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Comparison of ultra-fast microwave sintering and conventional thermal sintering in manufacturing of anode support solid oxide fuel cell

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Microwave sintering with selective susceptor and spacer has been proved to be an effective and facile method in the manufacturing of anode support solid oxide fuel cell (1). Two anode support SOFCs were fabricated by using microwave sintering and thermal sintering techniques, separately. The performances of the two cells were measured and compared in a temperature range of 700°C to 800°C. The microstructures of the two cells after the measurements were compared qualitatively based on SEM images. FIB-SEM technique was used to reconstruct the 3-D microstructure of both anode and cathode. The quantitative comparison of 3-D reconstructions shows the advantages of using microwave in both anode and cathode sintering processes.

1. Introduction

Microwave heating offers an ultra-fast method for ceramic with an ultra-large heating rate. The grain size uniformity increases because of a few orders higher densification rate in a short sintering time. In this paper, further comparison is conducted between microwave-sintered and conventional-sintered cells on their performances and microstructures.

2. Results and discussions

Details of the manufacturing procedures of both microwave-sintered and thermal-sintered SOFCs have already been introduced in our previous paper. Fig. 1 shows the comparison of I-V performances between microwave-sintered and conventional thermal-sintered cells. The Anode-Cathode open circuit potential of microwave-sintered cell is around 0.95 V, which is lower than the theoretical value 1.135 V. The lower open circuit potential indicates the possibility of certain leakage across the thin YSZ film, which is caused by micro-cracks formed in the extremely fast microwave sintering process or measurement heating up process. Besides, the non-uniform electromagnetic field within domestic microwave oven may also lead to the micro-cracks within non-uniform sintering process (1). Without leakage problem, the performance of microwave-sintered cell can be further improved.

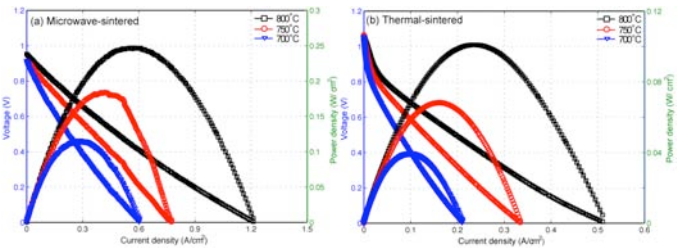

Fig. 1 The I-V characteristics comparison between microwave-sintered and thermal-sintered anode support SOFC at different temperatures. 3% H_2O, 97% H_2 as fuel and 100% O_2 as oxidant.

Fig. 2 shows the comparison of Anode-Cathode impedance spectra between microwave-sintered and conventional thermal-sintered cells. According to the high frequency spectra, the ohmic resistance of the cell sintered by microwave was about 0.55 Ω cm^2 at 800 °C which is only half of thermal-sintered cell. With the increase of temperature, the ohmic resistance slightly increases in both cases. From 800 °C to 700 °C, for microwave-sintered cell, the electrode polarization increases from 0.5 Ωcm^2 to 1 Ωcm^2, while for thermal-sintered cell, the increase is from 5.5 Ωcm^2 to about 31.5 Ωcm^2. Both of the impedance changes indicate that low-frequency polarization dominates the cell performance, especially for thermal-sintered cell.

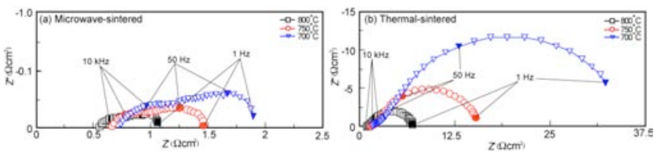

Fig. 2 Anode to cathode impedance spectra comparison between microwave-sintered and thermal-sintered cells.

The microstructures of the cells after testing were examined by SEM. Fig. 3 shows the SEM images of cross-sections, and the top surfaces of anode, electrolyte and cathode for both microwave-sintered and thermal-sintered cells. From the comparison it can be observed that, with the same materials used, microwave sintering results in very different microstructures from thermal sintering method. Microwave-sintered electrolyte is thinner than that of thermal-sintered one, and both methods resulted in fully densified YSZ film. The thiner electrolyte film in microwave sintering is mainly caused by the mechanical pressing applied by microwave susceptors. After sintering, microwave-sintered cell remained flat while thermal-sintered one was bent. Several microwave-sintered cells were tested, and similar deformations were obtained. For anode, microwave-sintering method produces finer and sharper particles than thermal sintering. For cathode, microwave sintering produced coarser LSM particle than thermal sintering, and the microwave-sintered LSM particle surface is rougher. Certain amount of sub-micron particles was observed uniformly on the particle surface. Besides the better performance obtained by microwave sintering, the cell durability was tested for the cell with constant current density. The cell performance presented no degradation in a 135 hours discharging process, after the initial increase of the performance.

In order to further investigate the anode microstructural differences between microwave sintering and thermal sintering methods, TPB densitiy was calculated based on 3D reconstructions of the microstructures of both anode (Fig. 4) and cathode (Fig. 5) by using centroid method (2). Results are shown in Table 1.

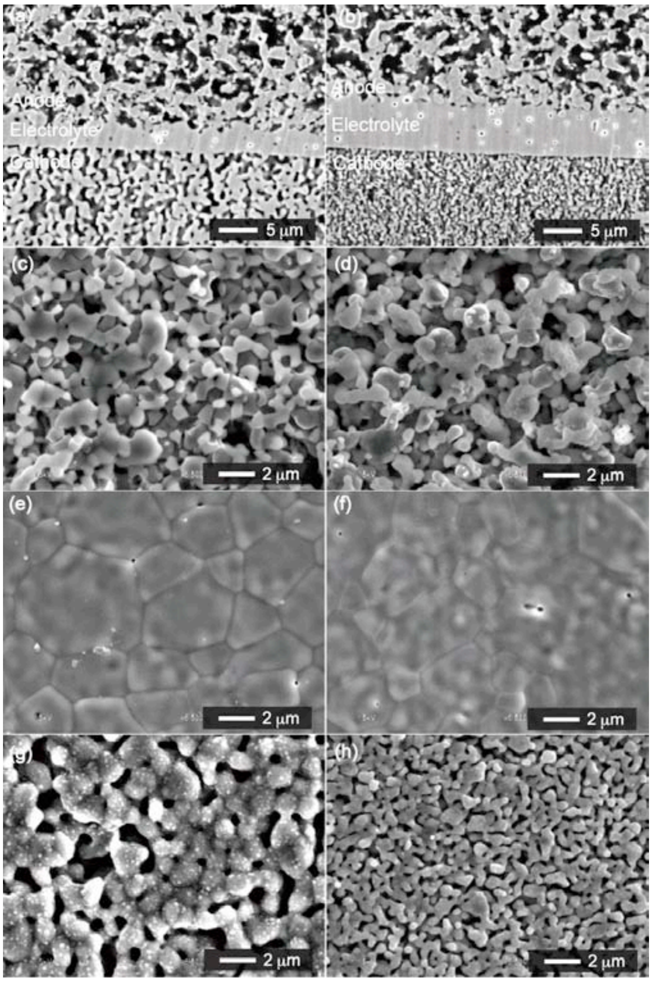

Fig. 3 SEM images of (a) microwave-sintered and (b) thermal-sintered cell cross-section, (c) microwave-sintered and (d) thermal-sintered anode, (e) microwave-sintered and (f) thermal-sintered electrolyte and (g) microwave-sintered and (h) thermal-sintered cathode.

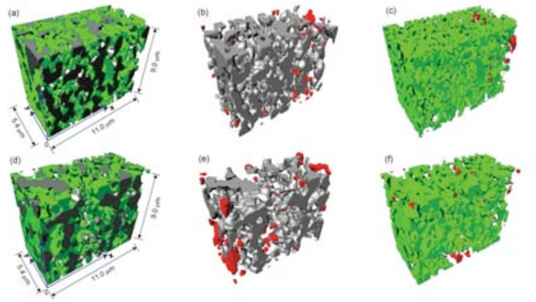

Fig. 4 3-D reconstructions of microwave-sintered (a) composite anode (b) Ni phase and (c) YSZ phase and thermal-sintered (d) composite anode (e) Ni phase and (f) YSZ phase. Red color indicates the non-pocolated particle clusters separated from the main phase network.

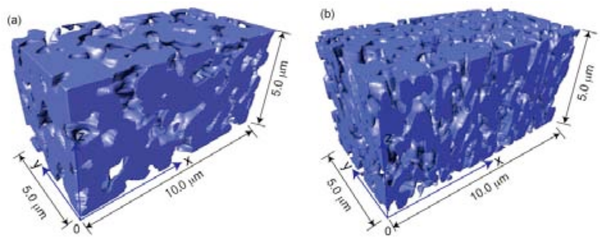

Fig. 5 3-D reconstructions of (a) microwave-sintered cathode and (b) thermal-sintered cathode.

3. Summary

Anode support SOFCs were fabricated by microwave-sintering and compared to thermal sintering one. The cell performances in the intermediate temperature range of 700-800^{o}C were measured. Microwave-sintered cell shows much better performance than thermal-sintered one. The reconstructed 3-D structures were used to quantify microstructural parameters such as porosity, percolation percentage and TPB density. The higher active TPB densities show the advantages of microwave-sintered anode. Microwave-sintered cathode is proven to have much better performance than thermal-sintered one because of the enhancement of active surface sites for oxygen adsorption.

Reference

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(2) N. Shikazono, D. Kanno, K. Matsuzaki, H. Teshima, S. Sumino, N. Kasagi, J. Electrochem. Soc. (2010) in press.

Table 1 TPB network properties of microwave-sintered and thermal-sintered anodes.

TPB density	Microwave-sintered	Thermal-sintered
Anode	$\mu m/\mu m^3$	$\mu m/\mu m^3$
Total 3-D TPB density	5.36	4.02
Active TPB density (x = 0→11.0 μm)	4.15	2.89
Active TPB density (y = 0→5.4 μm)	4.15	2.90
Active TPB density (z = 0→9.0 μm)	4.12	2.91
Active TPB density (x = 11.00→0 μm)	4.10	2.93
Active TPB density (y = 5.4→0 μm)	4.15	2.96
Active TPB density (z = 9.0→0 μm)	4.17	2.89
Cathode	$\mu m/\mu m^2$	$\mu m/\mu m^2$
2-D TPB density	1.7	4.0