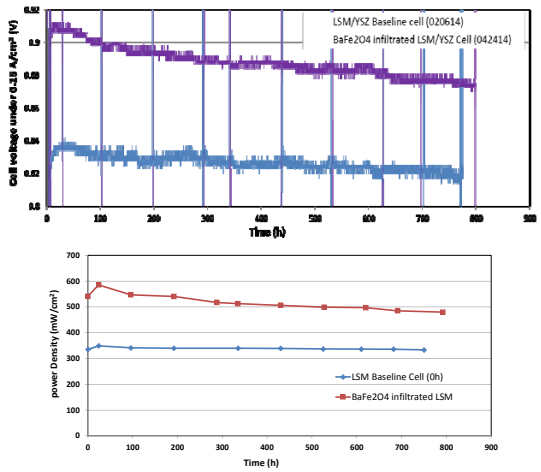
- $BaFe_2O_4$ and $SrFe_2O_4$ infiltrated LSM cell showed the best performance among all the metal ferrite infiltrated LSM/YSZ.
- $BaFe_2O_4$ and $SrFe_2O_4$ enhanced electrochemical performance in LSM/YSZ.

$BaFe_2O_4$ Infiltrated LSM Cell-SCTS TEST



- Bode plot: The impedance of infiltrated cell with frequency related to cathode (10-1000HZ) and anode (above 1000HZ) were both decreased significantly.
- Power density - current density plot: power density of $BaFe_2O_4$ infiltrated LSM/YSZ was increases by 50% for 792h compared with LSM/YSZ baseline cell.
- Nyquist plot: polarization resistance were decreased for $BaFe_2O_4$ infiltrated cell.

Stability Test of $BaFe_2O_4$ Infiltrated LSM



- $BaFe_2O_4$ infiltrated LSM/YSZ cell showed significantly higher voltage than that with baseline cell. Voltage of $BaFe_2O_4$ infiltrated LSM/YSZ reached highest in 24h, but decreased more quickly than that with baseline cell.
- Power density @0.5V of the infiltrated cell was significantly increased by 60% in zero hour, and reached the highest with performance increased by 68% in 24h. The performance was relatively stabilized after 200h for infiltrated cell.
- 790h operation of $BaFe_2O_4$ infiltrated Cell still showed 50% increased power density compared to the baseline cell.

Conclusions

- Seven MFe_2O_4 (M=Sr, Ba, Co, Cu, Mn and Ni) and $CuFeMnO_4$ infiltrated LSM/YSZ cells were tested in MCA. $BaFe_2O_4$ and $SrFe_2O_4$ showed the best performance among the seven tested metal ferrite infiltrated LSM/YSZ cells.
- Impedance of $BaFe_2O_4$ infiltrated cell with frequency related to cathode (10-1000HZ) and anode (above 1000HZ) were both decreased significantly.
- Power density of $BaFe_2O_4$ infiltrated cell was significantly increased by 60% in zero hour. Power density of $BaFe_2O_4$ infiltrated cell reached the highest in 24h with 68% increased performance compared to the baseline cell.
- Performance of $BaFe_2O_4$ infiltrated cell was slowly decreased after 24h, but stabilized after 200h.
- 790h operation of $BaFe_2O_4$ infiltrated cell still showed 50% increased power density compared to the baseline cell.
- The performance range measured for the various materials indicated that cathode activity can be customized by careful selection of infiltrated materials.

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