ELECTROPHORETIC DEPOSITION OF STABILIZED ZIRCONIA FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

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 with EPD method by using acetylacetone as a solvent. The open circuit voltages of SOFC, for which the YSZ films were obtained by the EPD method, increased with increasing number of deposition and calcination steps, and attained a theoretical open circuit voltage value above 5 repetitions. When the planar SOFC was fabricated by using La0.6Sr0.4MnO3 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 1.84 Wcm⁻², respectively.

1. INTRODUCTION

Yttria-stabilized zirconia (YSZ) is generally used as solid electrolyte in SOFC. A thin YSZ film without gas leakage is required for high power density SOFC because oxide ion conductivity of YSZ is not high. Various physical or chemical processes have been studied for preparing YSZ films[1,2]. In particular, electrochemical vapor deposition (EVD) method, which was developed by Westinghouse Electric Corporation, is very useful for preparing the dense YSZ films on porous substrate [3]. However, either of these processes proposed are costly and unsuitable for mass production. Electrophoretic deposition method, which is denoted hereafter as EPD method, is one of the colloidal processes in ceramic production [4] and has advantages of short formation time, little restriction on the shape of substrate, and being suitable for mass production. Preparation of ceramic films by EPD method is generally performed in aqueous suspensions. However, dense films are seldom obtained in aqueous suspensions, since oxygen and hydrogen gas are formed due to
electrolysis of water during electrophoresis of powders[5]. In this study, preparation of YSZ films as an electrolyte of SOFC was studied with EPD method by using various kinds of ketones as a solvent. Oxidation-reduction potentials of ketones are extremely high and consequently, their use is expected to give dense films [6].

2.EXPERIMENTAL

Suspensions of YSZ particles were prepared by mixing the prescribed amount of YSZ powder (Tosoh, TZ8Y), iodine, and ketones as solvent. Before the preparation of YSZ films, ultrasonic vibration was applied for 20 min for dispersing YSZ particles. A porous Ni–CaO stabilized ZrO2 (CSZ) cermet which contains 40 wt% Ni was calcined at 1723 K in air and then used as substrates for YSZ films. Electroless plating Pt electrode was applied on one side of the porous Ni–CSZ substrate. Porous Ni–CSZ substrate thus obtained was suspended in the center of a coiled Pt wire by a Pt wire connected at the side of Ni–CSZ disks as shown in Fig. 1. Constant dc voltage was applied between the cylindrical Pt wire (0.2 mm) as anode and the electroless plating Pt electrode on the Ni–CSZ substrate as cathode. Unless otherwise noted, voltage and period of applied dc were 10 V and 3.0 min, respectively. Obtained green YSZ films on the Ni–CSZ substrates were dried at room temperature for 1 h followed by sintering at 1673 K for 1 h. Deposition and sintering were repeated for a few times in order to eliminate the gas leakage. Powders of La0.6Sr0.4MnO3 were applied on the YSZ films as a cathode (5 mm diameter) followed by calcination at 1173 K for 10 min. Electrochemical characteristics of a single SOFC were measured by the four probe method using humidified hydrogen (2% H2O) as fuel and oxygen as oxidizing agent. It is also noted that the theoretical electromotive forces estimated from the Nernst equation at this condition is 1.10 V. Zeta potential of colloidal YSZ particles was measured with a zeta meter (Penkem, type 3000).

3.RESULTS AND DISCUSSION

Figure 2 shows the zeta potential of colloidal YSZ particles in aqueous solution as a function of pH. The isoelectric points of used YSZ powders were in the pH range from 4 to 5, and large positive zeta potential was exhibited below pH=4. Therefore, these YSZ powders were considered to be suitable for electrophoresis, provided that the acidic suspension is used, because a large deposition rate is predicted from large zeta potentials.

The quality of YSZ film prepared by the EPD method depended strongly on the kind of ketones used as the solvents. Effects of the kind of ketones on the amount of YSZ powder for 3 min deposition and also the property of obtained
film are summarized in Table 1. The thicknesses of the resulting films were nonuniform in thickness and the YSZ powders were sometimes deposited anomalously when methyl iso-buthyl ketone, 3-pentanone, or 4-methylaceto-phenone was used as solvent. Therefore, these ketones are unsuitable for the preparation of dense YSZ films. However, green films uniform in thickness and of good quality, were easily obtained in acetone, acetylacetone, or cyclo-hexanone suspension. In this study, preparation of YSZ film was further studied by using acetylacetone as a solvent for suspension because of its low volatility, lack of odor, and low required voltages for the electrophoresis of YSZ.

Zeta potentials of colloidal YSZ and the amount of deposited YSZ at 10 V for 3 min are plotted against the amount of $I_2$ in Fig. 3. Although the zeta potential of YSZ particles is almost 0 in pure acetylacetone, it increases remarkably with increasing concentrations of $I_2$ and attains a constant potential, 50 mV, above the $I_2$ concentration of 0.5 g/l. This suggests that protons are formed by the following reaction between $I_2$ and acetylacetone:

$$
\text{CH}_3\text{-C-CH}_2\text{-C-CH}_3 \rightleftharpoons \text{ICH}_2\text{-C-CH}_2\text{-C-CH}_2\text{I} + 2\text{I}^- + 2\text{H}^+
$$

The formed protons are adsorbed on the YSZ particles, and subsequently, YSZ particles charge positively by the addition of $I_2$. Corresponding to the increase in zeta potential, deposited amount of YSZ increased with increasing amounts of $I_2$ and attained a maximum at an $I_2$ concentration of 0.6 g/l. Therefore, the YSZ suspension with an $I_2$ concentration of 0.6 g/l was used in this study.

The deposition weight ($W$) per unit area of electrode is expressed by the following equation [5].

$$W = \frac{2}{3} C_i \varepsilon_0 \varepsilon_r \zeta \frac{1}{\eta} \frac{E}{L} t$$  \[1\]

where $C_i$ is the weight of particles per unit volume, $\varepsilon_0$ the permittivity of vacuum, $\varepsilon_r$ the relative permittivity of solvent, $\zeta$ the zeta potential of particles, $\eta$ the viscosity of suspension, $E$ the applied voltage, $L$ the distance between electrodes, and $t$ the period for deposition. The above equation suggests that the deposition weight is increases linearly with increasing applied voltage and a prolonged deposition period. In accordance with the theory, the increasing period for deposition and elevated applied voltages increased linearly the weight of deposited YSZ as shown in Fig. 4. Linear dependence of deposition 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. Consequently, the thickness of YSZ films can be controlled easily by the period and applied voltages in the EPD method.
The open circuit voltages of SOFC, for which the YSZ films were obtained by the EPD method, increased with increasing repetitions of deposition and calcination steps as shown in Fig. 5. 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, not cracks, had remained on the deposited YSZ films even after calcination at 1673 K. However, these pores can be removed by repeating the deposition and calcination cycle. Considering from open circuit voltages of SOFC, 5 times of repetitions are enough for obtaining YSZ film without gas leakage. In the electrophoretic deposition after second time, YSZ particles were deposited only at the pores or cracks due to the shield effect of the YSZ layer deposited in the first time. Therefore, relative densities of YSZ films were enhanced, but the thickness of films did not increase in spite of increases in the repetitions of deposition-calcination cycle. This is one of the great advantages of EPD method.

Figure 6 shows SEM photographs of YSZ films obtained by the EPD method at 5 V for 3 min (5 time repetitions of deposition and calcination cycle). The thickness of 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 of less than 1 µm. This is because larger particles of YSZ precipitate in suspension and consequently do not migrate in electrophoresis. Therefore, in spite of the porous substrate, the resulting films are extremely dense and uniform in thickness. Moreover, the thickness is only about 5 µm as shown in Fig. 6.

Figure 7 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 attained to be 1.03 V but it is slightly lower than an estimation (1.10 V) calculated by the Nernst equation from differences in oxygen partial pressure. This suggests that small amounts of pin holes may exist at the grain boundary in YSZ film. However, the maximum power density attained was 1.84 Wcm⁻² because the YSZ film used was gastight and only 5 µm in thickness. This study shows that the EPD method is very useful for preparing thin and dense YSZ films for the electrolytes of SOFC.

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| Solvent             | I₂ amount g/l | Voltage/V | Deposited YSZ/mg/cm² | Quality of film |
|---------------------|---------------|-----------|----------------------|----------------|
| acetyl-acetone      | 0.5           | 10        | 14.6                 | uniform        |
| acetone             | 0.1           | 100       | 19.7                 | uniform        |
| cyclo-hexanone      | 0.2           | 100       | 15.1                 | uniform        |
| ethanol             | 0.6           | 100       | 38.3                 | many cracks    |
| MBK<sup>a</sup>     | 0.2           | 100       | 13.8                 | many cracks    |
| 3-pentanone         | 0.2           | 100       | 5.6                  | deposited anomalously |
| MAP<sup>b</sup>     | 0.2           | 100       | 1.1                  | deposited anomalously |
| water (pH=2.5)      | 0             | 10        | trace                | spotted        |
| MEK<sup>c</sup>     | 0.2           | 300       | trace                | scarcely deposited |
| propiophenon        | 0.2           | 300       | trace                | scarcely deposited |

a) methyl iso-butyl ketone  b) 4-methylacetoephone  c) methylethylketone
Fig. 1 Schematic view of the apparatus for the electrophoretic deposition method.

Fig. 2 Zeta potential of colloidal YSZ particles in aqueous solution as a function of pH.
Fig. 3  Zeta potential and the amount of YSZ deposited at 10 V for 3 min as a function of I₂ concentration in acetylacetone suspension.

Fig. 4  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.
Fig. 5  Effect of repetitions of deposition and calcination cycle on open circuit voltage. EPD was performed at 5 V for 3 min and the resulting films was calcined at 1673 K for 1 h in each cycle.

Fig. 6 SEM photographs of YSZ film obtained by EPD method. (a) surface (b) fracture surface
Fig. 7 Generation characteristics of SOFC at 1273 K, for which YSZ film obtained by 5 repetitions was applied.