



Short communication

An ultra-fast fabrication technique for anode support solid oxide fuel cells by microwave

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ABSTRACT

An effective and facile technique has been developed for high temperature anode-electrolyte co-sintering of anode support solid oxide fuel cells by using microwave activated sparking plasma. A high sintering temperature of 1600 °C can be achieved in a few minutes time by discharging effect. Anode support substrate pellet is uniaxially pressed, and then dip-coated with a 10 μm yttria stabilized zirconia electrolyte layer. After the microwave co-sintering, La_{0.8}Sr_{0.2}MnO_x cathode is screen-printed onto electrolyte and sintered by conventional thermal method. The cell has stably operated in 3% humidified hydrogen for more than 130 h.

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1. Introduction

With the advantage of directly converting chemical energy to electrical power, fuel cell has been identified as an attractive technique in the recent few decades. In most of the papers published, the investigations of solid oxide fuel cells (SOFCs, hereafter) mainly focus on electrode materials and their fabrication processes based on the conventional thermal heating method. The properties of ceramic materials mainly depend on the fabrication method, and the use of microwave in ceramic materials processing has recently become an active area. The volumetric, selective, and ultra-fast nature of microwave heating can lead to the advanced ceramic material compositions and microstructures that cannot be achieved by using conventional thermal heating [1–6]. Microwave sintering leads to a higher heating rate and efficiency with a lower thermal stress gradient because of lower temperature gradient. The power absorbed by a dielectric material of volume V is estimated as [3], $P = (1/2)\epsilon_0\epsilon''\omega E^2V$ where ϵ 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 their temperature. Susceptors made by special material with large dielectric loss coefficient are needed as a pre-heater to raise temperature up to a critical value beyond which the material to be sintered can be self-heated [1–3].

Fujitsu et al. [3] used microwave energy to achieve the sintering of stabilized zirconia in a 2.45-GHz multimode microwave furnace with selective susceptors. The sintering temperature of zirconia was reduced by 100–150 °C comparing to the conventional sintering, and a finer grain size was obtained. 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 [7]. In this paper, a method of fabricating anode-support SOFC using microwave is presented. Comparing to previous sandwiching microwave sintering method [1,3], the microwave sintering technique achieved much higher sintering temperature and shorter sintering time by applying solid discharging effect, while the cell quality and the reproducibility of the fabrication process are also improved. The performance of the SOFC thus obtained is investigated experimentally.

2. Experimental materials and methods

NiO powder (1 μm) and yttria stabilized zirconia (YSZ, hereafter) powder (1 μm) were mixed at a ratio of 60:40 vol% and 10 wt% pore former was added to the mixture. The mixed powder was uniaxially compressed in a metal die at 100 MPa 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 before dip-coating the electrolyte.

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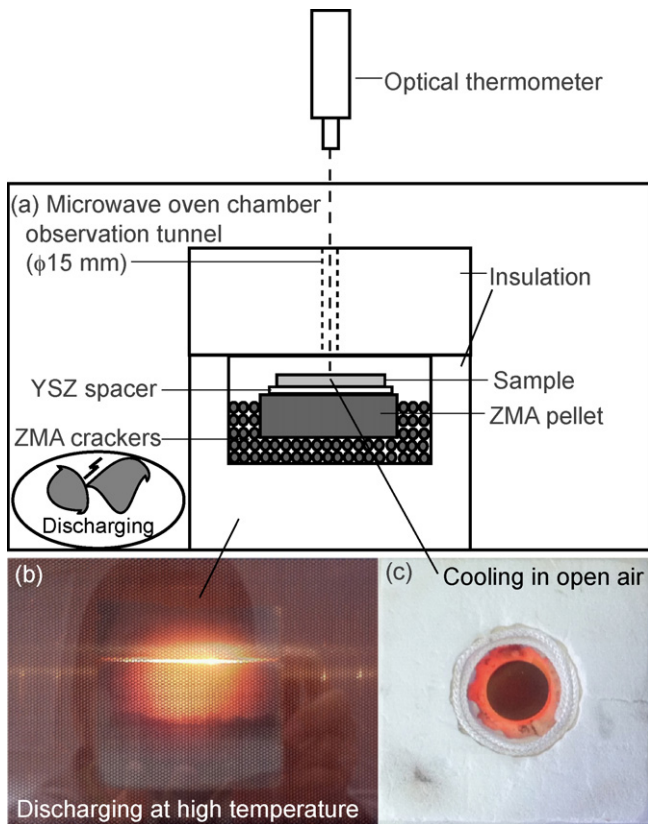


Fig. 1. Illustration of experimental setup.

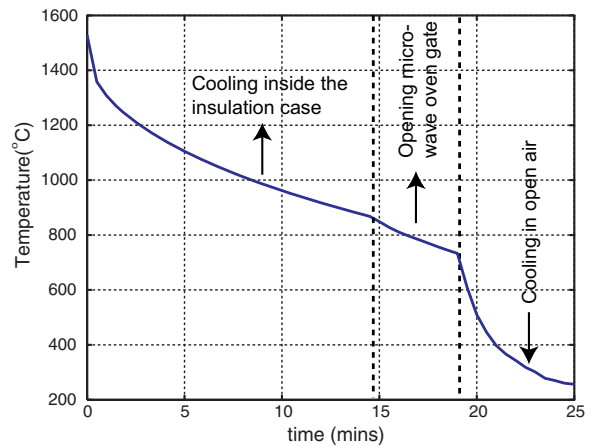


Fig. 2. Temperature history of the sample top surface in cooling process.

The material used for microwave susceptor is $72.5\text{ZnO}-27\text{MnO}_2-0.5\text{Al}_2\text{O}_3$, ZMA, hereafter [3]. ZMA was prepared by mixing zinc oxide, manganese dioxide and alumina powders (High Purity Chemical Laboratory, Sakado, Japan). The mechanically pressed susceptor pellets (30 mm in diameter, and 3 mm in thickness) were sintered in at 1300°C for 2 h. YSZ spacer pellets were put between the cell and the ZMA susceptor to prevent contamination.

The thin film YSZ electrolyte was dip-coated onto the substrate pellets, then the pellets were sintered in a domestic multimode microwave oven (SHARP, RE-T1, 700 W). The anode substrate pellet was put on YSZ spacer and then they were put on ZMA susceptor pellet, surrounded by small pieces ZMA crackers in a fibrous alumina-silica case (Kaowool 1700°C Board, Isolite Insulating Products Co. Ltd., Osaka, Japan), as shown in Fig. 1(a). An observation

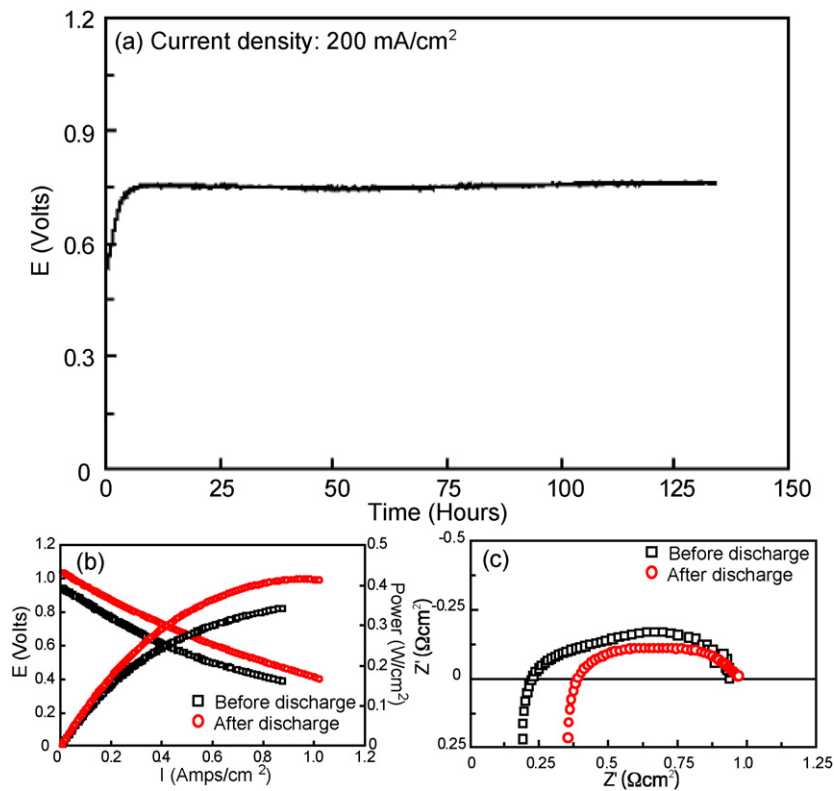


Fig. 3. (a) Anode-to-cathode terminal voltage versus time in discharge (current density: 200 mA cm^{-2}); (b) anode-to-cathode IV curves and (c) impedance spectra before and after discharge.

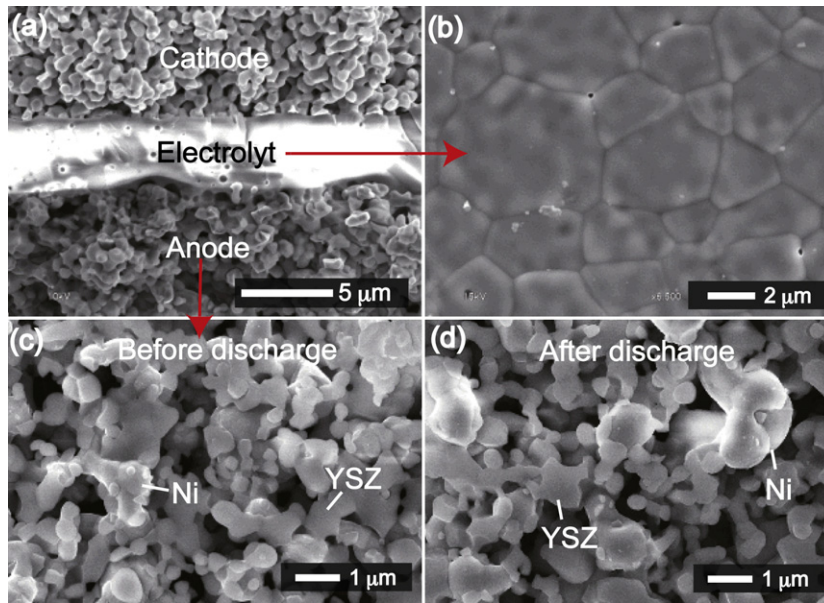


Fig. 4. Micro-scale SEM images of SOFC (a) cross-section, (b) densified electrolyte surface, (c) anode after reduction and (d) anode after discharge.

tunnel was made at the center of the case cover with a diameter of 15 mm for sample temperature measurement in cooling process. The power was turned to maximum and the cell was sintered for 8 min. In order to focus on the most challenging anode-electrolyte high temperature co-sintering process, conventional thermal heating method was used to sinter the cathode. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_x$ powder ($0.4\ \mu\text{m}$), was mixed with Tosoh YSZ powder in a ratio of 50:50 wt%, with terpeneol solvent and the ethylcellulose binder in agate mortar to obtain cathode slurry. The cathode was screen-printed and sintered at $1200\ ^\circ\text{C}$ for 2 h, with an effective area of $28.26\ \text{mm}^2$.

After turning on the power of the microwave oven, the inner temperature of the insulation case was raised up by the energy-absorbing effect of ZMA. With the increase of temperature, the mobility of ZMA surface ions increased a lot. The sharp corners of the ZMA crackers and the pellet enhanced the electric field at the contacting points. It has been simulated by Birnboim et al. [5] that the electric field generated during microwave sintering of ceramics exhibits strong variations in intensity. For a two-touching-spheres model the internal peak field in the neck region can be much larger than the average field, the local absorbed power can be 500 times larger than the averaged absorbed energy, so that a field emission current phenomena can be initiated. The ions were then tunneled out of the ZMA tips via tunneling and the large bias electric field and led to a very high local current density at the tip-contacting

point, since it came out of a very small area of the tip. The field created in the air near the neck can also be strong enough to ionize the ambient gas, and a very strong sparking plasma discharging effect was then observed. As shown in Fig. 1(b), from the gap between the case block and its cover, strong plasma flash can be observed, which made the chamber very shining. The temperature in this stage cannot be measured by top-located optical thermometer because of the interference of strong discharging effect. The local discharging effect propagated from certain points to the entire chamber in about 6 min. The strong discharging effect was maintained for 2 min for anode-electrolyte co-sintering, after which the power of microwave oven was switched off. In the discharging process, high-energy pulses at the points of inter-granular bonding lead to significant improvements over conventional thermal sintering.

Right after switching off the power, the temperature history of the sample top surface was recorded by the optical thermometer as shown in Fig. 2. The cover of the insulation case was removed when the temperature was down to about $700\ ^\circ\text{C}$, as shown in Fig. 1(c). It can be seen that the maximum temperature of sample surface reached by microwave sintering was about $1600\ ^\circ\text{C}$. After the sintering, it was observed that at the bottom of the case chamber, the insulation material was partially melted which meant that the local maximum temperature inside the chamber can reach more than $1700\ ^\circ\text{C}$. The initial average temperature increasing rate can

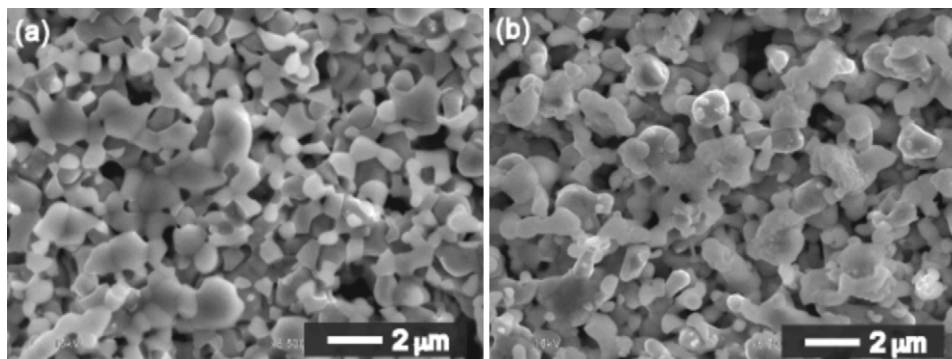


Fig. 5. SEM images of the top-views of (a) microwave sintered anode and (b) conventional thermal sintered anode after reduction (convention thermal sintering at $1400\ ^\circ\text{C}$, for 3 h).

be more than $300\text{ }^{\circ}\text{C min}^{-1}$, which is much higher than the previous report [3,4].

3. Results and discussions

The cell was then operated in 3% H_2O hydrogen at $800\text{ }^{\circ}\text{C}$ with a current density of 200 mA cm^{-2} . Measurement details have been described in Ref. [1]. The anode-to-cathode terminal voltage against time was plotted in Fig. 4(a). In about 130 h discharge, the cell performance increased initially and became stable afterwards. Fig. 4(b) shows the anode-to-cathode IV curves comparison before and after discharge, which shows that the cell anode-to-cathode performance was improved by the discharging process. It is also seen that the initial OCV was lower than the theoretical one (about 1.13 V), while the OCV was improved after the discharge. We have reported a similar phenomenon in Ref. [1]. The lower OCV may be caused by micro-cracker formed in the heating up process or the non-perfect glass sealing. In the discharging process, the leakage problem was improved. The anode-to-cathode impedance comparison before and after the discharge is shown in Fig. 3(c). After the discharge, the area-specific ohmic resistance increased while the area-specific polarization resistance decreased.

Fig. 4(a) and (b) shows the cross-sections and the electrolyte film surface of the anode support SOFC sintered by microwave after reduction. From the images we can see that dense film of YSZ electrolyte was achieved in the extremely short time sintering in microwave. Fig. 4(c) and (d) shows the anode microstructures before and after the discharge. The sintering of the YSZ network was established via inter-particle necks, which were formed around the contact area between two adjacent YSZ particles, since the microwave field intensity at neck can be amplified. So that particle growth of the starting powder materials was controlled, and it can be seen that YSZ particle original sharp-corner shape was kept after the short time sintering. The controlled sintering of YSZ particle led to smaller particle size so that larger TPB density in composite Ni-YSZ anode, which may explain the low polarization resistance of the cell, compared to conventional sintered cell [1]. It has also been reported by Singh et al. [8] that the cermets obtained from reduction of microwave processed composites have more uniform grain growth as compared to that obtained from conventionally processed composites. In this study, Fig. 5 shows the comparison of microwave sintered and conventional thermal sintered anode microstructures, from which we can observe the more uniform Ni-YSZ composite microstructure and sharper particle shape of microwave sintered anode. Besides, the microwave sintering favors

the cubic phase of YSZ while in the conventional sintered YSZ, monoclinic, tetragonal and cubic phases of zirconia existed instead of the pure cubic phase.

Ni phase was observed to become smoother than that before discharge. The aggregation of Ni phase and the accumulation of impurities at TPB may explain the increase of area-specific ohmic resistance, while cathode change in this study contributed little to the ohmic resistance increase according to previous experience. YSZ particles maintained the original size and shape with sharp corners, and sintering effect concentrated at the contacting area. The operation stability for a longer time and different gas environments will be reported in a later study.

4. Conclusions

In summary, the anode support SOFC anode-electrolyte co-sintering has been achieved by ultra-fast microwave activated sparking plasma sintering with an ultra high temperature ($1600\text{ }^{\circ}\text{C}$) reached. The initial durability of the cell at $800\text{ }^{\circ}\text{C}$ in humidified hydrogen was shown to be quite stable. The IV curve and impedance spectra changes showed that the cell performance was deteriorated by the increasing ohmic resistance rather than the electrode polarization. With the achievement of ultra-fast heating up process and uniform electromagnetic field in the sintering chamber, high quality SOFC can be manufactured with much higher time and energy-consuming efficiency compared to conventional thermal sintering.

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