

Short communication

Comparative study on the performance of tubular solid oxide fuel cells with various $\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3/\text{YSZ}$ cathode layers made by different processes

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Abstract

Tubular solid oxide fuel cells (SOFCs) with different $\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3/\text{YSZ}$ cathode layers made by slurry spraying, slurry dip-coating and paste brushing were assembled and compared in their performance. In order to improve cathode–electrolyte coherency and interface behavior, dip-coating process was also employed to make the dense electrolyte surface with porous morphology. Electrochemistry impedance spectroscopy (EIS) and current–voltage tests were carried out to characterize the interfaces and the cell performance. Compared with the cell made by normal paste brushing, the cells made by slurry spraying and dip-coating exhibited a decrease of about 50% in electrode polarization resistance and an increase of 67% in the peak power output at 750 °C.

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Keywords: Slurry spraying; Dip-coating; Paste brushing; Cathode layers; Cathode–electrolyte interfaces; Tubular SOFCs

1. Introduction

Compared with the planar SOFCs, the tubular SOFCs are a better alternative because it is easier to be sealed, made into stacks and scaled up. Plenty of research work has been devoted to developing cost-effective fabricating techniques to pursue high cell performance. Anode-supported SOFCs are usually prepared by co-sintering anode–electrolyte double layers, and then cathode layer is deposited on electrolyte surface. High temperature is required to form dense electrolyte in co-sintering process that usually makes the electrolyte surfaces very smooth. The rather poor cell performance reported in literature usually comes from the high resistance of cathode–electrolyte interface that is probably due to the preparation process. In order to deposit a cathode layer on the smooth ceramic surface, high viscosity slurry or sol is usually applied to coating on electrolyte surface by screen-printing [1,2], paste brushing [3], dip-coating [4,5] and painting [6]. Spraying process such as electrostatic spraying [7], plasma

spraying [8,9] is also a choice to be attempted in the fabrication of SOFCs. The comparative study on the cells with various cathode layers is definitely worth to do in order to control the interfaces structure and improve the cells performance.

In this study, we fabricated dense YSZ electrolyte membranes with porous surfaces, which would expect to improve cathode–electrolyte interfaces made by dip-coating. Slurry spraying and paste brushing were also employed to fabricate cathode layers of tubular SOFCs. SEM, EIS and current–voltage tests were carried out to characterize interfaces made by different methods.

2. Experimental

2.1. Fabrication of NiO/YSZ tubes and electrolyte membranes

The preparing process of tubular anodes and cells is similar to the previous studies [10,11]. Tubular NiO/YSZ green bodies were made by extrusion or gel-casting [12]. After being dried, the tubes were pre-calcined at 1000 °C for 2 h. The pre-calcined tubes were dipped into fine-NiO/YSZ slurry whose powders were made by co-precipitation. Then, the tubes were sintered

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at 1100 °C for 2 h to form modified coats. The tubes with fine-NiO/YSZ coats were dipped into fine and coarse YSZ (Fuel Cell Materials) slurry and sintered at 1400 °C for 5 h to form dense electrolyte membranes, and named half-cells. The surface of the YSZ electrolyte membrane was examined by a SEM (a Hitachi X-650 Scanning Electronic Microscope).

2.2. Fabrication of cathode layers and cells test

$\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3$ powders were synthesized by glycine–nitrite process, and the process was similar to the previous study [13]. The obtained ash was subsequently calcined at 800 °C for 2 h to get oxide powders. The XRD of the powders was carried out on a Philips X'Pert Pro Super Diffractometer with Cu K radiation ($\lambda = 0.15418$ nm) for phase analysis. Composite cathode powders were made by mixing oxide powders of $\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3$ and YSZ at a weight ratio of 6:4. Cathode layers were prepared by slurry spraying [14], dip-coating [15] and paste brushing [3], respectively on the surfaces of YSZ electrolyte. After being sintered at 1150 °C for 2 h, the cells made from these methods were named cells A, B and C, respectively. The cathode–electrolyte interfaces of the cells were examined by SEM. EIS (Chi604a, Shanghai Chenhua) was performed on the cells under open-current condition at 750 °C. The current–voltage curves of the cells were measured from 700 to 800 °C in a cell-testing system with hydrogen as the fuel, air as the oxidant.

3. Results and discussion

3.1. Microstructure of YSZ electrolyte surface and cathode–electrolyte interfaces

The dense electrolyte surfaces of the half-cells made by co-sintering are usually very smooth, and only high-viscosity slurry can be coated on it. In order to improve it, we prepared electrolyte membrane with porous surface showed in Fig. 1. The porous surface would provide capillarity force for coating with low viscosity slurry. The open current voltages (OCVs) of the cells were all about 1.05 V, as indicated dense electrolyte membrane.

Fig. 2 is the XRD pattern of as-prepared powders calcined at 800 °C which showed perovskite $\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3$ phase, and other characterization of it would be reported in detail in another paper. As can be seen in Fig. 3, porous cathode layer of cell A mad by slurry spraying had uniform thickness and good contact with YSZ membrane. The particles of cathode deposited tightly and connected each other for being sprayed on half-cell by compressed air. Meanwhile, half-cells were dipped into cathode slurry to coat cathode layer. In order to make cathode layers with enough thickness, dip-coating process was repeated for three times. Fig. 3 shows cathode layer of cell B is much good contact with YSZ membrane due to capillarity force during dipping. So the slurry had soaked into the porous surface of YSZ membrane because of low viscosity. However, the thickness of cathode layer was quite small, un-uniform and hard to control. It can be solved by further improving electrolyte surfaces and cathode slurry, which is also going on in our study. For com-

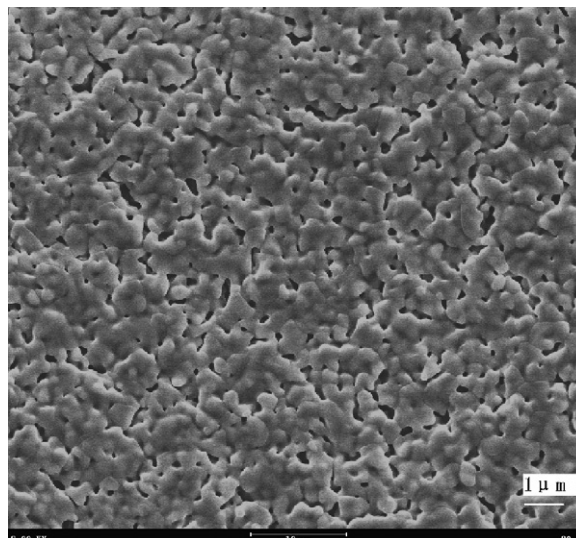


Fig. 1. the SEM photo of the YSZ electrolyte membrane surface with porous morphology.

parison, the cathode paste which used to be painted on smooth electrolyte films was brushed on half-cells by wool brusher. The paste could not be homogenously brushed on YSZ membranes because of high viscosity, especially for tubular SOFCs with large cathode area. Moreover, many air bubbles were remained in cathode layers and cathode–electrolyte interfaces during brushing. After being sintered, air bubbles became big pores, which were showed in Fig. 3 (cell C). The cathode particles of cell C were smaller than that of cells A and B and deposited more loosely. It was the reason that cell C made from the paste containing too much organic compound.

3.2. Electrochemistry characterization of cells

According to Fig. 4, the ohmic resistances of cells A, B and C at 750 °C were 0.53, 0.62 and 0.74 $\Omega \text{ cm}^2$, respectively, and the electrode polarization resistances were 0.49, 0.37 and 0.86 $\Omega \text{ cm}^2$, respectively. Since cells A, B and C were made from the same anode and electrolyte (half-cells), the differences in ohmic resistance and electrode polarization resistance

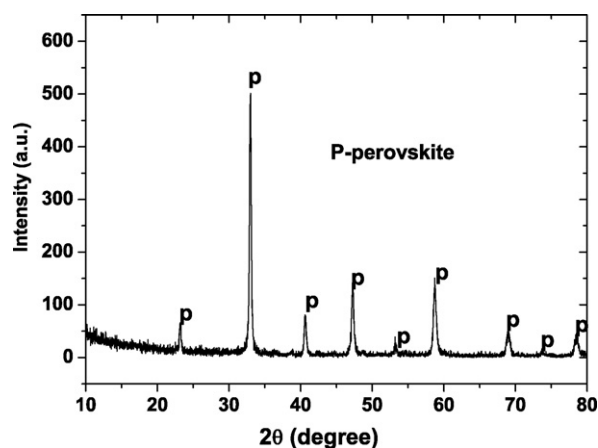


Fig. 2. The XRD pattern of $\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3$ powders calcined at 800 °C.

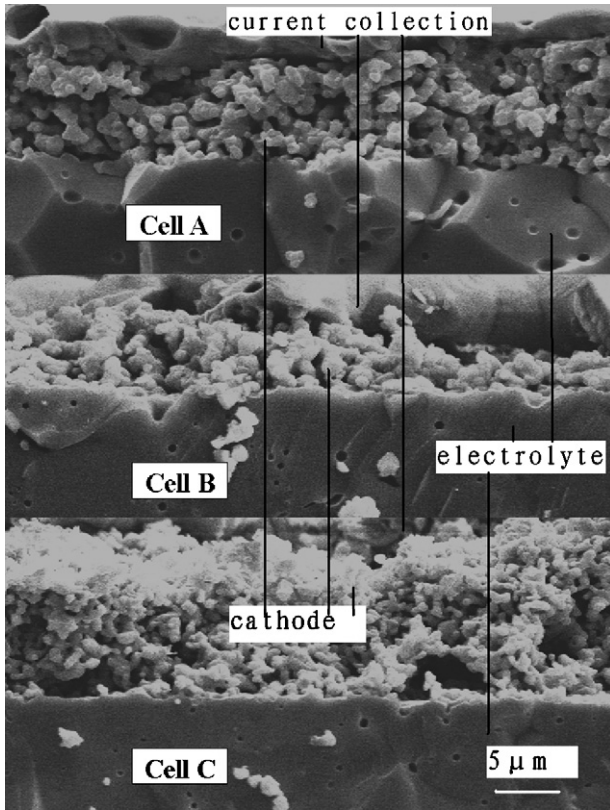


Fig. 3. The cathode–electrolyte interfaces of cells A, B and C.

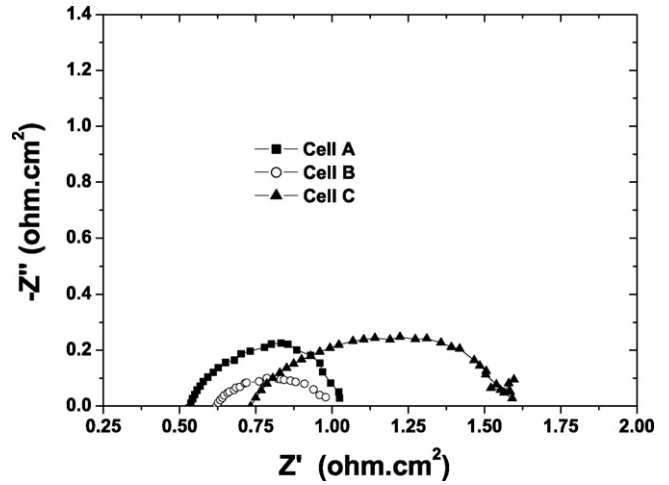


Fig. 4. The EIS of cells A, B and C tested at 750 °C.

must attribute to the different cathode ohmic resistances and cathode–electrolyte interfaces behavior. The cathode particles of cell A deposited tightly and good contact with YSZ membrane, so it showed lowest ohmic resistance. On the contrary, cell C showed highest ohmic resistance. Since some pores existed in cathode–electrolyte interface of the cell C, the effective cathode area would be reduced. Hence, cell C also showed highest electrode polarization resistance which were calculated by cathode area. Because capillarity made cathode layer much good contact with YSZ membrane, the cell B showed the lowest electrode polarization resistance.

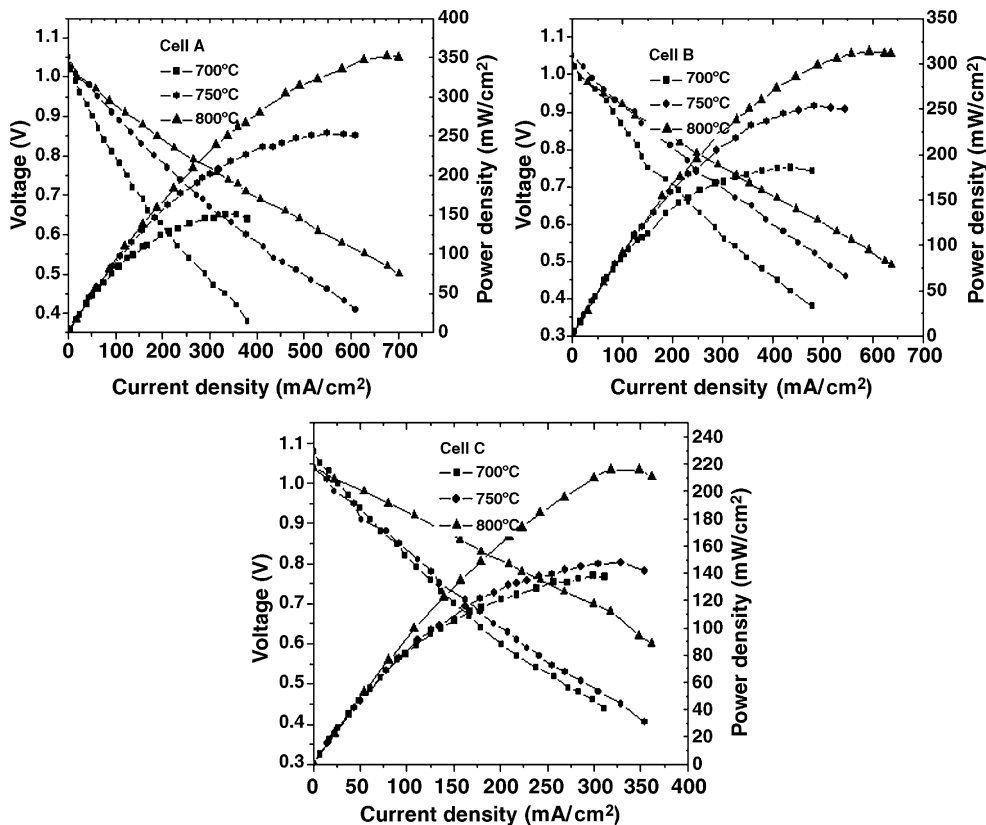


Fig. 5. The current–voltage and current–power curves of cells A, B and C.

The total resistances of the cells A and B were 1.02 and $0.99 \Omega \text{ cm}^2$, respectively, so they showed about the same peak power output (250 mW cm^{-2}) at 750°C showed in Fig. 5. The peak power output of cell C is only 60% as much as that of cells A and B because of higher total resistances ($1.60 \Omega \text{ cm}^2$). We also found the power output of cell B had smaller change with temperature than that of cells A and C. It was the reason that temperature had bigger effect on electrode polarization resistance than on ohmic resistance. So the dip-coating process may be suited for fabricating low and intermediate-temperature SOFCs for producing lower cathode polarization resistance.

4. Conclusion

Tubular SOFCs with various $\text{Pr}_{0.35}\text{Nd}_{0.35}\text{Sr}_{0.3}\text{MnO}_3/\text{YSZ}$ cathode layers made by three different methods were assembled and tested. The microstructure and cell performance were compared through SEM observation and electrochemical characterization. The results showed that slurry spraying and dip-coating had greatly improved cathode–electrolyte interfaces and cells performance, and would be potentially utilized for tubular SOFC commercialization. And dip-coating process made cells with lowest cathode polarization resistance.

Acknowledgement

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