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Effect of different electrode materials on electrophoretic depositional behavior of yttria-stabilized zirconia powder

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Abstract The electrophoretic depositional (EPD) behavior of yttria-stabilized zirconia (YSZ) powder with 8 mol% Y_2O_3, which is a common material for oxygen sensors as a solid electrolyte, was investigated on stainless steel and carbon based substrates. Ethanol + HNO_3 based suspensions were used for the EPD experiments, and three different YSZ powders, one commercially available powder and two own-made coprecipitated powders, were deposited. The latter powders were calcined at 900 and 1200 °C, respectively. The concentration of the suspension was 3 g/300 cm^3 and a small amount of HNO_3 solution was added as a dispersant. A DC electric field of 100–200 V/15 mm was applied between parallel electrodes. On stainless steel electrodes it was found that the own-made coprecipitated powder calcined at 1200 °C, showing the best deposition properties, whereas the commercial YSZ powder showed the best depositional properties on carbon electrodes. These characteristic depositional behaviors are discussed with regard to the adhesive force between the particles and the different electrodes, and some powder properties, e.g., particle size distribution and packing behavior.

A thick, continuous, free-standing YSZ film with a thickness of around 10 μm was successfully obtained after firing the deposit on the carbon electrode in flowing air.

Introduction

One of the attractive features of the electrophoretic deposition process (EPD) in ceramic processing is its very wide spectrum of applicable fields, for example, coatings, thick films with various microstructures or fiber reinforced ones, etc [1]. In many cases in electric device production, various ceramic powders are deposited on a metal substrate and are subsequently co-fired with it. After firing, the electrode works as an electrode of the device. In this case, the deposit is usually a thick film with a simple planer shape. The preparation of complex-shaped ceramic materials, even those of a micro-scale, is in higher demand these days. For example, some gas sensors require a very complex microstructure, which is composed of an O_2 pumping part and a sensing part [2]. One of the potential methods being considered for the preparation of three-dimensional complex ceramic materials is the EPD using a carbon electrode. A ceramic powder is deposited on a carbon electrode with a special shape which acts as a template of the ceramic material. In the next step, it is fired in air, the electrode is oxidized, burned out and the deposit is sintered into a thick film based component. Hayashi et al. prepared alpha-alumina thick films with various textures by this process using formed carbon powder as an electrode [3]. Conventionally such a structure is prepared basically by a tape-casting method; if the 3D-EPD method can be applied successfully, there are several merits in the production process. For example: decreasing process steps, saving binder materials, etc. For the successful EPD on a carbon electrode, which is expected to be somewhat different from that used on metal substrates, it is important that the deposition behavior be precisely investigated for various ceramic powders.

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Taking into consideration such characteristics, in this study, the EPD behavior of yttria-stabilized zirconia (YSZ), which is one of the most popular materials used for various gas sensors and solid oxide fuel cells, was investigated with the intent to clear the effect of substrates, stainless steel or carbon, on deposition behavior. There have been various studies for the EPD of YSZ, including the studies of Zhitomirsky et al. [4] and Negishi et al. [5], but the effect of electrode properties has not been made clear until now.

Experimental

Preparation of YSZ powder

As a starting material, a commercial YSZ powder (TZ-8Y, produced by Tosoh Co. Japan, stabilized with 8 mol% Y_2O_3) and own-made YSZ powders synthesized by the coprecipitation method, were used. TZ-8Y powder consists of agglomerates of some tens of micrometers, therefore we ground it by planetary potmilling at 200 rpm for 2 h with ethanol. In preparing of the own-made powders, zirconium chloride oxide octahydrate (0.92 mol), and yttrium chloride hexahydrate (0.16 mol) were dissolved in water (100 cm^3), and the solution was added to an 18% ammonia solution (200 cm^3). Obtained precipitate was filtered, washed, dried and calcined at 900 and 1200 °C for 1 h. These powders derived from the precipitate were ground by planetary potmilling at 200 rpm for 2 h with ethanol. The two synthesized samples were designated as S900 and S1200.

The starting powders were observed with a scanning electron microscope (SEM, S-4500, Hitachi Ltd., Japan). The specific surface area of the powders was measured by the one-point BET method (Macsorb model-1201, Mountech Co., Ltd., Japan) using N_2 gas. Primary particle size was calculated by assuming that the particles were spherical. Measurement of particle size distribution was performed by the laser-scattering method (SALD-2100, Shimadzu Co., Japan). The zeta potential of the powders was measured with an electrophoretic light-scattering spectrometer (CSA600, Otsuka electronics Co., Ltd., Japan).

EPD of YSZ powder on different electrodes

The concentration of the prepared YSZ suspensions was adjusted to 3 g/300 cm^3 using ethanol, in which 1 cm^3 of diluted (2.2×10^{-4} mol/cm^3) HNO_3 solution was added as a dispersant and used as the EPD suspension. A stainless steel electrode (cathode, a depositing electrode, austenitic stainless steel, containing ~18% Cr and ~8% Ni, $40 \times 20 \times 1$ mm^3) or a carbon electrode (an isotropic graphite plate, IG-43, produced by Toyo Tanso Co., Ltd., Japan, size equal to the steel electrode) and a platinum electrode (anode, a counter electrode, $40 \times 20 \times 0.5$ mm^3) were inserted in a parallel direction into the suspension and DC voltage (100–200 V) was applied between them for 1–5 min. The distance between the electrodes was 15 mm. The appearance of some deposit was observed and the amount measured using an electric balance.

Finally, the deposited carbon electrode was fired in an electric furnace ventilated with flowing air at a temperature of 1200 °C for 2 h. The obtained sample was observed with a SEM (JSM T-300, JEOL Ltd., Japan).

Results and discussion

Starting materials

The SEM micrographs of the two synthesized samples (S900 and S1200) and the one commercial sample (TZ-8Y), are shown in Fig. 1. The primary particle size of the samples determined by the BET method were 17 (S900), 154 (S1200) and 69 (TZ-8Y) nm, respectively. These values are congruent with the sizes shown in the SEM micrographs. S900, the synthesized sample, shows the finest particle size followed by TZ-8Y with medium sized particles and S1200 showing the largest particle size.

The particle size distributions of the three YSZ powders measured by the laser-scattering method are shown in Fig. 2. Median particle diameters of S900, S1200 and TZ-8Y samples were 0.58, 0.80 and 0.50 μm, respectively. This result illustrates that the particles in the samples formed agglomerates in the suspensions. The degree of agglomerate, which was estimated by the ratio of the particle sizes obtained by the laser-scattering and the BET methods, increased conjunctionaly with a decrease in BET-obtained particle size, i.e. S1200 < TZ-8Y < S900. The zeta potentials of the samples were 40 (S1200), 37 (TZ-8Y) and 29 (S900) mV, respectively. The lower zeta potential and finer particle size of S900 induced a greater manifestation of agglomerate than the other samples. In particular, large sized agglomerates with a diameter of some micrometers were contained in the S1200 sample.

EPD of YSZ powders

Figure 3a illustrates the depositional behavior of the three samples on the stainless steel substrate (applied voltage was 200 V). In this figure, open marks and

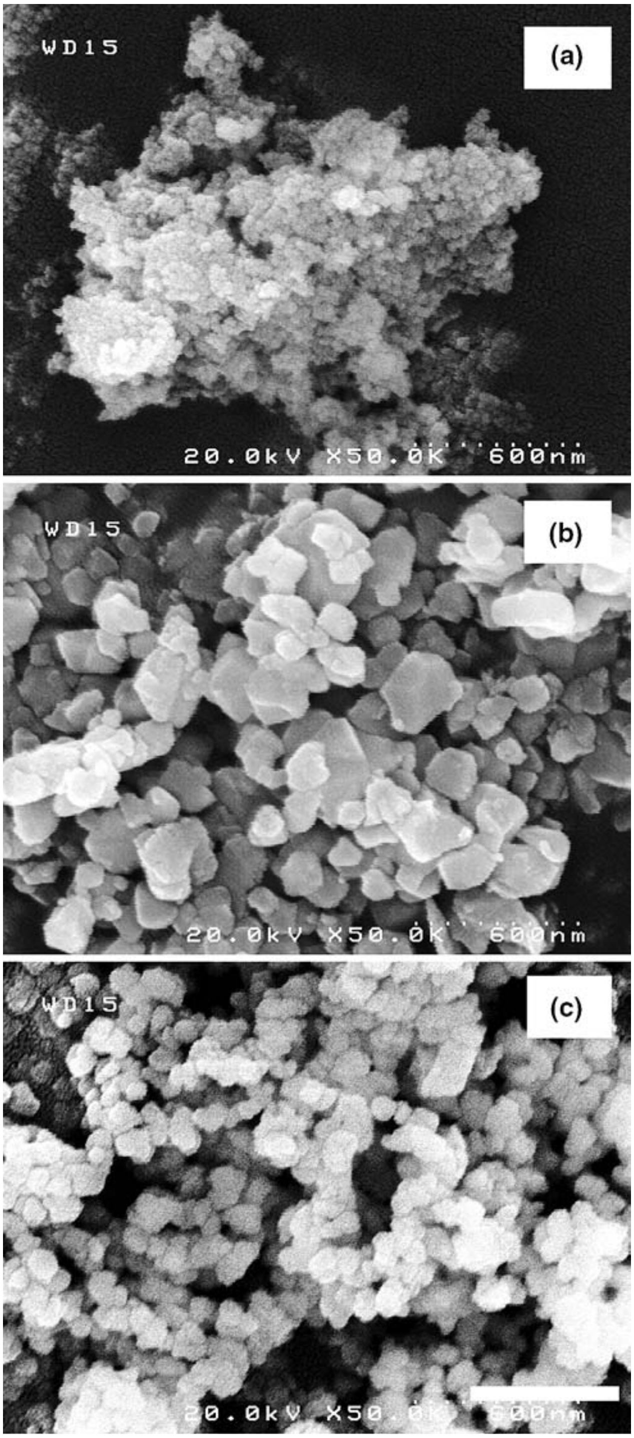

Fig. 1 SEM micrograph of the YSZ powders: (**a**) S900; (**b**) S1200; (**c**) TZ-8Y (bar = 0.5 μm)

broken lines show the data for the samples which illustrate cracking and/or peeling off. The only sample which showed a deposit able to withstand cracking for upto 5 min was S1200. The other samples were easily cracked and stable deposit was difficult to obtain. This experimental result can be explained by taking some

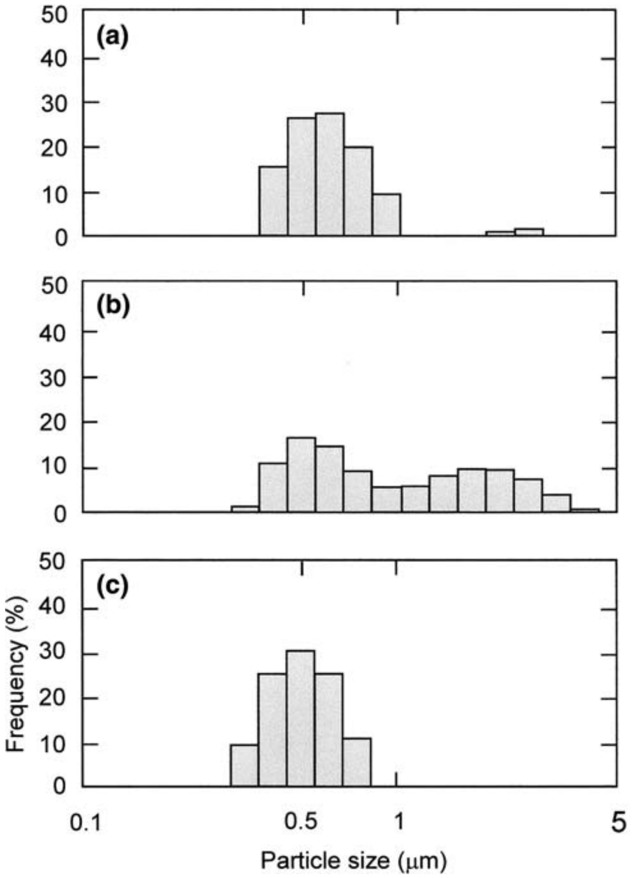

Fig. 2 Particle size distribution of the YSZ powders measured by the laser-scattering method: (**a**) S900; (**b**) S1200; (**c**) TZ-8Y

powder properties into consideration: As the particles were too fine (TZ-8Y and S900), the packing density of the deposit was low. Such deposit cracks easily while drying. When the particles are slightly larger (e.g., S1200), they can settle densely and a more stable deposit becomes obtainable.

However, the depositional behaviors of the three YSZ samples on the carbon electrode were largely different from those on the steel electrode, as shown in Fig. 3b. To illustrate, for S1200, which showed the largest amount of deposit on the steel substrate, the deposit was only slight on the carbon electrode. Conversely, a relatively large amount of the TZ-8Y powder deposit was obtained on the carbon electrode as opposed to that on the steel substrate. The deposit of S900, which consists of the finest particles, showed extensive cracking on the carbon electrode as well as on the steel electrode.

Figure 4 shows the appearance of the YSZ deposits on the two kinds of electrodes. As mentioned above and shown in Fig. 3, S900 deposits on both electrode types and TZ-8Y deposit on the steel electrode were

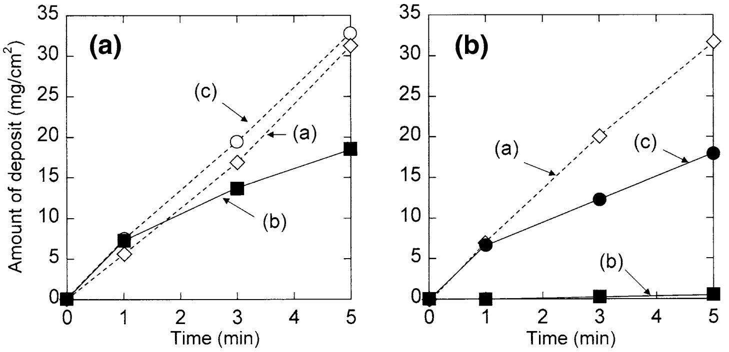

Fig. 3 EPD behavior of the three YSZ samples, (a) S900, (b) S1200 and (c) TZ-8Y on the stainless steel (**a**) and on the carbon substrate (**b**). Applied voltage was 200 V. Open marks and broken lines show cracked samples

cracked. Conversely, the amount of the deposit of S1200 on the carbon electrode is very small and only a trace can be seen on the surface. Observation of this sample showed that the particles definitely converged on the electrode when the DC power was applied, but they did not remain on the surface of the electrode upon being removed from the suspension. Another notable point is that the surface of the TZ-8Y deposit on the carbon electrode was very rough. The cause of this phenomenon will be elaborated on later.

These experimental results are complex and lack consistency, especially those for the TZ-8Y and S1200 samples. That is, if easy deposition is associated with the properties of the ZrO_2 powder, the S1200 sample should then deposit more easily than TZ-8Y, not only on steel but also on the carbon electrode. However, on the carbon electrode, TZ-8Y powder was more easily deposited than that of the S1200 sample.

In order to understand this phenomenon, a primary point of interest which should be considered is the surface property of the electrode. One possible reason why this characteristic depositional behavior may have occurred is the difference in the surface microstructures of both electrodes. Figure 5 shows the SEM micrographs of the surfaces of the electrodes. On the steel electrode, many striations are observed. These marks are almost parallel, and the distance between them and their depth are several micrometers. Conversely, on the carbon electrode, there are numerous hollows as if some graphite flakes had been peeled off. The width varies to a maximum of some tens of micrometers, and the depth also measures some micrometers. These results show that the surface structures of the electrodes are vastly different, but this alone cannot satisfactorily explain the cause of the complex depositional behavior. In particular, the reason why the large particles of the S1200 sample were only deposited successfully on the steel electrode cannot be explained regarding the surface structure of both electrodes.

Another possibility which may help to explain such depositional behavior may be understood through the differences in interaction. The adhesive force between the YSZ particles and the two kinds of electrodes resulted in the observed deposition behavior. If we assume the adhesive force between the YSZ particles and the steel electrode is great, both the deposit of relatively large particles and that of fine particles becomes possible. In this case, however, the deposit of fine particles results in cracking because the density tends to be low and the shrinkage in drying is large. This is congruent with the obtained experimental

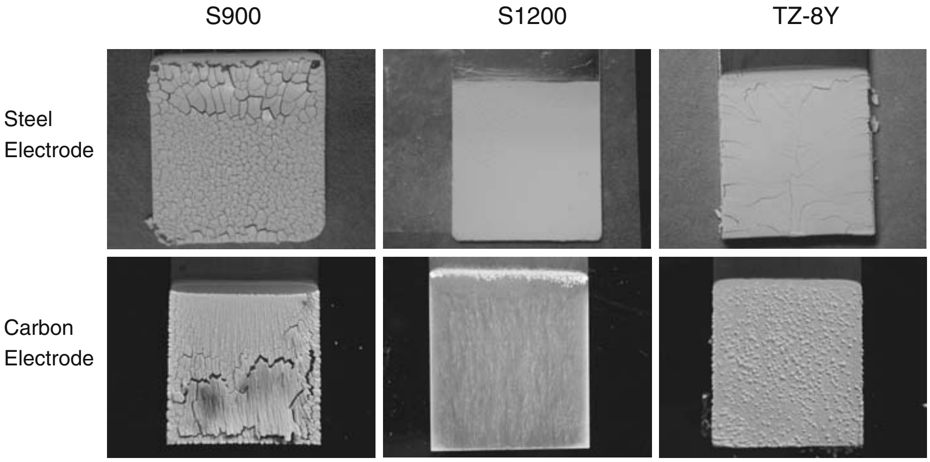

Fig. 4 Appearance of the YSZ deposits on the two kinds of electrodes

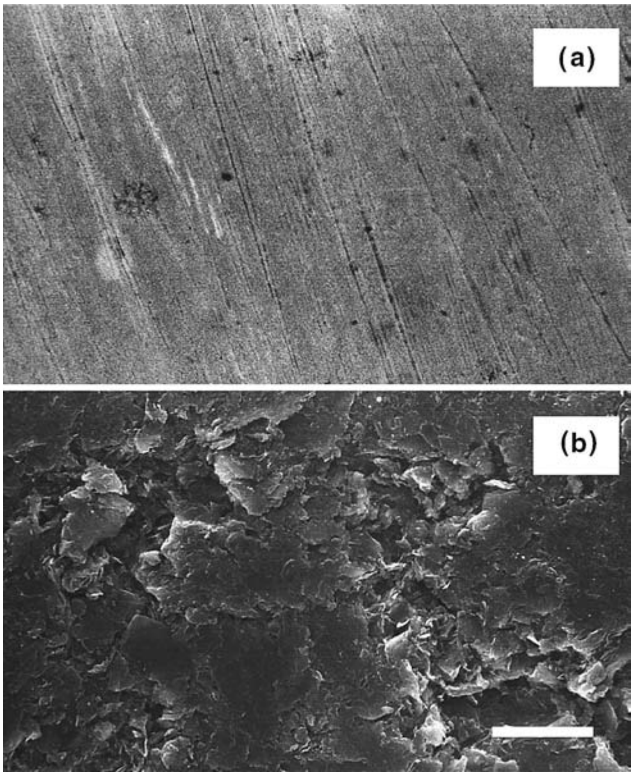

Fig. 5 Surface structure of the steel electrode (**a**) and the carbon electrode (**b**) observed by SEM (bar = 20 μm)

results. If the TZ-8Y or S900 sample was calcined and the particle size became much larger, similar depositional behavior involving S1200 would be observed.

In contrast, if we assume the adhesive force between the YSZ powders and the carbon electrode is weak, S1200 becomes difficult to deposit because this sample contains more and larger agglomerates than the other samples. This also agrees with the experimental results. One possible reason why the depositional behavior on the carbon electrode was so vastly different between S900 and TZ-8Y, in spite of the agglomerate size being almost the same, was that a part or all of the agglomerates in both samples were not rigid enough that the character of the primary particles would affect their depositional behavior.

Pertaining to the TZ-8Y sample, the deposit on the carbon electrode was obtained as a continuous thick film whereas that on the stainless-steel electrode was cracked. It is inferred that the reason for such a difference in deposit quality (i.e. packing density) on the different substrates is that only densely deposited TZ-8Y particles could remain on the carbon substrate because the adhesive force of the particles against the carbon electrode was less than that against the stainless steel substrate. Furthermore, the uneven surface of the TZ-8Y deposit on the carbon electrode seemed to be caused by the weak adhesive force. To further explain, at the beginning of deposition, deposits occurred sporadically at several points on the electrodes, where particles were able to fix with enough strength due to the mechanical effect of the rough surface. Such deposits grew laterally and finally merged into one continuous deposit. Therefore, the difference in the growth rates over the surface of the electrode caused the uneven surface of the deposit.

Unfortunately, the source of the adhesive force has not been specified in the present work. In summary, it is likely due to the interaction between the surface atoms and/or functional groups on a particle and a substrate surface. One conceivable source of adhesive force is surface energy. In other words, the surface hydrophilic/hydrophobic property of a particle and a substrate actually affect the EPD behavior. Tadanaga et al. showed the ‘‘selective’’ EPD of $PhSiO_{3/2}$ (phenylsilsesquioxane) on the hydrophilic/hydrophobic patterned substrate [6]. Similar phenomena may occur on the EPD of ZrO_2 particles on both the carbon and steel electrodes in this study. To elucidate, the adhesive force between the YSZ particles and the stainless steel electrode is likely to be larger than that between the YSZ and the carbon (graphite) electrode, because it is considered that the surface of the steel is generally hydrophilic, and that of the carbon is hydrophobic.

In this study, the simple characterization of the adhesive force between the deposit and the electrodes (i.e. a scratch test using a craft knife), or that of the electrode surface energy (i.e. observation of a water or ethanol droplet on the surface) were performed. However, no significant difference was found based on the different electrode materials. More precise investigation is necessary to achieve a better understanding of the source of the adhesive force and its effect on the EPD behavior.

One of the results of the firing experiment (1200 °C, 2 h) was shown in Fig. 6. The amount of the deposit was 6.2 mg/cm^2. As shown in this photograph, a continuous YSZ film with a thickness of around 10 μm was successfully obtained albeit no satisfying results were obtained in this work. Macroscopically, the film is somewhat warped, and microscopically it contains a lot of pores. Therefore, the film's density, which cannot be estimated because the volume of the film is difficult to measure, would be not so high. As deposited, the average relative density of the TZ-8Y deposit was not so high, around 35%. This would induce warping of the film and/or low density after firing. The quality of the film will presumably be improved by further investigation in the future. For

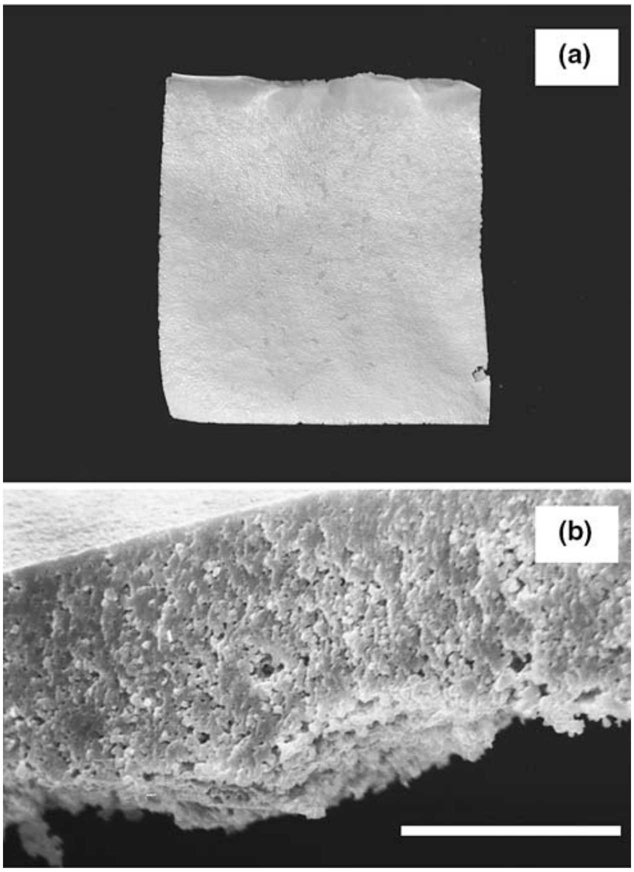

Fig. 6 Appearance (**a**) and SEM micrograph (**b**) of an obtained YSZ (TZ-8Y) thick film (bar = 10 μm)

instance, the addition of some binder to the suspension would be an effective way to obtain higher quality deposits on the carbon electrode, because the weak adhesive force between the YSZ powder and the electrode can introduce heterogeneity to the deposit, as mentioned above. Moreover, in this study, the pH of the suspensions was around 3.0, so it is possibile that yttrium ions can be dissolved from the YSZ particles [7]. If the conditions used in this study are actually applied in the production of YSZ components, special care must be taken, including ensuring the EPD process is limited to a very short time otherwise the excessive addition of the Y component to the starting powder will become necessary to obtain desirable properties.

Conclusions

EPD behavior of YSZ powders with 8 mol% Y_2O_3 on stainless steel and carbon substrates was investigated. For deposition on a stainless steel substrate, a deposit without cracks was only obtained from the own-made sample which contained relatively large particles (S1200). Conversely, for deposition on a carbon substrate a finer commercial sample (TZ-8Y) advantageously affected deposition. These characteristic experimental results can be explained by taking (a) the packing behavior of particles and (b) the adhesive force of particles on the two kinds of substrates into consideration. After the firing of the deposited carbon substrate, a free standing film of YSZ with a thickness of around 10 μm was successfully obtained.

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