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A study of process parameters of LSM and LSM–YSZ composite cathode films prepared by screen-printing

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Abstract

A screen-printing technique was developed to fabricate porous cathode film for solid oxide fuel cells. Several key process parameters such as the selection of binders, the mesh of screen, sintering temperature and sintering time were investigated and reported. SEM results showed that the selected process parameters exerted obvious influences on the structure of the screen-printed cathode film. Impedance spectra data were used to evaluate the performance of cathode films made by different process parameters. The optimized process parameters were as follows: ethyl cellulose used as a binder, 120 mesh screen-printing sintering at 1200 °C for 2 h. Based on the optimized parameters, the polarization resistance of pure LSM cathode was 0.396 Ω cm^2 at 800 °C; the LSM–YSZ composite cathode displayed R_p value of 0.2027 Ω cm^2 at 850 °C, 0.2463 Ω cm^2 at 800 °C and 0.5168 Ω cm^2 at 750 °C, respectively. The performance of the LSM–YSZ composite cathode improved significantly after being polarized at 300 mA cm^{-2} and 800 °C for 150 h. After 150 h, the over-potential of the composite cathode was stable.

Keywords: SOFC; Cathode; Process parameter; Screen-printing; Impedance spectra

1. Introduction

In recent years, there has been an intense focus to develop solid oxide fuel cells (SOFCs), which are capable of delivering high energy at reduced temperatures [1]. For intermediate temperature planar anode-supported cells, the resistance of electrolyte has been reduced to acceptable (or negligible) levels but the performance of the electrodes, especially at the cathode, becoming the limiting factor. Theoretical and experimental work has shown that the dominant loss was attributed to the cathode in the cell operating at the range of 600–850 °C [2–4]. There are two approaches to resolve this concern. One is to develop new cathode materials with higher performance than conventional strontium-doped lanthanum manganites ($La_{1-x}Sr_xMnO_3$, LSM) cathode materials, such as $La_xSr_{1-x}Fe_yCo_{1-y}O_3$ [5,6]. The other method is to optimize the microstructure of the LSM cathode [7,8]. Recently, there has been significant progress in the development of intermediate temperature anode-supported SOFCs with conventional LSM cathode. For example, de Souza et al. [9] reported that a thin-film SOFC with a yttria-stabilized zirconia (YSZ) electrolyte of ∼10 μm, a Ni/YSZ anode and a LSM-based cathode could achieve a high power density of ∼1.8 W cm^{-2} at 800 °C.

To improve the performance of the cathode, many groups have studied the relationship between the cathode microstructure and the electrochemical performance [10,11]. The electrode microstructure is controlled by several factors, such as the thickness of the cathode film, the particle size of electrode materials and the sintering conditions [7,12]. Choi et al. [7] reported that the LSM (mean diameter of 1.54 μm) showed a favorable activity in the initial stage, but this activity declined quickly. When the particle size was 11.31 μm, the LSM cathode possessed unsatisfactory initial activity, but this activity was quite stable due to a negligible change in the microstructure. A trade-off between the number of active sites and the particle growth rate was likely made at the intermediate size (about 5 μm) [7]. JØrgensen et al. [11] reported that the electrode microstructure was found to be less dense and contained smaller grains with the sintering temperature decreasing in the range from 1300 °C to 1150 °C. This resulted in a decrease in polarization resis-

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tance with the corresponding sintering temperature decreasing. It has been generally accepted that the electrochemical performance of SOFC cathodes can be improved by mixing the cathode materials with electrolyte materials to increase the three-phase boundary (TPB) sites. Murray and Barnett [13] reported that the polarization resistance of LSM–YSZ50 composite cathode was 1.31 $\Omega\,cm^2$ at 750 °C under open circuit on YSZ electrolyte substrate. It was lower than the polarization resistance of pure LSM cathode (3.5 $\Omega\,cm^2$). This result showed that composite cathodes have better performance than pure cathodes since the TPB could be extended three-dimensionally into the composite cathode [10,13–16].

The screen-printing technique is one of the most important methods to fabricate cathode film. Process parameters may affect the electrochemical active area, the electronic conductivity of the electrodes and the gas diffusion for the reactants. However, reports related to the influences of the process parameters on microstructure and performance of screen-printing LSM and LSM–YSZ composite cathode films were insufficient. In this work, the effects of several important process parameters comprising of the selection of binders, the mesh of screen, sintering temperature and sintering time were studied.

2. Experimental

The $La_{0.8}Sr_{0.2}MnO_3$ (LSM) powders were prepared as the cathode materials for SOFCs by the co-precipitation method. $Mn(NO_3)_2{\cdot}6H_2O$, $La(NO_3)_2{\cdot}6H_2O$ and $Sr(NO_3)_2$ (all with a purity level of >99.9%, Gansu rare earth) were dissolved with the stoichiometric composition into water and then titrated into $NH_4HCO_3/NH_3{\cdot}H_2O$ buffer solution which was stirred constantly. The co-precipitated products were washed by deionised water and dispersed in *n*-butanol, then azeotropic distilled to obtain the LSM precursors. The precursors were subsequently heated at 1000 °C for 2 h to obtain the LSM powders.

A YSZ (Tosoh, Japan) electrolyte pellet was prepared by being sintered at 1550 °C for 6 h with the size of 15 mm in diameter and 0.6 mm in thickness. Three-electrode setup was used to measure the electrochemical performance. The LSM powders were made into slurry by being mixed with 1 mass% binder (ethyl cellulose or polyvinyl-butyral) and organic solvent (terpineol). For the composite cathode, 80 wt% LSM and 20 wt% YSZ (30 wt% sintered at 700 °C for 2 h and 70 wt% un-sintered YSZ) powders were mixed homogeneous and made into slurry. The slurries were screen-printed (The mesh material was silk) onto one side of the electrolyte pellet before being sintered at different temperatures to prepare cathode (WE). The cathode area was 5 mm × 5 mm. A commercial Pt paste (PC-Pt-7840, sino-platinum metals) was painted on the cathode side as reference electrode (RE) and painted to the other side of the electrolyte pellet as the counter electrode (CE) (Fig. 1). The counter area was 7 mm × 7 mm. The Pt electrodes were fired at 850 °C for 30 min. The electrochemical performance of the cells was measured using a potentiostat/galvanostat (model PARSTAT® 2273, Princeton applied research). The impedance frequency range was 10 mHz to 10^5 Hz with a signal amplitude of 5 mV. The impedance fitting analysis was controlled with software (Zsimpwin). The microstructures of the surface and the interface between cathode and electrolyte were studied by scanning electron microscopy (SEM, HITACHI, S-4700).

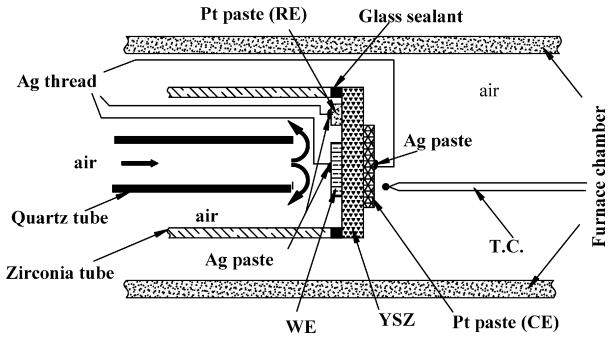

Fig. 1. Holder of three-electrode setup for high temperature electrochemistry measurement.

3. Results and discussions

3.1. Selection of binder for screen-printing slurry

The LSM cathode powders were made into slurry by being mixed with the binder and organic solvent before screen-printing. The selection of the binders would influence the microstructure of the cathode film. The binders for screen-printing cathode, ethyl cellulose and polyvinyl-butyral were evaluated. The fabricating process parameters were listed in Table 1 (sample A for ethyl cellulose as binder and sample B for polyvinyl-butyral as binder). The microstructures of the electrode films were measured by SEM (Fig. 2). It can be read-

Table 1
Process parameters for fabricating cathode films and impedance spectra data (measured at 800 °C)

Sample	Binder	Mesh screen	Sintering temperature (°C)	Sintering time (h)	Series resistance R_s ($\Omega\,cm^2$)	Polarization resistance R_p ($\Omega\,cm^2$)
A	Ethylcellulose	120	1200	2	0.8365	0.3961
B	Polyvinyl-butyral	120	1200	2	0.9567	0.7113
C	Ethylcellulose	100	1200	2	0.9577	0.8214
D	Ethylcellulose	140	1200	2	0.8576	0.909
E	Ethylcellulose	120	1150	2	1.11	0.95
F	Ethylcellulose	120	1250	2	1.261	0.851
G	Ethylcellulose	120	1300	2	1.237	1.205
H	Ethylcellulose	120	1200	1	0.899	1.0965
I	Ethylcellulose	120	1200	3	0.95	0.767