CHEMISTRY LETTERS, pp. 943-946, 1992. © 1992 The Chemical Society of Japan

Preparation of Yttria-Stabilized Zirconia Films for Solid Oxide Fuel Cells by Electrophoretic Deposition Method

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The electrophoretic deposition (EPD) method was applied for the preparation of yttria-stabilized zirconia (YSZ) films for a solid oxide fuel cell (SOFC). Dense YSZ films with uniform thickness can be readily prepared by EPD method. When the planar SOFC was fabricated by using $La_{0.6}Sr_{0.4}MnO_3$ as a cathode and electroless plating Pt as an anode, the open circuit voltage and the maximum power density attained were 1.03 V and 1.87 Wcm^{-2}, respectively.

Solid oxide fuel cells (SOFC) have attracted great attention as a new electric power generation system because of the high energy conversion efficiency. Yttria-stabilized zirconia (YSZ) is generally applied for solid electrolyte in SOFC. However, a thin YSZ film without gas leakage is required for SOFC due to low ionic conductivity of YSZ. Various physical or chemical processes have been studied for preparing YSZ films.[1-3] In particular, electrochemical vapor deposition method, which was developed by Westinghouse Electric Corporation, is very useful for preparing the dense YSZ films.[4] However, either of process proposed is costly and unsuitable for mass production. Electrophoretic deposition method, which is denoted hereafter as EPD method, is a colloidal process used in ceramic production,[5] and has advantages in short formation time, little restriction on the shape of the substrate, and being suitable for mass production. In this study, YSZ films were prepared on porous substrate by the EPD method, and the generation characteristics of SOFC, for which the YSZ thin films obtained by EPD method were applied, were further studied.

Suspensions of YSZ particles were prepared by mixing the prescribed amount of YSZ powder (Tosoh, TZ8Y), iodine, and acethylacetone which was used as a solvent in the YSZ suspension due to its high redox potential. Before the preparation of YSZ films, ultrasonic vibration was applied for 20 min. A porous Ni-CaO stabilized ZrO_2 (CSZ) cermet which contains 40 wt% Ni was calcined at 1723 K in air and then applied for the substrates of YSZ films. Electroless plating Pt electrode was applied on one side of the porous Ni-CSZ substrate. Positive YSZ particles dispersed in the acethylacetone were deposited on the Pt electrode by the EPD method. Constant dc voltage was applied between the cylindrical Pt wire (0.2 mm) as an anode and the electroless plating Pt electrode on the Ni-CSZ substrate as a cathode. Obtained green YSZ films on the Ni-CSZ substrates were sintered at 1673 K for 1 h followed by drying at room temperature for 1 h. Deposition and sintering were repeated for a few times in order to eradicate the gas leakage. Powders of $La_{0.6}Sr_{0.4}MnO_3$ were applied on the YSZ films as a cathode, and generation characteristics of a single SOFC were measured by the four probe method using humidified hydrogen (2% H_2O) as a fuel and oxygen as an oxidizing agent. The zeta potential of the colloidal YSZ particle was measured with a

zeta meter (Penkem, type 3000).

Zeta potentials of colloidal YSZ, conductivity of slurry, and the amount of deposited YSZ at 10 V for 3 min were plotted versus I_2 concentrations in Fig. 1. Although the zeta potential of YSZ particles is almost 0 in pure acethylacetone, it increases remarkably with increasing concentrations of I_2 and attains a constant potential, 50mV, above the I_2 concentration of 0.5 g/l. This is because proton are formed by the reaction between I_2 and acethylacetone. The formed protons were adsorbed on the YSZ particles, which have isoelectric points in the pH range from 4 to 5, and YSZ particles charge positively by the addition of I_2. Corresponding to the increase in zeta potential, deposited amounts of YSZ increased with increasing amounts of I_2 and attained a maximum at an I_2 concentration of 0.6 g/l. On the other hand, conductivity of suspension increases linearly with increasing amount of I_2. This suggests that protons start to carry the charge in YSZ suspension at an I_2 concentration above 0.6 g/l because the concentration of protons seem to become too high. This is why the amount of YSZ deposited decreases with increases in the I_2 concentration above 0.6 g/l. Therefore, the YSZ suspension with an I_2 concentration of 0.6 g/l was used in the EDP method in the following study because of the highest deposition rate.

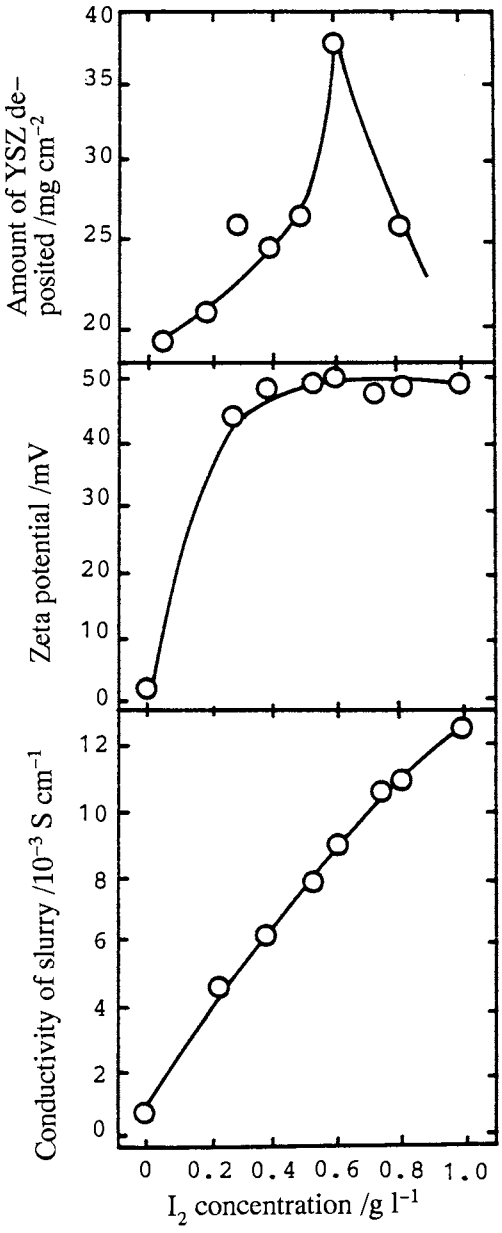

Fig. 1. Zeta potential, conductivity of slurry, and the amount of YSZ deposited at 10V for 3 min as a function of I_2 concentration.

The amount of deposited YSZ is shown in Fig. 2 as a function of the applied voltage and deposition time. Not only the period for deposition but also the elevated applied voltages increased linearly the weight of deposited YSZ. Linear dependence of deposited weight of YSZ on time and applied voltages suggest that the shield effect of deposited YSZ layer on the following electrophoretic deposition was negligibly small in the range of times and voltages examined. Therefore, the thickness of YSZ films can be controlled easily by period and applied voltages in the EPD method.

The open circuit voltages of SOFC, for which the YSZ films prepared by EPD method was applied, increased with increasing repetitions of deposition and calcination (Fig. 3). When deposition and calcination was repeated more than 5 times, the open circuit voltages higher than 1.0 V were obtained. This suggests that small amounts of open pores or cracks had remained on the deposited YSZ films even after

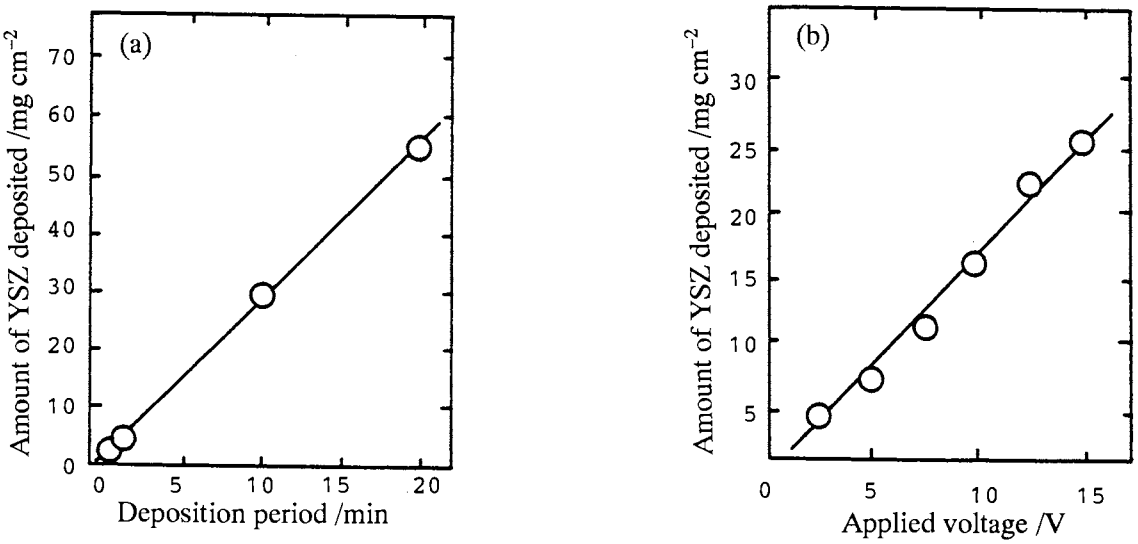

Fig. 2. The amount of YSZ deposited as a function of (a) the deposition period at the applied voltage of 10 V and (b) the applied voltages for 3 min.

calcination at 1673 K. However, these pores or cracks can be removed by repeating the deposition and calcination cycle. Upon the electrophoretic deposition after second times, YSZ particles were deposited only at the pores or cracks due to the shield effect of the YSZ layer deposited in the first time of electrophoretic deposition. Therefore, relative densities of YSZ films were enhanced, but the thickness of films did not increase with increase in repetitions of deposition-calcination cycles. As a result, repetitions of deposition and calcination greater than 5 times are required to obtain YSZ films without gas leakage.

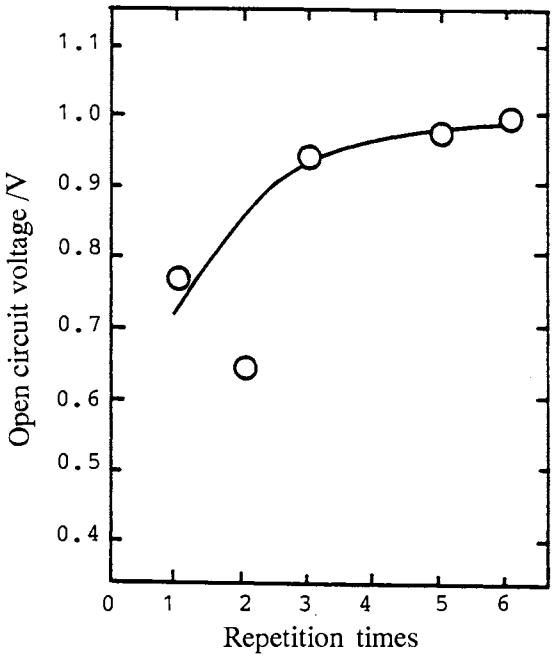

Fig. 3. Effect of repetitions of deposition and calcination cycles on open circuit voltage. Electrophoretic deposition of YSZ was performed at 5 V for 3 min in each cycles.

Figure 4 shows SEM photographs of YSZ films obtained by the EPD method at 5 V for 3min (5 time repetitions of deposition and calcination cycles). The thickness of the YSZ films obtained are about 5 μm, but no large pores or cracks were recognized on the surface of the films. Green YSZ film obtained by the EPD method consists of uniform sized YSZ particles. This is because the large particles of YSZ were precipitated in suspension and so do not migrate in electrophoresis. Therefore, in spite of the porous substrate, the resulting films are extremely dense and uniform in thickness. Moreover, their thickness are only about 5 μm as shown in Fig. 4.

Figure 5 shows the I-V and I-P characteristics of a single SOFC, for which the YSZ film by EPD method was applied. Since the gas leakage in the YSZ film is negligibly small, open circuit voltage of the cell is as high as 1.03 V but it is slightly lower than an estimation (1.10 V) given by the Nernst equa-

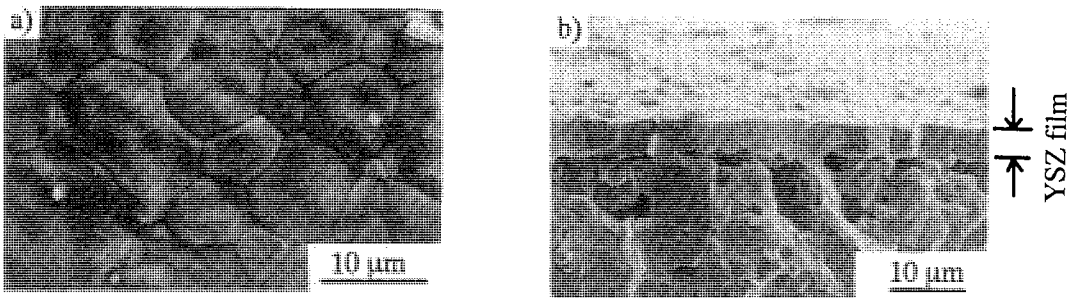

Fig. 4. SEM photographs of YSZ film obtained after 5 times repetitions of deposition and calcination cycles. Electrophoretic deposition of YSZ was performed at 5 V for 3 min in each cycles.
(a) surface of YSZ films (b) fractured surface of YSZ films

tion from differences in oxygen partial pressure. Although large pores or cracks could not be recognized on the surface of YSZ films by SEM observation, small amounts of pin holes may exist on the YSZ film. However, the maximum power density attained was 1.87 Wcm^{-2} because the YSZ film used was only 5 μm in thickness. The maximum power density of a tubular type SOFC developed by Westinghouse Electric Corporation is reported to be about 0.7 Wcm^{-2}.[4] Therefore, the maximum power density of the planer SOFC prepared by the EPD method is higher than that of Westinghouse Electric Corporation's, albeit far smaller size and different experimental conditions. This study revealed that the EPD method is very useful for preparing thin and dense YSZ films for the electrolytes of SOFC.

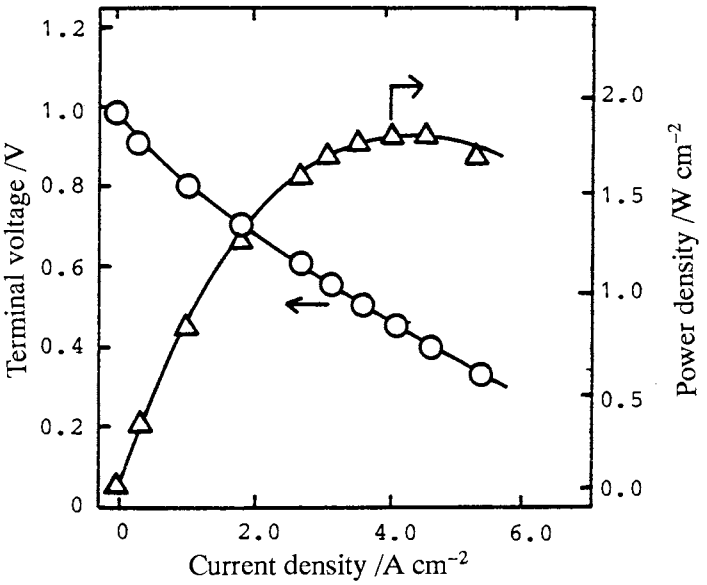

Fig. 5. I–V and I–P characteristics of SOFC at 1273 K., for which YSZ film obtained by 5 times repetitions was used.

The authors acknowledged to Dr. S. Nishimura (Government Industrial Research Institute, Kyushu) for the measurement of Zeta potential.

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(Received March 6, 1992)