Journal of Power Sources 195 (2010) 151–154

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Performance of an anode support solid oxide fuel cell manufactured by microwave sintering

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ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 4 July 2009
Accepted 6 July 2009
Available online 30 July 2009

Keywords:
SOFC
Microwave sintering
Susceptor

ABSTRACT

An effective and facile method has been developed to manufacture anode support solid oxide fuel cells in a multimode domestic microwave oven with selective susceptors. Anode support substrate pellets are prepared by an uniaxial pressing method, and then a thin YSZ electrolyte film is coated by a spray coating method. The electrolyte thickness is kept less than 10 μm. The anode supported electrolyte is co-sintered being sandwiched by two spacers and two susceptors in the microwave oven. A cathode is then screen-printed onto the sintered dense electrolyte film and sintered again in the microwave oven with only one spacer and one susceptor. The whole solid oxide fuel cell is sintered at lower temperatures compared to conventional thermal sintering temperature. The performance of the present solid oxide fuel cell is measured in an intermediate temperature range of 650–800 °C. The maximum power densities of 0.09, 0.12, 0.2 and 0.26 W cm^{-2} are obtained at operating temperatures of 650, 700, 750 and 800 °C, respectively.

1. Introduction

With the advantage of directly conversing chemical energy to electrical power, fuel cell has been identified as an attractive technique in the recent few decades. Solid oxide fuel cell (SOFC, hereafter) working in a high-temperature environment is attracting more attention because of its fuel flexibility and high efficiency. In order to achieve long time stability and reduce the equipment cost of the power conversion system, low temperature anode support SOFC has been investigated by many researchers with an emphasis on reducing the thickness of electrolyte, which dominants the fuel cell resistance. As a result, anode is always sintered with a thickness in a milimeter or sub-milimeter scale, while the thickness of electrolyte is kept less then 10 μm, and this kind of cell is called anode support SOFC.

Zhang et al. [1] reported a novel method for fabricating of thin film electrolyte. In their experimental procedures, 10- μm thick YSZ film was fabricated onto an anode substrate by revolving a rod at low rotation speed. Their cell shows a maximum power density of 1.4 W cm^{-2} at 800 °C. The anode substrate with thin film electrolyte is sintered at a temperature of 1400 ° C for 4 h, and the cathode screen-printed on the electrolyte layer is sintered at a temperature of 1200 ° C for 2 h. In most of the papers published, the investigations of SOFC mainly focus on electrode materials and their fabrication processes, and all the cells are sintered by the conventional heating method.

The conventional sintering method is time- and energy-consuming, so that some researchers have shown a possibility of using microwave energy for rapid sintering [2,3]. It is a self-heating process which is accomplished by absorbing electromagnetic energy by a dielectric material. Higher heating speed and efficiency can be obtained with a low thermal stress gradient by microwave volumetric heating. The energy absorbed by a dielectric material per volume is estimated as [2]:

$$P = \frac{1}{2}\varepsilon_0 \varepsilon'' \omega E^2 V \quad (1)$$

where ε_0 is the dielectric constant in a vacuum, ε'' is the dielectric loss factor of the material, and ω is the angular frequency of the external electromagnetic field. At room temperature, most of the ceramics have low dielectric loss factor so that it is impossible to raise the temperature. Susceptors made by special material with large dielectric loss coefficient are needed as a pre-heater to raise temperature to the critical value beyond which the material to be sintered can be self-heated.

In the microwave sintering method, the material itself generates heat and this volumetric heating mechanism makes the sintering process rapid and selective. Fujitsu et al. [2] used microwave energy successfully to achieve the sintering of stabilized zinconia in a 2.45-GHz multimode microwave furnace with selective susceptors. The full sintering temperature of zinconia was reduced by 100–150 ° C

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doi:10.1016/j.jpowsour.2009.07.009

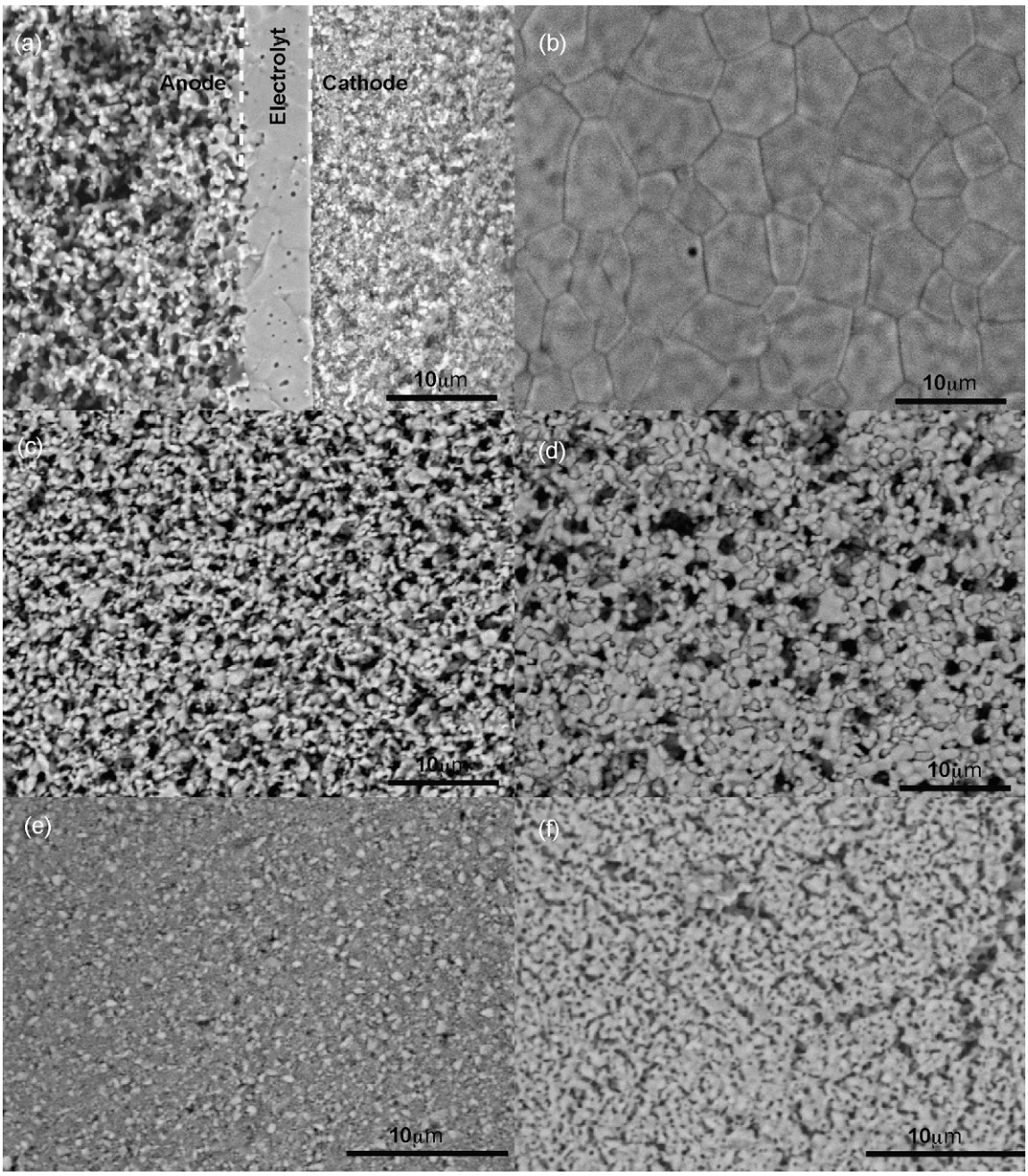

Fig. 1. SEM images of (a) microwave sintered anode support SOFC cross-section, (b) microwave sintered electrolyte film surface, (c) microwave sintered anode microstructure, (d) conventional sintered anode microstructure (1400 °C, 3 h) [1], (e) microwave sintered cathode microstructure, and (f) conventional sintered cathode microstructure(1200 °C, 2 h) [1].

as compared to the conventional sintering, and a finer grain size was obtained. In a review of this technique, Clark [4] summarized the fundamentals, benefits, and major research issues of microwave processing of materials.

Microwave heating offers an ultra-fast method for ceramic with an ultra-large heating rate. The grain size is smaller than the grain sintered by conventional method, while the grain size uniformity increases because of a few orders higher densification rate in a short sintering time. According to authors' knowledge, only a few groups have investigated the use of microwave sintering to manufacture SOFC [5]. In this paper, a new method of manufacturing anode support SOFC with microwave sintering is presented. The performance of the SOFC thus obtained is investigated experimentally.

2. Experimental procedures

2.1. Preparation of anode substrate and microwave susceptor pellets

NiO powder (1 μm) and YSZ powder (1 μm) were used to prepare NiO–YSZ anode substrate pellets. The powders were mixed at a ratio of 50:50 wt%. In order to maintain a sufficiently porous structure, pore former was added to the powder mixture. The final mixed powder was uniaxially compressed in a metal die at 30 MPa pressure to make anode substrate pellets with a diameter of 20 mm and a thickness of 0.8 mm. The pellets obtained were then pre-sintered at 1100 ° C for 2 h in a conventional sintering furnace to improve the mechanical strength.

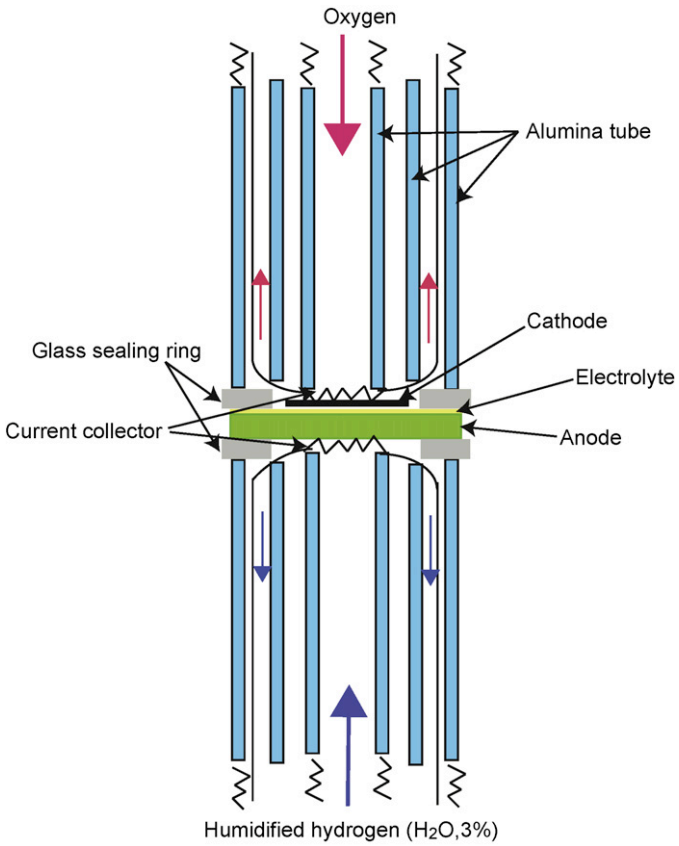

Fig. 2. Schematic of SOFC measurement setup.

Microwave susceptor pellets were prepared before the microwave sintering experiments. The microwave susceptor pellets (30 mm in diameter and 3 mm in thickness) were made by the same technique as substrate pellets, while the material used is $72.5ZnO–27MnO_2–0.5Al_2O_3$, ZMA, hereafter. ZMA was prepared by mixing zinc oxide, manganese dioxide and alumina powders (High Purity Chemical Laboratory, Sakado, Japan) [2]. YSZ spacer pellets (20 mm in diameter and 0.8 mm in thickness) were made by YSZ powder (0.3 μm, Tosoh Co., Japan) and then sintered in furnace at 1350 ° C for 2 h. The spacers were used between the cell and the ZMA susceptor to prevent contamination, and at the same time contributed to the temperature rise up to 1300 ° C as discussed in the previous section.

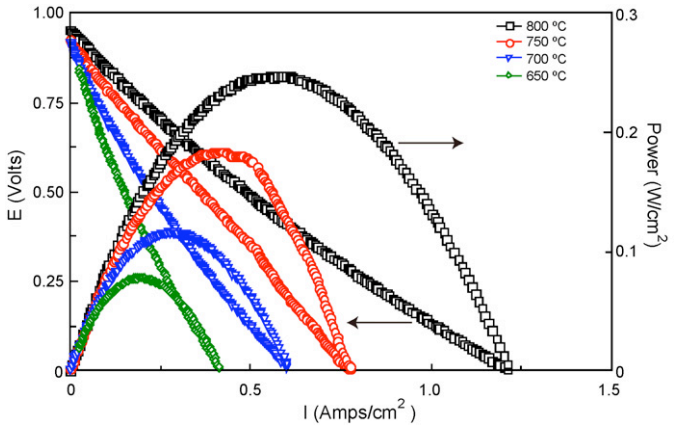

Fig. 3. The *I–V* characteristic of microwave sintered anode support SOFC at different temperatures. 3% H_2O, 97% H_2 as fuel and 100% oxygen as oxidant.

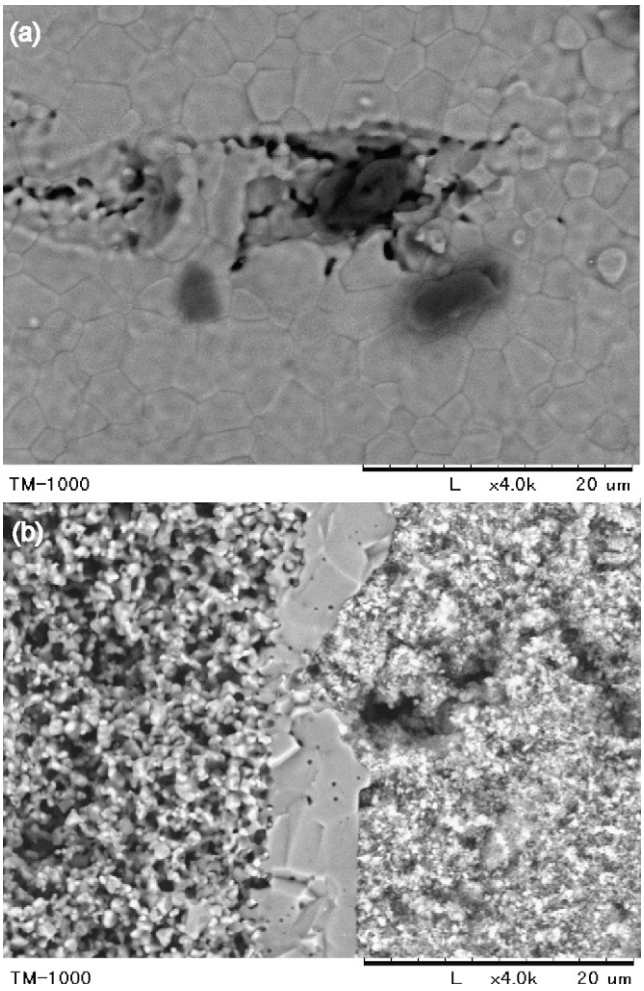

Fig. 4. (a) Micro-cracks on free electrolyte surface. (b) Micro-cracks at anode–electrolyte–cathode cross-section.

2.2. Fabrications of thin film electrolyte and cathode

The thin film electrolyte was spray-coated onto the substrate pellets by using a nozzle. The spraying coating slurry was prepared by YSZ powder (0.3 μm) from Tosoh Co., Japan. A mixture of isopropyl alcohol and terpineol was used as solvent, while ethyl cellulose was used as an organic binder. The organic binder was mixed with YSZ powder first, then added into the solvent. The slurry was ball mixed for 24 h to obtain a homogeneous slurry, which contains 0.33 g solid per microliter slurry. The slurry was then sprayed onto substrate pellets by using the nozzle under slight air pressure (≈ 0.7 MPa).

After spray coating, the pellets were dried in the air for 24 h, and then the pellets were sintered in a multimode microwave oven. The anode substrate pellet was sandwiched by two YSZ spacer pellets and then they were sandwiched by another two ZMA susceptor pellets. The pellet series were then put into a fibrous alumina–silica case (Kaowool 1700 Board, Isolite Insulating Products Co., Ltd., Osaka, Japan) for thermal insulation. The isothermal case was then put at the center of the turning table with a kaowool board as spacer between the case and the glass table. The power was turned to maximum and the cell was sintered for 20 min.

$La_{0.8}Sr_{0.2}MnO_x$ (LSM) powder (0.4 μm) was used as a cathode material in this study. LSM powder was mixed with Tosoh YSZ powder in a weight ratio of 60:40 wt%. The powder was then mixed with the terpineol solvent and the ethyl cellulose binder in agate mortar to obtain cathode printing paste. The LSM–YSZ mixture paste was

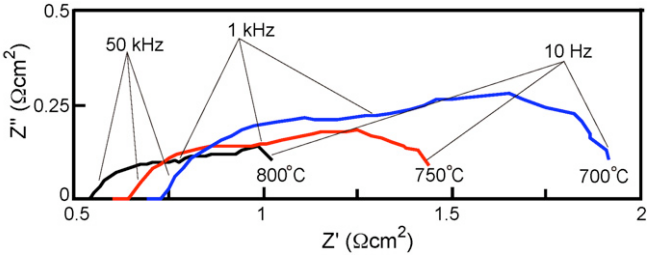

Fig. 5. Anode to cathode impedance spectra of microwave sintered SOFC at different temperatures.

then screen-printed onto the electrolyte film and sintered in the microwave oven for 10 min, with an effective area of 28.26 mm^2. For cathode sintering, only one ZMA susceptor with one YSZ spacer was applied as the sintering base to reduce the sintering temperature.

3. Results and discussion

The microstructure morphology of the sintered SOFC was examined by Hitachi Miniscope TM-1000 (Tokyo, Japan) scanning electron microscope (SEM). Fig. 1(a) and (b) shows the cross-sections and the electrolyte film surface of the anode support SOFC sintered by microwave. From the images we can see that dense film of YSZ electrolyte was obtained in a short time sintering in microwave. Porous anode and cathode structures were obtained and certain residual pores can be observed in the electrolyte layer.

Fig. 1(e) and (f) shows the comparison between microwave sintering and conventional sintering [1]. For conventional sintering, temperature was raised so that dense electrolyte layer was obtained. The anode and the electrolyte layer were co-sintered at 1400 ° C for 3 h, and then the cathode was sintered at 1200 ° C for 2 h. It is seen that the microwave sintering method results in finer microstructure than the conventional sintering method. For mechanical strength, the microwave sintered cell is slightly weaker than the conventional method sintered one. This is mainly because of shorter sintering time. The sintering at inter-particle boundary was enhanced by the microwave driven high-frequency ion vibration, while the short time of sintering process inhibits the grain growth.

The SOFC performance measurement setup is shown in Fig. 2. Pt meshes were used as current collectors, which were pressed against the electrodes of the cell by springs. Glass rings were used as the seals between two outer alumina tubes, and the two outer tubes were also pressed against the cell by spring. After the temperature was increased beyond 600 °C, the glass seals were melted and covered both edges of the cell and the two outer tubes completely, which resulted in perfect sealing. The performance of SOFC was evaluated at different temperatures by using humidified hydrogen and oxygen. *I–V* characterization and ac impedance (frequency range 1– 10^5 Hz) measurements were conducted with a Solatron frequency analyszer and a Solatron interface.

Fig. 3 shows the *I–V* performance of the microwave sintered anode support SOFC with a 8- μm thick YSZ electrolyte film. The cell was tested by introducing H_2 with humidity of 3% steam, and pure oxygen. It is shown that the maximum power densities are 0.09, 0.12, 0.2 and 0.26 W cm^{-2} at 650, 700, 750 and 800 °C, respectively. The open circuit potential is about 0.95 V, which is smaller than the theoretical value 1.135 V. The decreased open circuit potential indicates a possibility that there was leakage across the thin YSZ film, which is caused by residual pore or micro-cracks formed in the measurement heating up process.

Fig. 4 shows two examples of the micro-cracks on free electrolyte surface and anode–electrolyte–cathode cross-section. It is known that, in the home-use microwave oven, the electromagnetic field intensity is not uniform. In such kind of microwave sintering process, certain thermal stress can be formed in the process of ultra-fast sintering. Although the residual thermal stress was not strong enough to break the cell, micron-scale cracks can be formed easily and cause the cross-over leakage problem, especially when the cell was pressed by alumina tubes in high-temperature environment. In the future, this problem can be resolved by replacing the current home-use microwave oven by a professional designed microwave oven which offs a stable and uniform electromagnetic field.

Fig. 5 shows three impedance spectra under open circuit condition at three different temperatures. According to the high measurement frequency region, the total ohmic resistance of the cell at 800 ° C was about 0.55 Ω cm^2, of which 0.15 Ω cm^2 comes from the measurement system. With the increasing of temperature, the cell area specific ohmic resistance slightly increases while the electrode polarization increases drastically. This fact means that the electrode polarization dominates the cell performance.

Several microwave sintered cells were tested with humidified H_2 as fuel and oxygen as oxidant, and similar results were obtained. Because of the micro-cracks which was caused by the non-uniform sintering by home-use microwave oven. Some cell samples were even cracked by the serious asymmetric deformation, so did the spacers. Besides, the power output of the microwave oven cannot be precisely controlled, while the initial large power output resulted in large temperature gradient across the sandwich structure in the first few minutes, and this also influenced the cells quality. In the future, if the cell after reduction can be processed in such special designed device, the value of ceramic adhesion to the metal can be increased by 200–300% [6], and the enhancement can be used to improve the interactions between YSZ and nickel particles so that SOFC durability can be improved.

4. Conclusions

Anode support SOFC was successfully sintered by using microwave energy. The cell performance in the intermediate temperature range of 650–800 ° C was presented. The cross-over electrolyte leakage problem makes the open circuit potential lower than the theoretical value. The impedance spectra show that the cell performance was deteriorated by the electrodes polarization rather than the ohmic resistance. The cell quality can been improved if a professional microwave oven with precise electromagnetic field controlling can be applied in the sintering process. With the achieving of ultra-fast heating up process and uniform electromagnetic filed in the sintering chamber, good performance SOFC can be manufactured in much higher efficiency compared to conventional sintering.

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