Short communication

Preparation of $Pr_{0.35}Nd_{0.35}Sr_{0.3}MnO_{3-\delta}$/YSZ composite cathode powders for tubular solid oxide fuel cells by microwave-induced monomer gelation and gel combustion synthesis process

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Abstract

A microwave-induced monomer gelation and gel combustion synthesis process was successfully developed to synthesize well-dispersed $Pr_{0.35}Nd_{0.35}Sr_{0.3}MnO_{3-\delta}$ (PNSM)/YSZ composite cathode powders for tubular solid oxide fuel cells (SOFCs). The thermo-gravimetric (TG) analysis of as-prepared ash indicated the decomposition process of most of metal nitrates during gel combustion. The X-ray diffraction (XRD) pattern of the powders calcined at 1000 °C showed only pure PNSM and YSZ phase. Transmission electron microscopy (TEM) revealed that the morphology of powders was characterized with the YSZ particles enwrapped by fine PNSM particles so that PNSM/YSZ composite powders were much better-dispersed compared with the powders made simply by mechanical mixing process. The cell made from PNSM/YSZ composite powder showed lower cathode ohmic resistance and polarization resistance, and produced higher power density subsequently.
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1. Introduction

The performance improvement of solid oxide fuel cells (SOFCs) has attracted much research work mainly devoted to designing and synthesizing cell materials. Compared with mature anode and electrolyte materials, cathode materials have been studied more actively. In order to avoid reaction between the La in $La_{0.7}Sr_{0.3}MnO_3$ or $La_{0.6}Sr_{0.4}CoO_3$ cathode and the Zr in YSZ electrolyte, La was substituted by Pr [1] and Nd [2], respectively. In this study, we used $Pr_{0.35}Nd_{0.35}Sr_{0.3}MnO_{3-\delta}$ as cathode material, and the characterization of it would be reported in detail in another paper. The cathode layers of anode-supported cells should exhibit high electro-catalysis and have good contact with electrolyte films. So the cathode/electrolyte composite powders are usually used to fabricate cathode layers.

A wide variety of methods have been used to synthesize cathode powders for laboratory use, such as the solid-state reaction method [2], the glycine-nitrate process [3], the citrate method [4], the combined citrate-EDTA method [5], etc. Gel-casting process has also been demonstrated as a good choice to fabricate materials for SOFCs, including anode [6], electrolyte [7,8], and cathode [9]. Among these methods, combustion synthesis is more suitable for high activity cathode powders. The powders made by combustion synthesis have low depositing density and large contacting area between particles, which would increase the porosity and electrical conductivity of cathode layers, respectively. However, the powders made by gel-casting process aggregate to some degree and are required to be ground carefully.

Composite cathode powders are usually made by the mechanical mixing of cathode and electrolyte powders [10,11]. In this study, we developed a microwave-induced monomer gelation and gel combustion process to synthesize PNSM/YSZ composite cathode powders. For comparison, we also fabricated composite cathode powders by mechanical mixing. The TG

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analysis, phase, morphology, and electrochemical properties in cell of as-prepared powders were characterized.

2. Experimental

2.1. Synthesis of PNSM/YSZ powders

First, stoichiometric Pr_6O_{11}, Nd_2O_3, $SrCO_3$, and $MnCO_3$(all in 99.9%, Sinopharm Chemical) were dissolved in calculated amount of nitrate, and formed a cation solution. Organic monomer (acrylamide, AM) and cross-linker (*N,N*-methylenebisacrylamide, MBAM) were dissolved in deionized water to prepare a premix solution. Secondly, commercial YSZ powder, the cation solution, and the premix solution were mixed and ball-milled for 10 h, and a suspension was obtained. Then, the beaker containing the suspension was heated by a microwave oven (MA-2270EGC, 700W) for 10 min, and the suspension was gelated and combusted subsequently. Lastly, the as-prepared ash was calcined at temperatures ranging from 700 to 1000 °C for 2 h, and formed the PNSM/YSZ composite powders. For comparison, pure PNSM powders were also synthesized by the same process and mixed with commercial YSZ powder by ball-milling in ethanol. After being dried at 80 °C, the PNSM + YSZ powders were obtained.

2.2. Characterization of powders

The thermal, structural and morphological properties of as-prepared powders were characterized by several techniques.
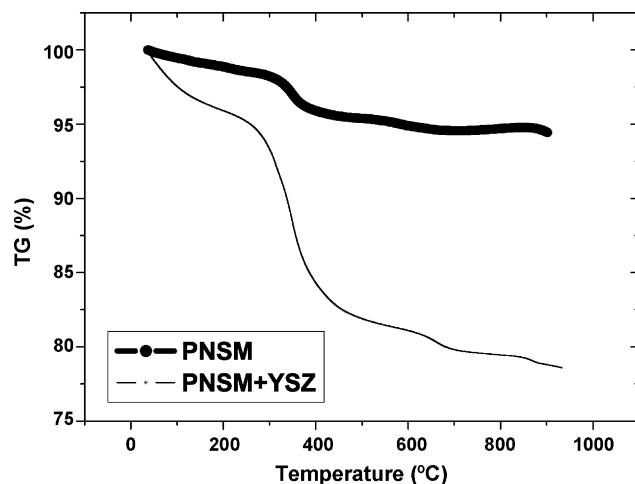

Fig. 1. Picture of the as-prepared cell.

Fig. 2. TG curves of as-prepared PNSM and PNSM/YSZ ash.

The TG analysis of the powders was carried out with Perkin-Elmer Diamond TG from room temperature to 950 °C at a heating rate of 10 °C min^{-1}. The XRD of the PNSM/YSZ powders, as well as pure PNSM and pure YSZ, was carried out on a Philips X'Pert Pro Super Diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm) for phase analysis. The particle size and morphology of powders were observed by TEM (JEOL-2010).

2.3. Preparation and test of cells

The process of fabricating tubular NiO/YSZ anodes with dense YSZ films was described in previous study [12]. The PNSM/YSZ composite powder and the PNSM + YSZ powder were deposited on YSZ electrolyte films by slurry spraying, and sintered at 1100 °C for 2 h to form cells. The cells made with PNSM/YSZ composite powder and PNSM + YSZ powder were named cell A and B, respectively. Fig. 1 shows the appearance of as-prepared cell. Electrochemistry impedance spectroscopy (Chi604a, Shanghai Chenhua) was performed on the cells under
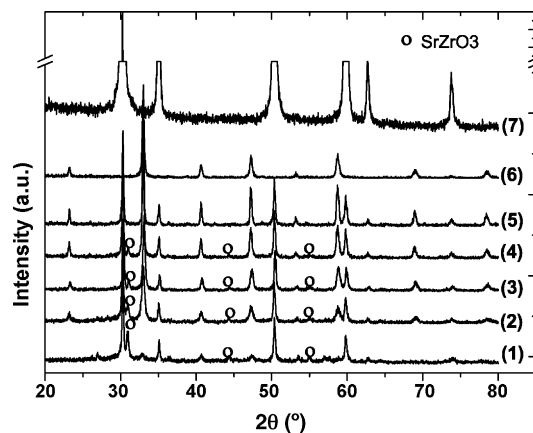

Fig. 3. XRD patterns of as-prepared powders and commercial YSZ: (1) the PNSM/YSZ powders without being calcined; calcined at: (2) 700 °C, (3) 800 °C, (4) 900 °C and (5) 1000 °C; (6) pure PNSM calcined at 800 °C; (7) commercial YSZ.
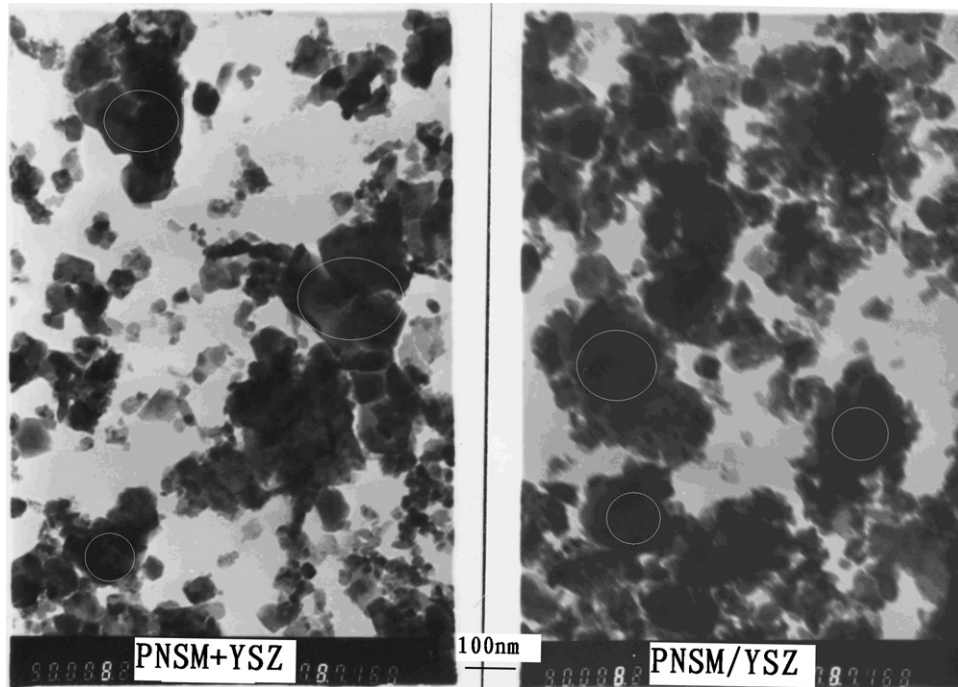
Fig. 4. Morphologies of the PNSM/YSZ powders and the PNSM + YSZ powders observed by TEM.

open-current condition with amplitude of 5 mV over the frequency range of 0.01 HZ to 100 kHz at 750, 800, and 850 °C. The current–voltage curves of the cells were obtained at the same temperatures in a cell-testing system. Hydrogen, as the fuel, flowed through anode tubes, and the cathode layers of cells were exposed in air, which was as the oxidant. The cathode layers of cells were characterized by scanning electronic microscope (Philips XL30 ESEM).

3. Results and discussion

3.1. TG analysis

The TG curves of the PNSM/YSZ and PNSM powders were given in Fig. 2. In the temperature range of 300–400 °C, there is a large mass loss owing to the combustion of organic compound [13], which indicated that organic compound cannot be combusted completely during gel combustion. The small mass loss at the temperature ranging from 400 to 700 °C could be attributed to the decomposition reactions of remained metal nitrates and forming perovskite phase, which indicated that most of metal nitrates had been decomposed during combustion process. The mass loss of the PNSM/YSZ powders during being heated was larger than that of the PNSM powders, and it was the reason that the YSZ powders in gel restrained organic compounds from combusting. Above 800 °C, there was still a little mass loss, which might be due to the loss of oxygen during forming perovskite phase.

3.2. Phase analysis

Fig. 3 shows different XRD patterns for as-prepared powders calcined at different temperatures. The as-prepared ash showed intense cubic YSZ phase and many other weak oxide phases. According to the XRD pattern of pure PNSM calcined at 800 °C, the PNSM/YSZ powders calcined at 700 °C already showed PNSM phase. With the increase of calcining temperature, crys-
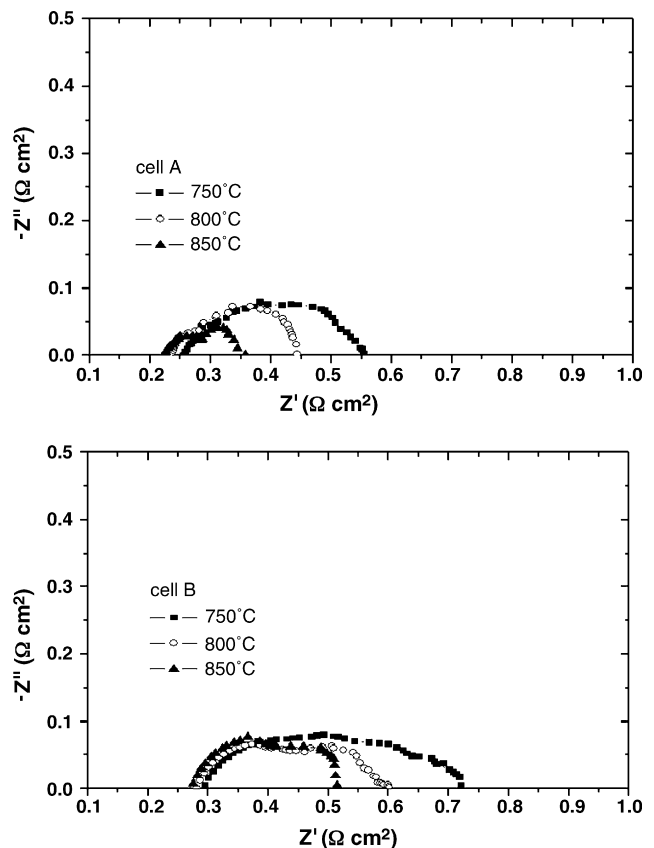

Fig. 5. EIS of cells A and B measured at 750, 800 and 850 °C.

tallinity increased subsequently. The data was in agreement with the TG analysis. Though a little $SrZrO_3$ phase (shown in Fig. 3), which was not found in pure PNSM powders, existed in powders calcined below 1000 °C, the powders calcined at 1000 °C showed pure PNSM and YSZ phases. So there was no impure phase in the final cells calcined at 1100 °C.

3.3. Powders morphology

The morphologies of the PNSM/YSZ powders and the PNSM + YSZ powders are shown in Fig. 4. The YSZ particles (about 100 nm, marked in Fig. 4) in the PNSM/YSZ powders were well-dispersed and enwrapped by fine PNSM powders, while YSZ particles (marked in Fig. 4) in the PNSM + YSZ powders aggregated and separated severely from aggregated PNSM particles. The difference could be attributed to different synthesis processes. First, while YSZ particles were ball-milled before gelation, organic monomer and cross-linker acted as dispersants and made YSZ particles disperse homogenously in suspension. Then, instantaneous gelation induced by microwave immobilized YSZ particles, which prevented YSZ particles from aggregating again in the following process. Lastly, the ash was adsorbed around YSZ particles after combustion.

3.4. Electrochemical properties in cells

The well-dispersed PNSM/YSZ powders would show higher electrical conductivity and electro-catalysis in the final cell than the aggregated PNSM + YSZ powders. It could be proved by the EIS of cells in Fig. 5. The cell A made with the PNSM/YSZ powders showed lower ohmic resistance and polarization resistance. Since, cells A and B had the same anode and electrolyte, cell A showed lower cathode ohmic resistance and polarization resistance. As a result, the cell A exhibited higher power density shown in Fig. 6. Compared with cell B, cell A showed obvious concentration polarization at a voltage of about 0.6 V. The reason of it could be that the well-dispersed PNSM/YSZ powders showed higher sintering activity and produced fewer pores in the cathode layer of cell A, which could be proved by the microstructure of cathode layers shown in Fig. 7. The cathode layer of cell B made from aggregated PNSM + YSZ powders was made up of big and small particles with poor connection, while the cathode layer of cell A made from well-dispersed PNSM/YSZ powders contained uniform small particles with good connection. Therefore, compared with the cathode layer of cell B, the cathode layer of cell A showed lower porosity, ohmic resistance and polarization resistance. The performance of cell A
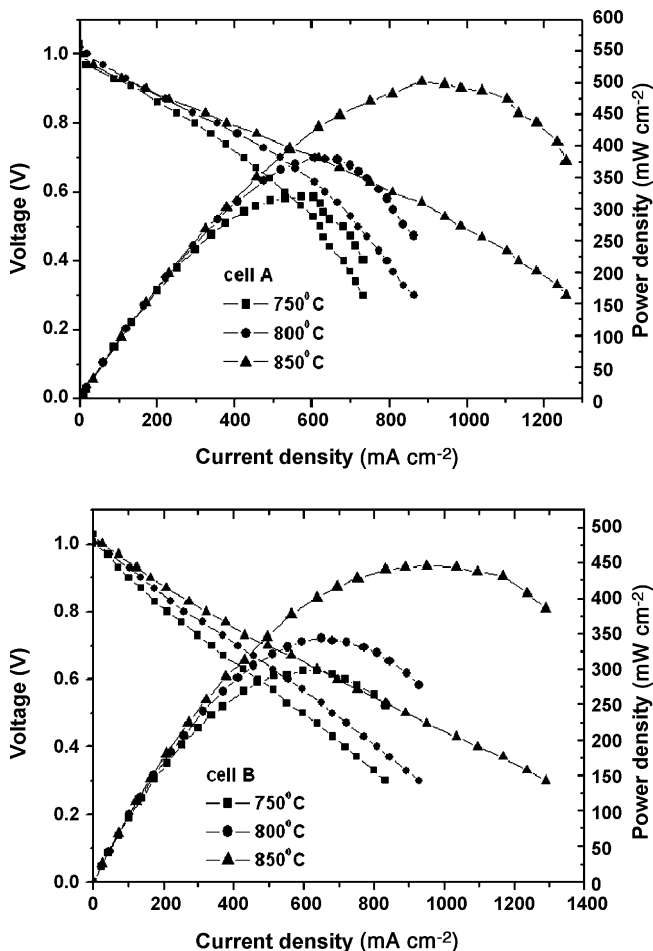

Fig. 6. Current–voltage and current–power curves of cells A and B measured at 750, 800 and 850 °C.
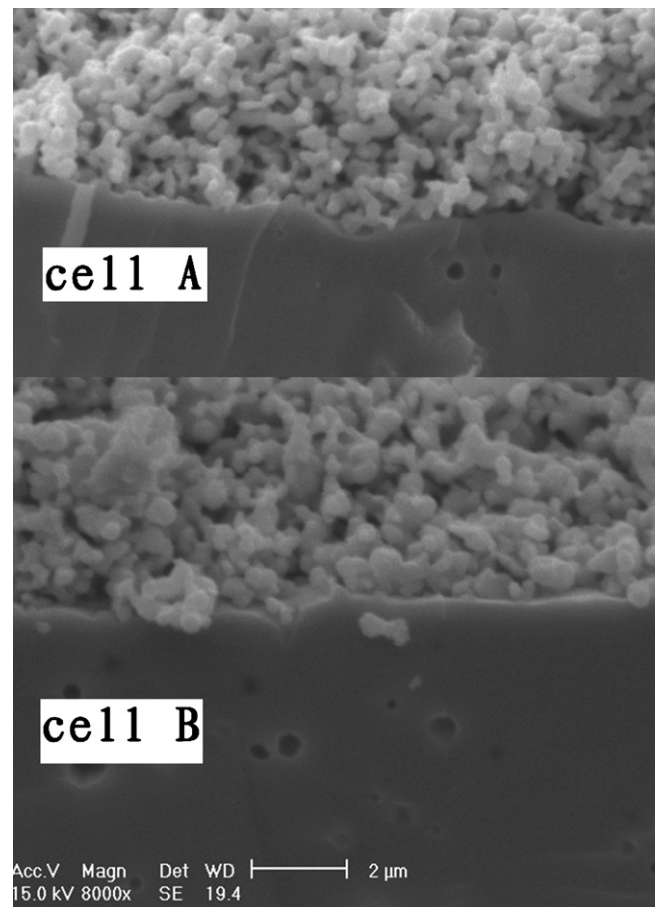

Fig. 7. Cathode layers of cells A and B.

could be further improved by increasing the porosity of cathode layer.

4. Conclusions

The well-dispersed PNSM/YSZ composite cathode powders were synthesized conveniently by a microwave-induced monomer gelation and gel combustion process. XRD pattern proved there had been no impurity phase in the powders calcined at 1000 °C. Compared with the commonly mixed PNSM + YSZ powders, the PNSM/YSZ powders showed higher electrical conductivity and electro-catalysis, and improved the final cell performance.

Acknowledgements

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