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SOFC Powders and Unit Cell Research at NIMTE

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$(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$(LSM), $(La_{0.6}Sr_{0.4})_{0.9}Co_{0.2}Fe_{0.8}O_{3-\delta}$(LSCF), $La_{0.6}Sr_{0.4}CoO_{3-\delta}$(LSC), $Ce_{0.9}Gd_{0.1}O_{1.95}$(CGO) nano-powders and LSM+YSZ, LSCF+CGO, LSC+CGO composite cathodes have been researched, and reported in this paper. Microstructure characterizations and electrical properties measurements showed resultant powders to be of high purity, single phase, with slight aggregation with grain size less than 100 nm and high performances. Excellent polarization resistance of 0.18 $\Omega.cm^2$ at 750°C, 0.12 $\Omega.cm^2$ at 700°C, and 0.12 $\Omega.cm^2$ at 650°C were obtained respectively in the LSM+YSZ/YSZ/LSM+YSZ, LSCF+CGO/CGO/LSCF+CGO and LSC/CGO/YSZ/CGO/LSC symmetric cells. Anode supported cells with configuration of Ni+YSZ/YSZ/LSM+YSZ, Ni+YSZ/YSZ/CGO/LSCF+CGO and Ni+YSZ/YSZ/CGO/LSC+CGO exhibited maximum power densities of 0.63 W/cm^2 at 750°C, 0.54 W/cm^2 at 700°C and 0.42 W/cm^2 at 650°C (H_2/air, active electrode area of 4×4 cm^2), respectively. These results indicated that the YSZ-based anode supported cells with LSM–YSZ, LSCF-CGO, LSC-CGO composite cathodes have the feasibility to be operated at 750–650°C with an acceptable power density.

Introduction

Ningbo Institute of Material Technology & Engineering (NIMTE) currently runs the largest activity in Solid Oxide Fuel Cell research and development in mainland China (1). A division named Fuel Cell and Energy Technology (FCET) has been established focusing on the development of SOFC key materials, cell fabrications, stack designs and assembly as well as system integration since the end of 2006. The powders and unit cells research group is one of the five groups in the FCET division. The research in this group is to focus on the ZrO_2-based SOFCs, especially the planar anode supported cells. In this paper, recent research on SOFC powders and unit cells at NIMTE is described.

Experimental

Powders Synthesis and Characterization

Four kinds of nano-powders, $(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$ (LSM), $(La_{0.6}Sr_{0.4})_{0.9}Co_{0.2}Fe_{0.8}O_{3-\delta}$(LSCF), $La_{0.6}Sr_{0.4}CoO_{3-\delta}$(LSC), and $Ce_{0.9}Gd_{0.1}O_{1.95}$(CGO) were prepared by a modified sol-gel process using citric acid as complexing agent (2-5). Phase formation and crystallinity of the resulting powders were characterized by means of X-ray diffraction (XRD) in a Bruker D8 Advance with Cu Kα radiation. The microstructures of the powders and sintered samples were observed by field emission scanning electron microscope (Hitachi S-4800). The purity of the synthesized powders was measured by XRF (Rigaku ZSXPrimus II). The electrical conductivity of the sintered LSM, LSCF and LSC samples was measured by four-probe DC measurement in the temperature range of 25–800°C in air. The electrical properties of the sintered CGO samples were studied using impedance measurement by two-probe four-wire method with platinum electrodes.

Symmetric Cells Fabrication and Measurement

Symmetrical cells were prepared to study the electrochemical properties of the three kinds of composite cathodes, LSM+YSZ, LSCF+CGO, and LSC+CGO, on GDC or YSZ electrolyte. The YSZ component in the composite electrodes is a commercial powder, TZ-8Y (ZrO_2 with 8 mol% Y_2O_3, Tosoh Corporation). An ethanol-based slurry consisting of powders, binder, dispersion was produced by ball milling and sprayed on both sides of an approximately 200 µm thick YSZ or CGO foil using airborne spraying. The sintered cathode layer thickness was around 20 µm. All the symmetric cells were coated with Pt for current collection and cut into approximately 7.1×7.1 mm^2 for electrochemical measurements from 600°C to 850°C in air. The tests were performed as two-electrode four-wire measurements, and the polarization resistance was determined as half of the measured electrode polarization resistance (6-9). Impedance measurements were carried out using a Solartron 1260 frequency response analyzer over the frequency range from 2 MHz to 0.1 Hz and 20 mV excitation voltage.

Unit Cells Fabrication and Measurement

Three kinds of anode supported Cells with configuration of Ni+YSZ/YSZ/ LSM+YSZ, Ni+YSZ/YSZ/CGO/ LSCF+CGO and Ni+YSZ/YSZ/CGO/LSC+CGO were prepared and measured. The unit cells were produced by tape casting the anode support, spraying the NiO–YSZ active anode and YSZ electrolyte layer, followed by co–sintering. The GDC interlayer and cathode layer were prepared by spraying the slurry on the electrolyte substrates and sintering at different temperatures. The unit cell with an active electrode area of 4×4 cm^2 was tested in a ceramic–test housing using hydrogen as fuel and air as oxidant.

Result and Discussion

Results of Powders Research

Figures 1 and 2 show the XRD patterns and SEM photos of these four kinds of powders. From XRD patterns only the patterns of crystalline LSM, LSCF, LSC and CGO were observed; no impurity phases were observed in these XRD patterns. The crystallite size of these powders was 20-30 nm as deduced from the XRD pattern by Debye–Scherer equation after subtraction of the equipment widening. From SEM photos, it can be seen that all powders have few aggregates, and the particles are spherical and the particle sizes are less than100 nm with a narrow distribution.

The XRF results show that the purity of these four kinds of powders is all higher than 99.9%. In view of all microstructure characterizations, the powders are high purity, single phase, homogeneous with slight aggregation with grain size less than 100 nm. The conductivities of the sintered samples prepared from these nano-powders were also measured, and the conductivities of LSM, LSCF, LSC and CGO sintered bulks reached 200, 279, 1950 and 0.033 S/cm, respectively, at 750°C. Table I shows the conductivities of the sintered samples.

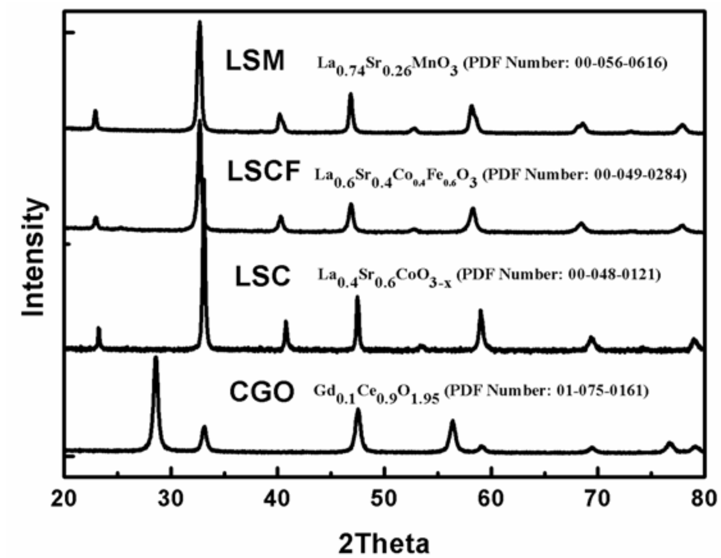

Figure 1. XRD patterns of LSM, LSCF, LSC, and CGO powders.

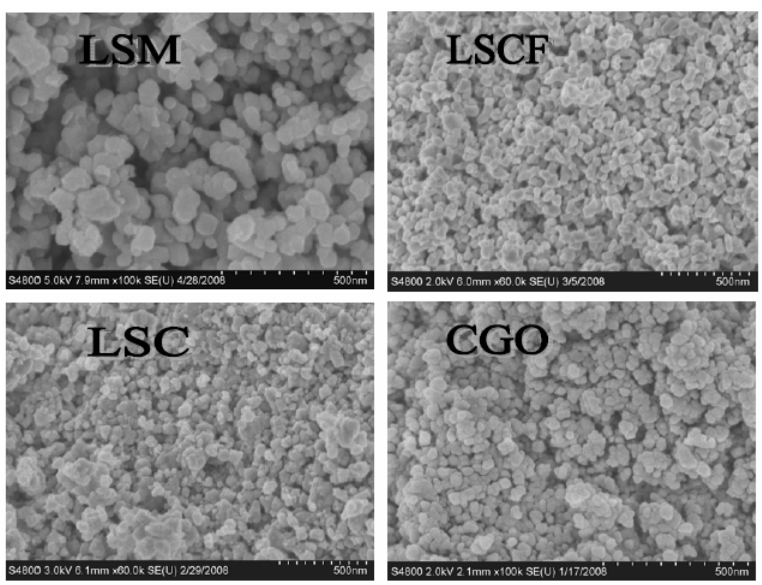

Figure 2. SEM photos of LSM, LSCF, LSC, and CGO powders.

TABLE I. The conductivities of four kinds of sintered samples.

Powder Composition	**Sintering Schedule**	**σ (S/cm) at 650°C**	**σ (S/cm) at 700°C**	**σ (S/cm) at 750°C**
$(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$	1300 °C -5h	198	199	200
$(La_{0.6}Sr_{0.4})_{0.9}\ Co_{0.2}\ Fe_{0.8}O_{3-\delta}$	1300 °C -5h	283	284	279
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	1250 °C -5h	2000	1905	1950
$Ce_{0.9}Gd_{0.1}O_{1.95}$	1400 °C -12h	0.022	0.027	0.033

Symmetric Cells Measurement

Three kinds of symmetric cells, LSM+YSZ/YSZ/LSM+YSZ, LSCF+CGO/ CGO/LSCF+CGO, and LSC/CGO/YSZ/CGO/LSC, were measured. Figure 3 shows the Arrhenius plot of the *R*p obtained from the impedance spectra of all symmetric cells. For comparison, the results reported in Ref. (5) are also shown in this figure. The excellent polarization resistance (Rp) of 0.18 $\Omega.cm^2$ at 750°C was obtained in the LSM+YSZ/YSZ/LSM+YSZ sample, Rp of 0.12 $\Omega.cm^2$ at 700°C was obtained in the LSCF+CGO/CGO/LSCF+CGO sample; Rp of 0.12 $\Omega.cm^2$ at 650°C was obtained in the LSC//CGO/YSZ/CGO/LSC sample. These performances indicated that the YSZ-based anode supported cells with LSM+YSZ, LSCF+CGO, LSC+CGO composite cathode have the potential to be operated at 750–650°C with an acceptable power density.

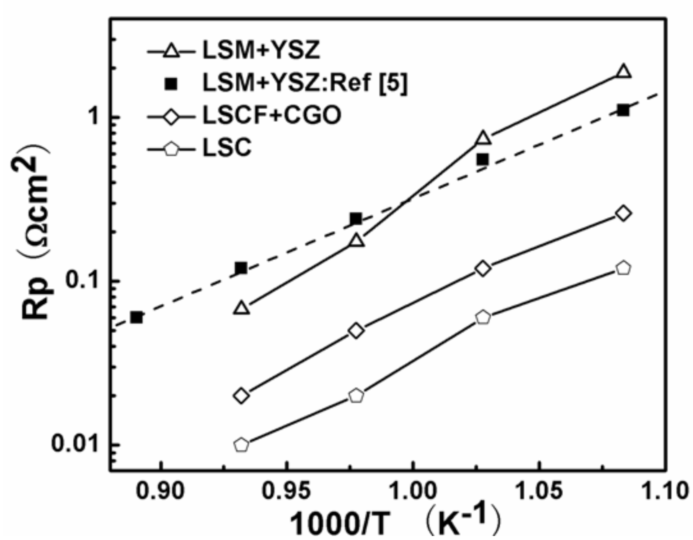

Figure 3. Arrhenius plot of the LSM+YSZ, LSCF+CGO and LSC cathode area specific polarization resistance, obtained from impedance measurements.

Unit Cells Measurement

Three kinds of anode supported cells with configuration of Ni+YSZ/YSZ/ LSM+YSZ, Ni+YSZ/YSZ/CGO/LSCF+CGO and Ni+YSZ/YSZ/CGO/LSC+CGO exhibited the maximum power densities of 0.63 W/cm^2 at 750°C, 0.54 W/cm^2 at 700°C and 0.42 W/cm^2 at 650°C (H_2/air, active electrode area of 4×4 cm^2), respectively, which are shown in Figure 4.

The microstructures of the LSM, LSCF and LSC unit cells were studied by FESEM, and are shown in Figure 5. The cathode layer is about 20 μm thick and has a very fine structured composite with uniformly distributed grain and pores. The individual grains are clear and round. The grain size is approximately 100-200 nm. Furthermore, the cathode layers are well adhered to the YSZ substrate. Almost all the available “branches” of the LSM–YSZ network or CGO at the interfacial region are connected to the YSZ layer. Such connected network offers large extended contacts between electrolyte and electrode. Porous structure with very small grain size enlarges the number of the active TPBs. Good electric and chemical performance is believed to be related to such homogeneous porous composite nanostructure, which can increase the length of the active TPBs, thereby lowering the cathodic polarization (2,10).

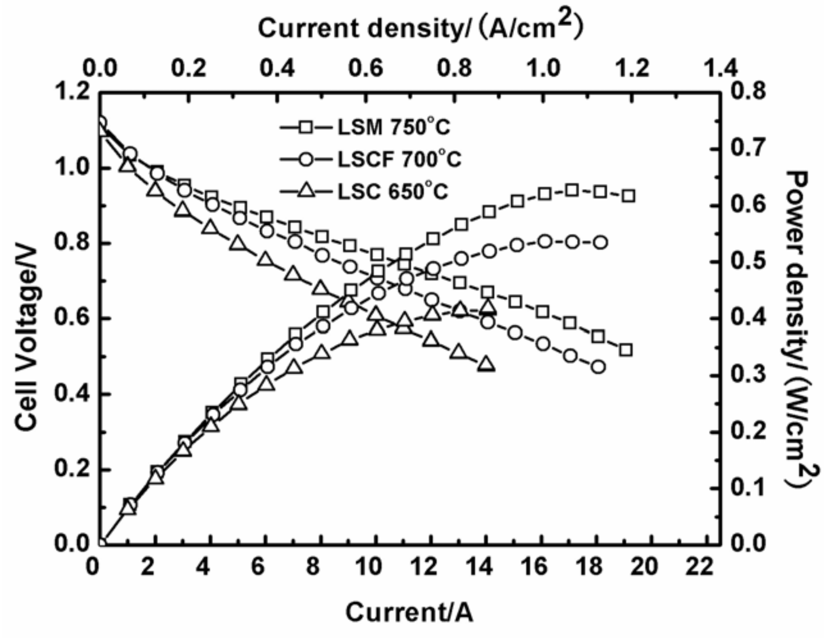

Figure 4. I-V characteristics of LSM、LSCF and LSC cells.

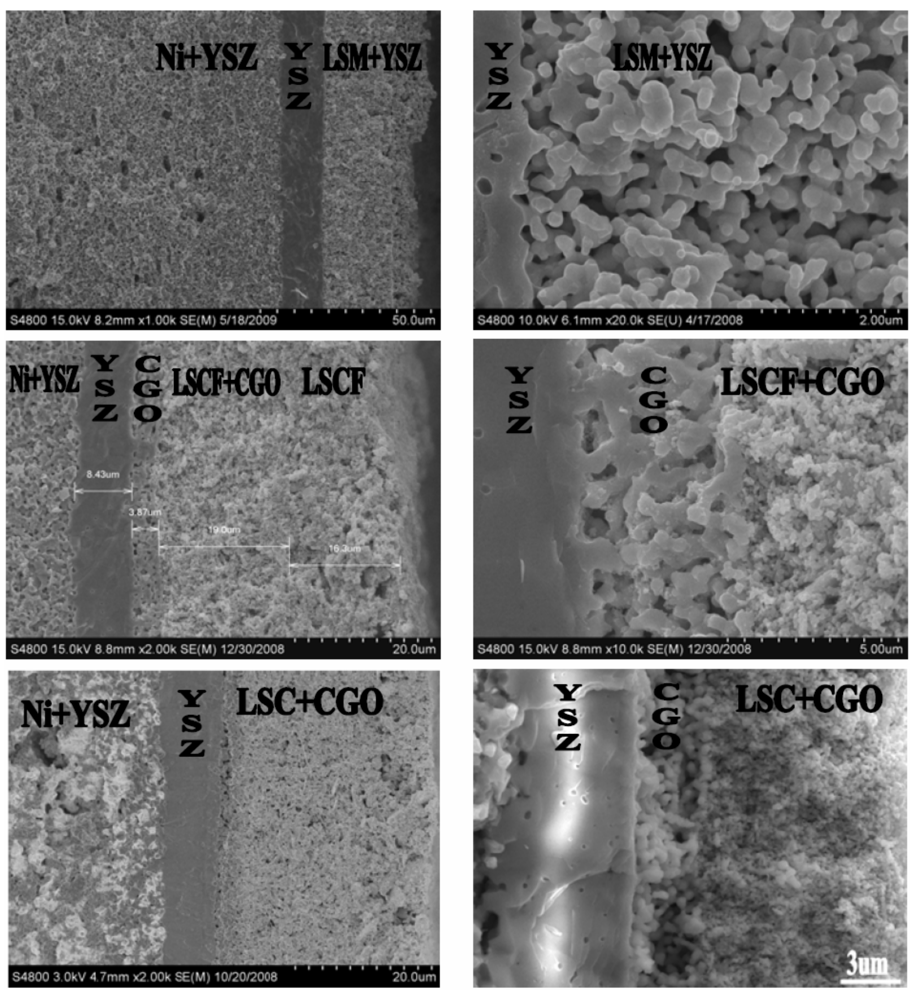

Figure 5. SEM micrographs of LSM, LSCF and LSC cells.

Conclusions

$(La_{0.75}Sr_{0.25})_{0.95}MnO_{3\pm\delta}$, $(La_{0.6}Sr_{0.4})_{0.9}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$, and $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders were prepared and characterized. Microstructure characterizations and electrical properties measurements showed these powders to be of high performance. Excellent polarization resistances of 0.18 $\Omega.cm^2$ at 750°C, 0.12 $\Omega.cm^2$ at 700°C, 0.12 $\Omega.cm^2$ at 650°C were obtained, respectively, in the LSM+YSZ/YSZ/LSM+YSZ, LSCF+CGO/CGO/LSCF+CGO and LSC/CGO/YSZ/CGO/LSC symmetric cells. Anode supported cells with configuration of Ni+YSZ/YSZ/LSM+YSZ, Ni+YSZ/YSZ/CGO/LSCF+CGO and Ni+YSZ/YSZ/CGO/LSC+CGO exhibited the maximum power densities of 0.63 W/cm^2 at 750°C, 0.54 W/cm^2 at 700°C and 0.42 W/cm^2 at 650°C (H_2/air, active electrode area of 4×4 cm^2), respectively. These results indicated that the YSZ-based anode supported cells with LSM-YSZ, LSCF-CGO, LSC-CGO composite cathode have the feasibility to be operated at 750–650°C with an acceptable power density.

Acknowledgments

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