Spark-plasma sintering the 8-mol% yttria-stabilized zirconia electrolyte

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The 8-mol% yttria-stabilized zirconia (YSZ) is a widely chosen electrolyte for solid oxide fuel cells (SOFC) and oxygen sensors because of its excellent high-temperature ionic conductivity [1–4]. The ionic conductivity and mechanical strength of the electrolyte are strongly related to the microstructure of the electrolyte [5]. Gibson *et al.* [6] investigated the relationship between YSZ sample density and its corresponding ionic conductivity. Tomonari Takeuchi *et al.* [7] reported that different sintering methods of the electrolyte could get distinct microstructure and induce variety of the ionic conductivity of the electrolyte.

Spark plasma sintering (SPS) method enables the manufacture of dense materials in a short period at low sintering temperatures compared with current methods. SPS method is a manufacturing technology for materials, which utilizes the high energy of a high temperature plasma (discharge plasma) generated when pulse-formed electric energy is applied to the space among fine particles [8]. SPS has been employed to study alloys [9], functionally gradient materials [10, 11] and several ceramics such as SiC [12], ZrO_2 [13], Al_2O_3 [14], Zr_2O/Al_2O_3 [15] and TiC/Al_2O_3 [16]. However, for SPS sintered ZrO_2 ceramics, the past research was interesting mainly for its microstructural and mechanical properties, In this article, the electrical properties of the 8-mol% YSZ sintered by SPS was studied in comparison to conventional sintering.

Commercial 8-mol% YSZ powder (TZ-8YS, Tosoh Corp., Tokyo, Japan) with an average particle size of ca. 0.1 μm was used as starting material. The YSZ powder was sintered to disks by SPS with Dr. Sinter LAB 515 System (Sumitomo Coal Mining, Kanagawa, Japan) or by conventional sintering in air. For SPS, the following sintering steps were taken: YSZ powder ($\sim$2 g) was placed in a graphite die (15 mmϕ), and the SPS system was evacuated to 5 Pa and uniaxial pressure of 28 Mpa was applied. During theses procedures, the sintering temperature was increased to 1350 °C at a rate of ca.160 °C min^{-1} and maintained at 1350 °C for 10 min. Then the sample was cooled to room temperature naturally (SPS pellet). The SPS pellet were annealed in air at 1000 °C for 2 hrs to remove carbon contamination. For conventional sintering (CS), the green pellet with a dimension of 15 mm in diameter and approximately 4 mm in thickness was formed by die compaction at similar uniaxial pressure of 140 MPa to ensure the comparable green density. The pellets were then sintered at 1450 °C for 4 hrs by electrical resistance furnace and cooled to room temperature naturally (CS pellet).

The sintered densities of the samples were obtained using the conventional Archimedes technique and a digital micrometer measuring the exact diameters and thickness. The Jeol JSM-5900LV (Jeol Pte Ltd., Tokyo, Japan) scanning electron microscope (SEM) and X'Pert Pro MPD X-ray Diffraction System (Philips, Netherlands) were employed to study the microstructural characteristics of the sintered samples. The sintered electrolytes were coated with platinum paste on both sides as electrodes and fired at 1200 °C for 2 hrs. The ionic conductivity of the sintered samples was measured by AC impedance analyzer (HP4194A, USA). The measuring frequency range is from 100 Hz to 1 MHz with an applied voltage of 100 mV. Measurements were carried out between 300–850 °C at an increment 50 °C.

The relative density of the SPS pellet and CS pellet are 99 and 97% respectively. The XRD patterns for the SPS pellet and CS pellet as shown in Fig. 1, indicated a cubic unit cell (Fm3m). Using the value of full width at half maximum (FWHM) of the peak (111). The calculated finer crystallite size of the SPS pellet is 154 nm and that of the CS pellet is more than 1 μm.

Fig. 2 shows SEM micrographs of the surface of the SPS pellet and CS pellet, and shows that the average grain size of SPS is 0.8 μm and they are in close contact with each other. In contrast to the SPS pellet, the grain size of the CS pellet increased to more than 3 μm, as reported previously for dense 8YSZ ceramics sintered by conventional heating [17].

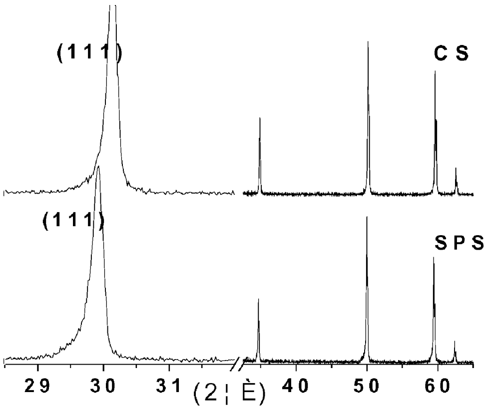
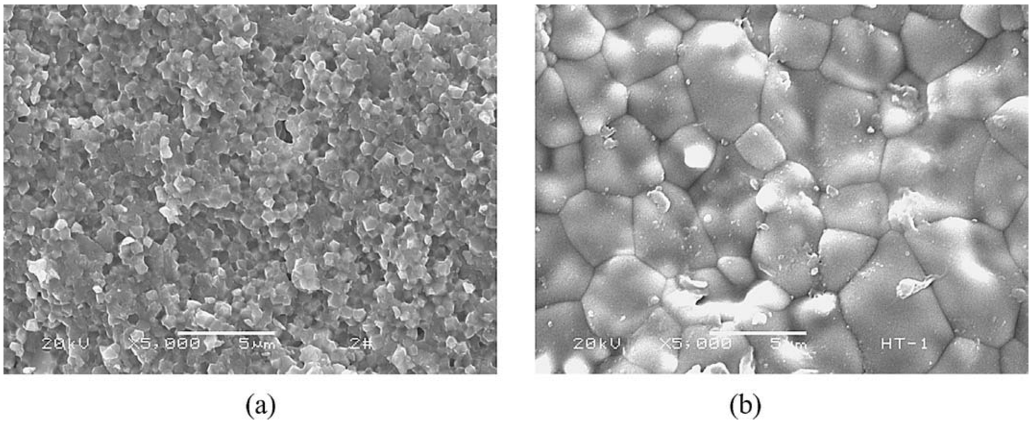


Figure 1 X-ray diffraction patterns of the SPS pellet and CS pellet.



(a) (b)

Figure 2 SEM images of the surface of the SPS pellet (a) and CS pellet (b).

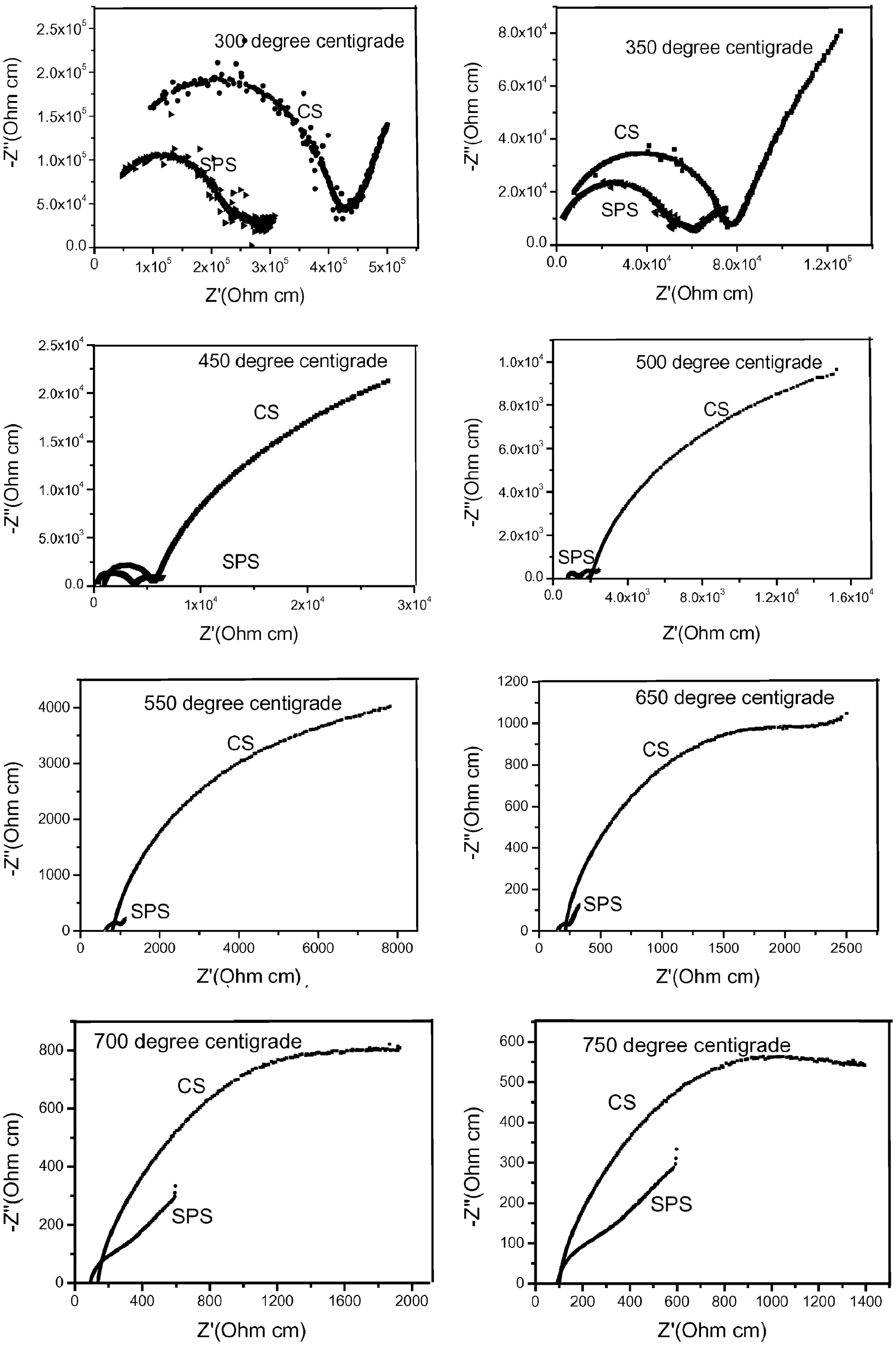


Figure 3 The AC impedance spectroscopy for both SPS and CS pellet at different measuring temperature.

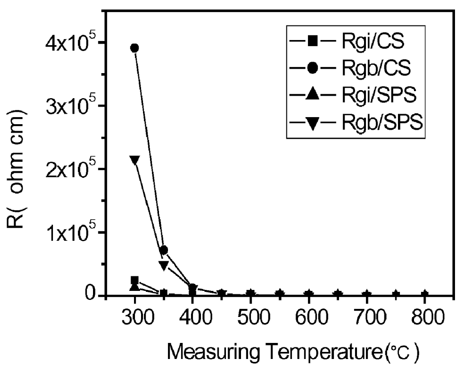


Figure 4 The plot of resistance of grain and grain boundary vs. measuring temperature.

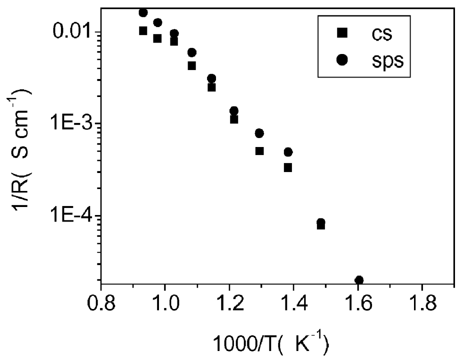


Figure 5 AC ionic conductivity of solid electrolyte vs. reciprocal temperature.

Fig. 3 shows the AC impedance spectroscopy for both SPS and CS pellet at different measuring temperatures in air. By these AC impedance diagrams, the resistance of grain and grain boundary and ionic conductivity of solid electrolyte at each measuring temperature was obtained [18] and shown as in Figs. 4 and 5.

Between 300–850 °C, the resistance of grain of SPS pellet is less than that of CS pellet, but, under 400 °C the resistance of grain boundary of SPS is less than that of CS pellet, however, above 400 °C the resistance of grain boundary of SPS is higher than that of CS pellet and at high temperature the value of resistance of grain boundary of SPS and CS all go to zero.

The total ionic conductivity of SPS is higher than that of CS between 300–850 °C. For example, at 450 °C, ionic conductivity of SPS and CS pellet are 4.8949E-4 and 3.3216E-4 Scm^{-1}, respectively; and at 800 °C, they are 0.01608 and 0.0102 Scm^{-1}, respectively.

The activation energy for the SPS , estimated from the slop in the rang of 400–800 °C, is 91 KJ mol^{-1}, which is in good agreement with CS pellet (96 KJ mol^{-1}), indicating that the conduction mechanism in SPS ceramics is similar to that in CS ceramics.

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