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Fabrication of electrolyte materials for solid oxide fuel cells by tape-casting

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Abstract

In this research, solid oxide fuel cell electrolytes were fabricated by aqueous tape-casting technique. The basic compositions for SOFC electrolyte systems were focused on yttria-stabilized zirconia (YSZ) system. The powders used in this study were from different sources. ZrO_2-based system doped with 3, 8, and 10 mol% of Y_2O_3, and 8YSZ electrolyte tape illustrated the desirable properties. The grain size of the sintered electrolyte tapes was in the range of 0.5–1 μm with 98–99% of theoretical density. Phase and crystal structure showed the pure cubic fluorite structure for 8–10 mol% YSZ and tetragonal phase for 3 mol% doped. The electrolyte tapes sintered at 1450 °C for 4 h had the highest ionic conductivity of 30.11×10^{-3} S/cm which was measured at 600 °C. The flexural strengths were in the range of 100–180 MPa for 8–10 mol% YSZ, and 400–680 MPa for 3 mol% YSZ.

Keywords: C. Ionic conductivity; Water-based tape-casting; YSZ; Solid oxide fuel cells

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1. Introduction

Fuel cell technology is being investigated for its potential use in power generation and transportation applications in many countries in the world. Fuel cells have the capacity to supplant various conventional technologies with cleaner and more efficient systems. They are categorized by their electrolytes, the alkaline, phosphoric acid and solid polymer types are all past the fundamental development stage and are being tested or used in commercial applications.

Two main issues in SOFC development can be identified as driving forces during recent years: cost reduction with respect to low-cost materials and simpler processing techniques, as well as the improvement of durability in long-term operation [1]. For the environmental impact, and the lowering the manufacturing cost, the significance of this study is to be able to fabricate the SOFC electrolyte by water-based tape-casting technique which can meet the desirable properties for high performance fuel cell stack reactor.

2. Experimental procedure

2.1. *Tape casing process*

In this study, the basic compositions for SOFC electrolyte systems are yttria-stabilized zirconia (YSZ) which were mainly from two sources, Magnesium Elektron Inc., U.K. (MEL) and Tosoh Corporation, Japan [2]. First, the electrolyte powder (3YSZ, 8YSZ, 10YSZ) was mixed with de-ionized water in a ball-mill with a small amount of water-based acrylic polymer binder (Röhm and Haas), dispersants, and defoamer for 16 h. Before discharging the slurry, more aqueous binder, and defoamer were added into slurry to adjust viscosity and then stirred by a magnetic stirrer for 4 h. The slurry composition prepared in this study is based on formulation shown in Table 1. In addition, the summary table shows the average particle sizes of the starting zirconia electrolyte powders (Table 2). The slurry was then casted by a doctor-blade tape-casting machine. Then, green tape was dried at room temperature overnight and sintered at various temperatures. The samples were initially heated up to 600 °C and soaked for 30 min. The sintering temperature was at 1400–1450 °C for 2 and 4 h with the heating rate of 3 °C/min and cooling rate of 5 °C/min to room temperature to study the

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Table 1
Slurry composition and formulation prepared for tape-casting in this study

Ceramic slurry composition	Weight%
Ceramic powder (3YSZ, 8YSZ, 10YSZ)	62
De-ionized water	20
Acrylic polymer binder (B1000, Röhm & Haas)	17.6
Defoamer (B3005, Röhm & Haas)	0.2
Dispersant (Dispex, Allied Colloids Ltd., UK)	0.2

Table 2
Summary of particle sizes of starting raw materials and theoretical density (%)

Starting powders	Average particle size (μm)	Theoretical density (%) (sintered at 1400–1450 °C for 2–4 h)
8YSZ (MEL)	0.37	97.5–99.0
8YSZ (Tosoh) (spray-dried)	5–100	98.0–99.0
10YSZ (MEL)	0.41	97.0–99.0
3YSZ (MEL)	0.42	99.5–99.8

influence of sintering conditions to the microstructure and the ionic conductivity of the electrolyte tape.

2.2. Characterizations

Phase and crystal structures of electrolyte tapes were investigated by X-ray diffraction (Cu Kα; JEOL: JDX-3530). The microstructures were examined by scanning electron microscopy (JEOL: JSM-6301F) for 5000–15,000× magnifications.

The ionic conductivity of the sintered tapes was measured from 275 to 600 °C in air by two-probe impedance spectroscopy (Solartron 1260). Pt-electrodes were used as the termination applied to both sides of samples. Since the electrolyte material for SOFC components will later be integrated into a cell structure with other electrodes, therefore, the thermal expansion behavior is also critical to get the value matching with both anode (NiO/YSZ) and cathode (LSM-based) materials. A dilatometer, Anter Unitherm 1161 was used to determine the thermal expansion coefficient (TEC) of the sintered specimens. The TEC of the sintered specimens were investigated at temperature range from 50 to 1000 °C with a heating rate of 3 °C/min.

The electrolyte is a critical component of the fuel cell stack, particularly in the planar with the electrolyte self-supporting design. Then the mechanical properties were measured on the samples whose ionic conductivity had been favorable. A Universal Testing Machine, Instron 4502 was used to measure the three-point bending strength at room temperature on a sample of dimension 50 mm × 10 mm × 0.15 mm.

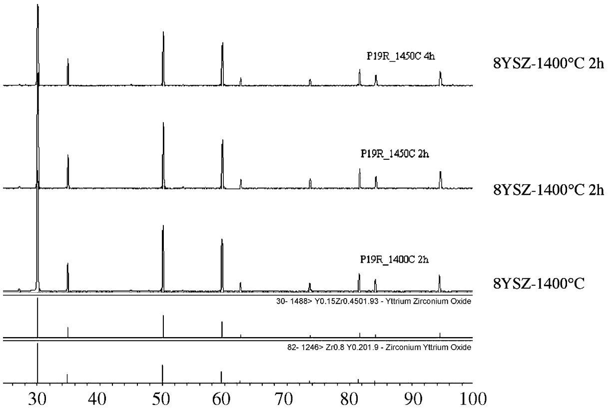

Fig. 1. XRD patterns of 8YSZ (MEL) sintered electrolyte tape at 1400 and 1450 °C for 2 and 4 h.

3. Results and discussion

3.1. Phase and crystal structure

The XRD study of the sintered electrolyte tapes showed the pure phase of tetragonal structure for 3YSZ following JCPDS no. 50-1089, and Fig. 1 showed pure cubic phase for 8YSZ following JCPDS no. 30-1468. All patterns and did not have any evidence of impurity phase.

3.2. Microstructure evaluation

From these SEM results, it was evident that as the sintering temperature increased from 1400 to 1450 °C, most electrolyte samples showed higher density as the porosity was reduced. However, it is evident that some grain growth occurred as the sintering temperature and time increased from 1400 °C for 2 h to 1450 °C for 4 h for fully stabilized ZrO_2 (8YSZ, MEL) as shown in Fig. 2. The result showed that sintered tapes had grain growth of about 3 μm (1400 °C for 2 h), and even larger grains (>5 μm at 1450 °C for 4 h), whereas the average particle size

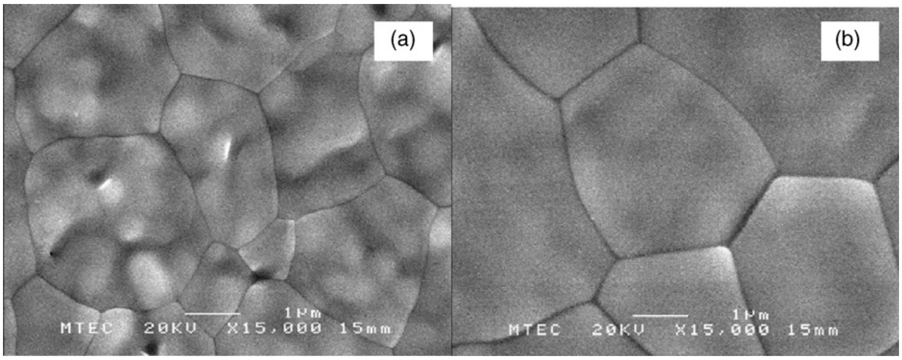

Fig. 2. SEM microstructure of 8YSZ (MEL) tape sintered at (a) 1400 °C for 2 h and (b) 1450 °C for 4 h.

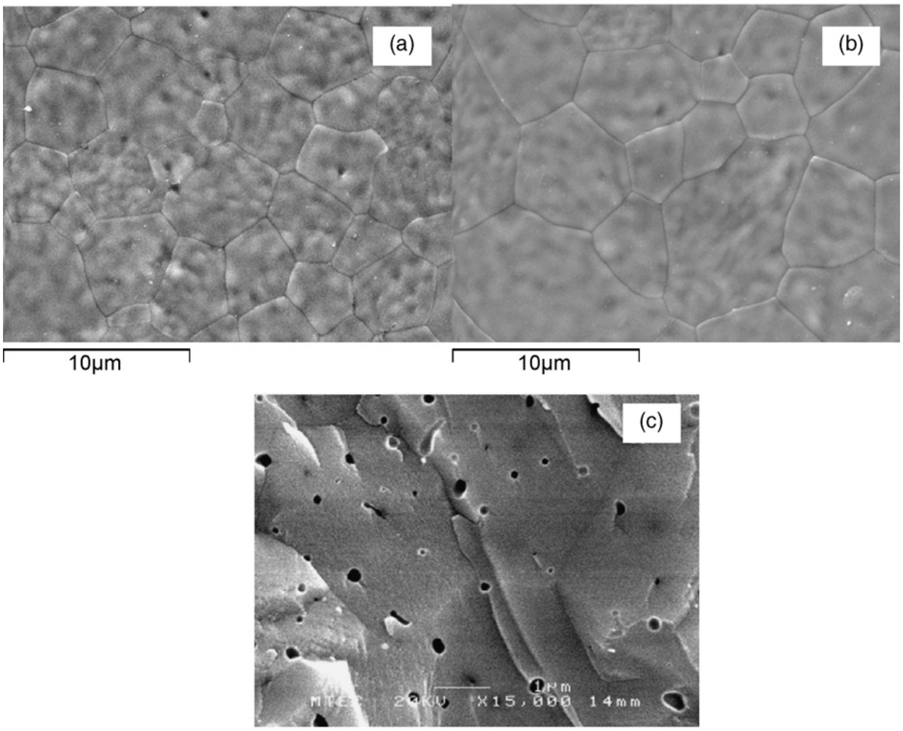

Fig. 3. SEM microstructure of 8YSZ (Tosoh) tape sintered at (a) 1400 °C for 2 h, (b) 1450 °C for 4 h, and (c) cross-sectioned of the sintered tape at 1400 °C for 2 h.

of the starting powders was about 0.37 μm (Table 2). Similar grain growth results were found in 8YSZ (Tosoh) in Fig. 3, only larger particle sizes at the starting powder (see also in Table 2).

Fig. 4 showed the SEM micrographs of 10YSZ (MEL) electrolyte tapes (sintered at 1400 °C for 2 h and 1450 °C for 4 h). The results clearly showed that sintered tapes at 1450 °C for 4 h had a significant grain growth compared to that of lower temperature. It can be summarized that the electrolyte batches prepared, including 3YSZ, 8YSZ, and 10YSZ were found to be well-sintered at 1450 °C for 4 h and the microstructures found to be as dense as 98.2–99.7% theoretical density.

3.3. Electrical conductivity

The total conductivity of which the major contribution was from the ionic conductivity of sintered tapes was measured by the two-probed impedance spectroscopy (Solartron SI1260). The measurements were taken every 25 °C interval started at 275 °C during the specimens were heated from room temperature to 600 °C. The complex impedance measurements were commonly used to determine the ionic conductivity of stabilized zirconia electrolyte. The complex impedance plots for all electrolyte batches could be found elsewhere [2]. An example plot of the imaginary part (Z'') versus the real part (Z') for equivalent circuits over a wide range of frequencies resulted in three semicircles as shown in Fig. 5. The high frequency semicircle (first from left) represented the bulk resistance and capacitance of the interior of the grains; the intermediate frequency semicircle provides the grain boundary resistance and capacitance; and the low frequency semicircle provides the information on the oxygen-ion transfer at the electrodes. In real measurement, the circular arcs rather than semicircles are often observed because the structure of the actual grain boundaries is more complicated than predicted in the equivalent circuit. It

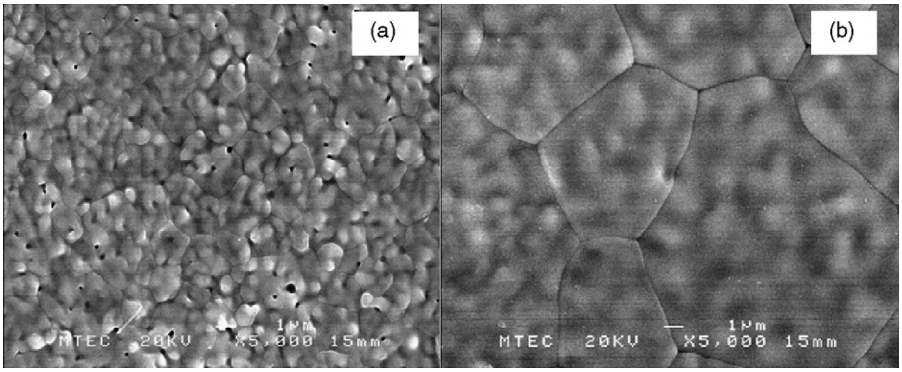

Fig. 4. SEM microstructure of 10YSZ (MEL) surface tape sintered at (a) 1400 °C for 2 h and (b) 1450 °C for 4 h.

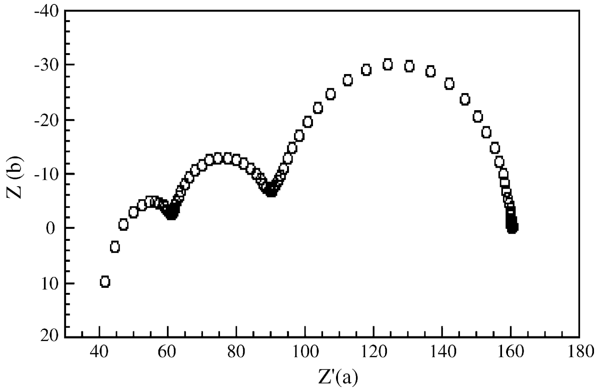

Fig. 5. An example of impedance spectra plot of 8YSZ electrolyte sintered at 1450 °C for 2 h, recorded at 275 °C in air. The *X*-axis represented the imaginary part (Z'), and *Y*-axis represented the real part (Z'') of resistance, which units in ohm.

should be noted that the influence of grain boundaries on conductivity varies depending on temperature [3]. Therefore, the complex impedance plot (number and size of semicircles) may also vary with temperatures.

The Arrhenius plots in Fig. 6 showed the ionic conductivity of 3–10 mol% YSZ electrolytes after sintering at 1450 °C for 4 h from the various sources of suppliers versus temperature in air. The electrolyte, 8YSZ (MEL) had the highest ionic conductivity compared to the others. The 8YSZ (Tosoh) showed lower ionic conductivity which may cause from the porosity trapped after sintering as shown in SEM study (Fig. 3c). The average particle size of the starting powders of Tosoh was much larger (>5–100 μm) than 8YSZ (MEL) which was 0.37 μm. Other researchers [4–7] reported that at higher sintering temperature the electrolyte specimens were found to have higher density, larger crystal grain sizes, and lower activation energy. As shown in Fig. 7, it was evident that longer sintering time also increased the electrical conductivity of 8YSZ (MEL). The activation energy of the fully sintered 8YSZ (1450 °C for 4 h) was calculated from the slope of the Arrhenius plot to be 11.46 kJ/mol compared to the reported value of 113 kJ/mol of bulk YSZ [8].

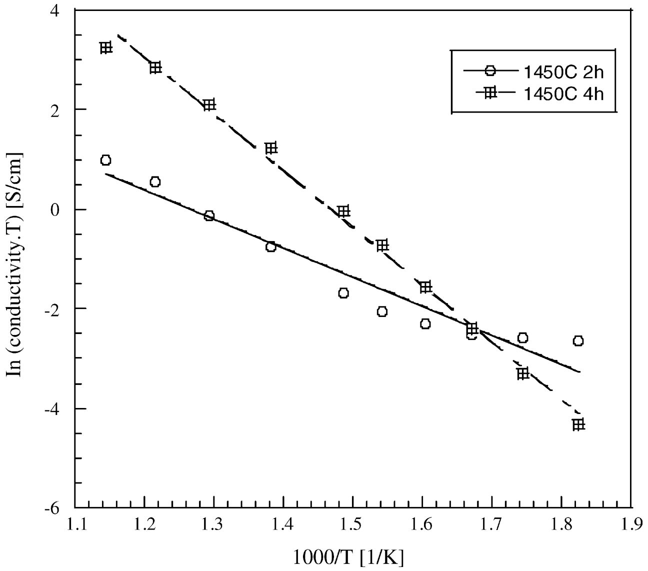

Fig. 7. Arrhenius plots of the ionic conductivity for 8YSZ (MEL) as the function of sintering time.

In summary, the higher sintering temperature leads to higher electrical conductivity, which may be due to denser specimens. Apart from the sintering temperatures, the longer sintering time shows the higher electrical conductivity as well.

3.4. Mechanical property

The measurement was done only on the sintered electrolyte specimens, which showed the satisfied electrical conductivity results. The sintering conditions played an important role to the flexural strength of the electrolyte tapes (YSZ materials) as it trended to decrease with increasing temperature and time. The

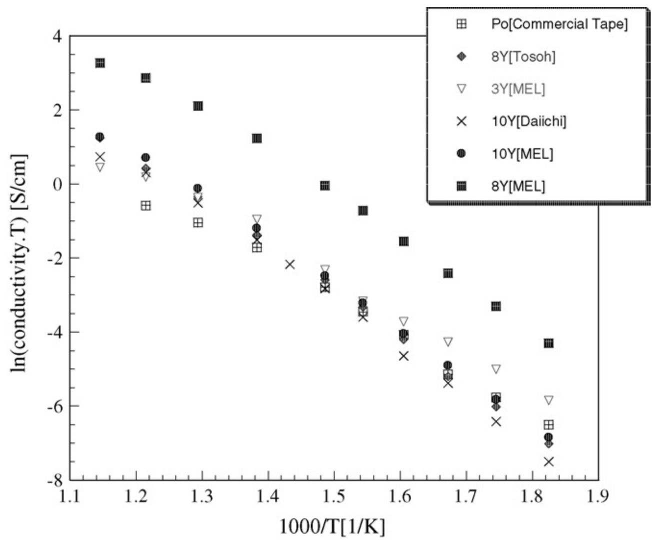

Fig. 6. Arrhenius plots of YSZ electrolytes sintered at 1450 °C for 4 h with various mol% of dopants.

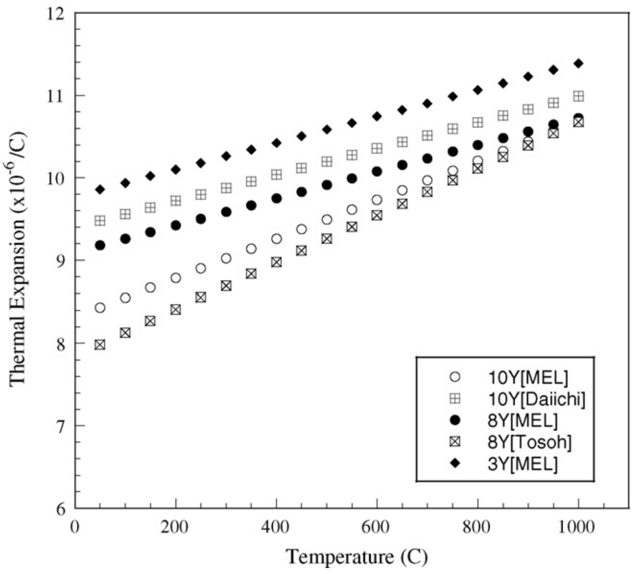

Fig. 8. Thermal expansion coefficients of SOFC electrolyte materials at the temperature range of 50–1000 °C (from various sources).

flexural strengths were in the range of 100–180 MPa for 8–10 mol% YSZ, and 400–680 MPa for 3 mol% YSZ. Therefore, to improve the mechanical properties of the electrolyte materials, we may need to consider doping with high strength materials such as TZP (tetragonal zirconia phase).

3.5. Thermal expansion

Fig. 8 showed the thermal expansion behavior of electrolyte materials for SOFCs, the 3YSZ tetragonal structure had TEC about $11.4 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$ and 8 and 10 mol% Y_2O_3 stabilized ZrO_2, cubic fluorite structure group has TEC around 10.7–$11 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$, which had a good match with the TEC values for electrode materials [3] for SOFCs as the following report:

- anode (NiO/YSZ) TEC $11.5 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$;
- cathode (LSM-based) TEC $11 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$

4. Conclusions

The YSZ electrolyte systems with varying mol% of Y_2O_3 from 3 to 10 mol% were studied and successfully fabricated by water-based tape-casting technique regarding the optimized composition of 62 wt.% ceramic powder, 18 wt.% organic binders, and 20 wt.% water. The sintering temperature and time for the highest electrical conductivity and density (>99.07% of theoretical density) was at 1450 °C for 4 h. From the XRD results, the electrolyte specimens showed the single phase of cubic for 8–10 mol% YSZ, and tetragonal phase for 3 mol% YSZ. SEM micrographs suggested that as the sintering temperature increased, most of the samples have higher density as the porosity reduced, while some batches showed lower density due to grain growth. The highest electrical conductivity of the electrolyte specimens found to be as high as 30.11×10^{-3} S/cm for 8YSZ (MEL) after sintering at 1450 °C for 4 h measured at 600 °C. The flexural strength values of the sintered electrolytes tape were in the range of 100–180 MPa for 8–10 mol% YSZ, and 400–680 MPa for 3 mol% YSZ. The thermal expansion coefficients of the electrolyte system prepared in this study are reported as the followings: for 8–10 mol% YSZ (cubic) at 1000 °C $\sim 10.7\text{–}11 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$, for 3YSZ (tetragonal structure) $\sim 11.4 \times 10^{-6}\,^{\circ}\mathrm{C}^{-1}$.

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