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Influence of rheological characteristics of YSZ suspension on the morphology of YSZ films deposited by electrostatic spray deposition

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Abstract

The effect of polyvinyl butyral (PVB) on the dispersion in nonaqueous yttria stabilized zirconia (YSZ) suspension and the influence of rheological property of the YSZ suspension on morphology of deposited films by electrostatic spray deposition (ESD) were investigated. The results showed that a gradual increase of PVB (5 wt.%, 10 wt.%, 15 wt.%) enabled the suspension to be more viscose. Also, adding PVB helped to better get dispersed and decrease the size of agglomerated particles (580 nm with 5 wt.% PVB, 830 nm with 10 wt.%, and 910 nm wt.% with 15 wt.%, respectively) compared to when YSZ suspension does not contain PVB. The dense 5 μm thick YSZ film was obtained at 15 wt.% PVB suspension, and this optimal condition resulted from the optimized viscosity and the steric stabilization of suspension.

Keywords: A. Suspensions; E. Fuel cells; Yttria stabilized zirconia; Electrostatic spray deposition

1. Introduction

Yttria stabilized zirconia (YSZ) is the most widely used as a solid electrolyte material for solid oxide fuel cells (SOFCs). In order to achieve sufficient ionic conduction, an SOFC with the YSZ electrolyte must be operated at a high temperature between 800 °C and 1000 °C. Though YSZ electrolyte shows enough mechanical property in the range of the temperatures, this high operating temperature of the YSZ based SOFC causes some problems related to durability of the SOFC and becomes a major obstacle when it comes to commercialization. Therefore, the most of the recent research on SOFC has been focused on how to lower the operating temperature below 800 °C. However, the ionic conductivity is decreased at the lowered operating temperature and, hence, overall polarization resistance of each component of the cell rapidly increase by lowering the operating temperature [1]. To solve this issue, thin film type electrolyte can be used to compensate the decrease in ionic conductivity and reduce the ohmic polarization resistance of electrolytes operating at an intermediate-low temperature (500–800 °C) [2]. Conventionally, the YSZ electrolyte has been coated by several methods such as screen printing [3] and tape casting [4] using slurries. However, these types of technique are not suitable to fabricate films thinner than ~10 μm [5]. The electrostatic spray deposition (ESD) technique using a high electric force to atomize and spray liquid suspension or precursor solution has been used at many coating industries. Also, it can produce ultra fine droplets with narrow size distribution [6] and deposit films with uniform morphology by controlling variables such as an applied voltage, flow-rate and deposition time, thus, it is benefit to fabricate uniform thin films [7]. However, the morphology of films deposited by ESD highly depends on the characteristics of slurries such as viscosity and dispersion of suspensions [6]. Polyvinyl butyral (PVB) can act both as a binder and as a dispersant which is demonstrated by in terms of a polymer adsorption [8]. In this study, the effect of PVB on the dispersion characteristics of YSZ suspension was observed and the influence of rheological property of the PVB added YSZ suspension on morphology of deposited films was investigated using electrostatic spray deposition (ESD).

2. Experimental

To prepare YSZ suspensions, yttria-stabilized zirconia (8 mol% yttria, Tosoh Corp., Japan) was used as a solid

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constituent. Isopropyl alcohol (IPA) and toluene (Daejung Chemicals & metals Co., Ltd., Korea) as solvents, Menhaden fish oil (MFO) as a dispersant, Dibutyl phthalate as a plasticizer (Sigma–Aldrich, USA), and Triton X-100 (Daejung Chemicals & metals Co., Ltd., Korea) as a surfactant were utilized. Various amounts of polyvinyl butyral (PVB, Sigma–Aldrich, USA) were used as a binder and a dispersant. The PVB was first dissolved in the IPA and toluene mixed solvent, and a required amount of dispersant, surfactant, plasticizer and YSZ powder were added to the suspension in order and stirred for 1 h, and then ultrasonicated for 1 h.

The effect of various amounts of PVB on the YSZ slurry dispersion was estimated from the measurement of slurry viscosity as a function of the PVB concentration. The slurry viscosities were measured at shear rates ranging from 1 to $1000 s^{-1}$ using a concentric cylindrical rotational viscometer (RVDV-II, Brookfield, USA). Also, zeta potential and agglomerated particle size of the YSZ suspension with different PVB contents were measured with zeta potential & particle size analyzer (ELS-Z, Otsuka Elec., Japan). The ESD system applied to deposit the YSZ thin film in this work consists of a heating table, a syringe pump, a nozzle, and a power supply. The YSZ suspension is fed through a needle (0.03 mm inner diameter) of the nozzle toward a porous NiO-YSZ substrate by the syringe pump (KD Scientific Co.). The NiO-YSZ substrate was fabricated by uni-axial dry pressing in the weight ratio of 60 (NiO, Sumitomo Chemical Co., Japan): 40 (YSZ, Tosho Co., Japan). At the end tip of the needle, the suspension is atomized by the electrostatic force supplied from the DC power source between the needle and the substrate. The atomized and sprayed droplets fly to and are deposited on the substrate. All processes take place under ambient atmosphere and the cone-jet, one of the spray modes in the ESD, is applied in this study. The microstructure of deposited films with the YSZ suspension by the electrostatic spray deposition (ESD) was investigated by scanning electron microscopy (SEM).

3. Results and discussion

Rheological behaviors of the YSZ suspensions in the bi-solvent system were evaluated as a function of the PVB concentration and the result is shown in Fig. 1. The viscosity measurement was carried out with pure suspension without precipitated particles. The suspensions with various PVB contents exhibited significant shear thinning behavior, that is, a decrease of viscosity with ascending shear rate. The shear thinning behavior can be explained by considering agglomerates as primary flow units. The increasing shear rate leads to breakdown process of the aggregated particles, and the liquid mobility in agglomerates is improved because the size of agglomerated particles is reduced [8]. As can be seen in Fig. 1, the slurry with no (without) PVB showed the lowest viscosity because almost all YSZ powders were precipitated down to the bottom. Adding more PVB contents increased the apparent viscosity. With PVB addition, the YSZ particles were well dispersed in the suspensions and the amount of precipitated particles was decreased. As seen in Fig. 2, the sedimentation

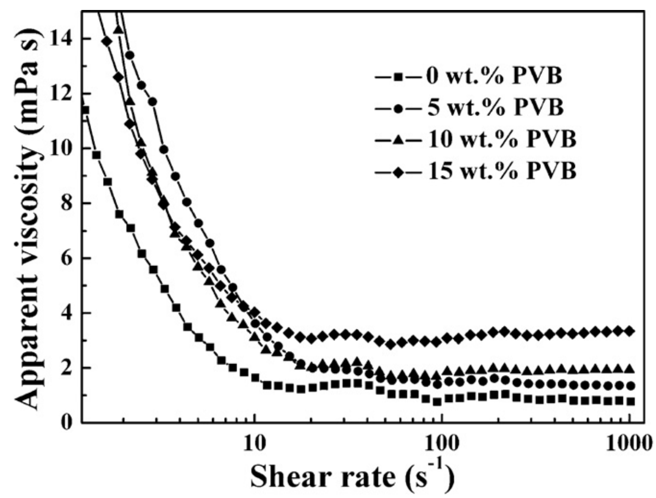

Fig. 1. Log plots of apparent viscosity as a function of shear rate for YSZ suspension with varying PVB concentration.

height sharply decreased after the PVB was added and the height slightly grew with increasing the PVB contents though the suspension still maintained well dispersed state. To investigate dispersion mechanism of the PVB adding YSZ suspensions, zeta potential measurement was carried out and the result is shown in Fig. 3. As increasing the PVB contents in the YSZ suspensions, the pH and zeta potential values did not show remarkable changes and were closely positioned at isoelectric points (IP). This minor variation in zeta potential cannot explain the drastic change in the dispersion of the YSZ suspensions, which suggests that a well dispersed state of the PVB adding suspension was not a result of electrostatic stabilization. Agglomerated particle sizes were also measured to confirm the effect of steric stabilization and it is shown in Fig. 4. The mean agglomerated particle size in the suspension was about 1920 nm for the suspension with no PVB addition. For this suspension, the YSZ powder was not dispersed and most of the YSZ particles were settled to the bottom. However,

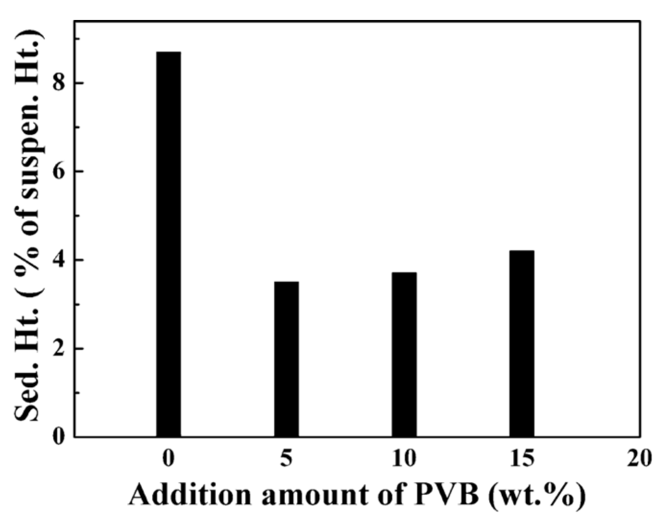

Fig. 2. Sedimentation height of YSZ particle in the suspension as a function of addition amount of PVB.

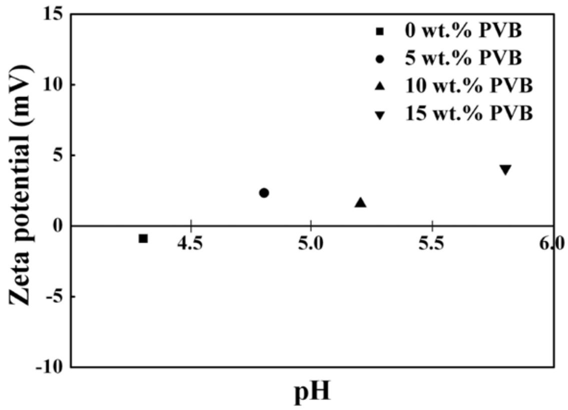

Fig. 3. Zeta potential as a function of pH of YSZ suspension with various PVB contents.

the particle size remarkably decreased to about 580 nm in the suspension with 5 wt.% PVB. However, the particles tended to aggregate in the suspensions at more addition of PVB and the aggregated size increased to about 830 nm in 10 wt.% and 910 nm in 15 wt.% PVB added suspensions, respectively. These results explain that the PVB acts positively as a dispersant with the PVB addition below 5 wt.% and a binder over 5 wt.% PVB concentration and also indicate that the steric stabilization is the major stabilization mechanism. This phenomenon can be described by polymer adsorption. Long linear polymer molecules in solution can be adsorbed onto the solid particle surface and the particles are dispersed and stabilized by these adsorbed polymer layers on solid surfaces due to the fact that the adsorbed polymer weakens the van der Waals attraction force and increases the repulsive force among the solid particles [9]. However, excessive polymer adsorption can cause reflocculation by the linkage between lengthened polymer chains. This is the reason why the agglomerated particle sizes precipitously decreased and increased again as shown in Fig. 4. Thus, the PVB acted both as a dispersant below 5 wt.% and as a binder over 5 wt.%. in the YSZ suspension. This dual role of PVB has been discussed in terms of viscosity

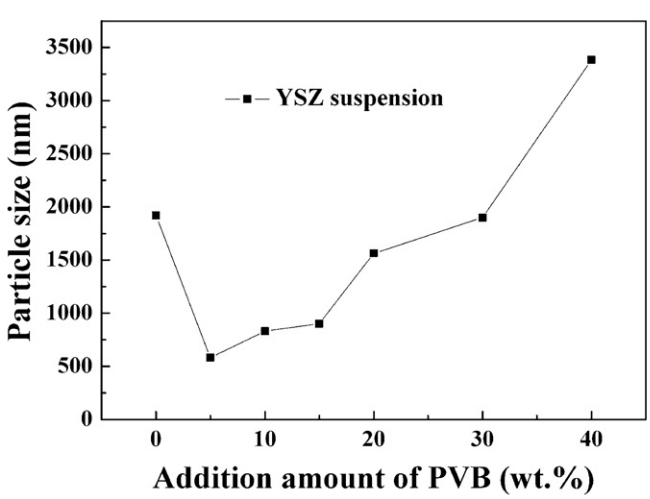

Fig. 4. The variation of an agglomerated particle size in YSZ suspension as a function of PVB concentration. If the PVB contents exceed over 20 wt.%, the suspension cannot be atomized and sprayed with the ESD system.

for ceramic suspensions in previous reports [8–10]. Bhattacharjee et al. [10] demonstrated that the PVB acted as a dispersant for the barium titanate suspension at low concentration levels (PVB < 1.6 vol%), while it changed to a binder with markedly increased viscosity as the concentration was further increased.

Three types of suspensions with different viscosities and agglomerated particle sizes (580 nm, 830 nm and 910 nm) were prepared by varying PVB concentration and used to deposit YSZ films by the ESD technique. The suspension without PVB was excluded in this study because of poor dispersion stabilization and low quantity of YSZ particles. Fig. 5 shows the images of deposited YSZ films on NiO-YSZ anode substrate. Fig. 5(a), (c) and (e) are surfaces and (b), (d) and (f) are cross-sectional images of the films. As shown in Fig. 5, the morphologies of deposited films by the ESD were changed from porous to dense. For the suspension with 5 and 10 wt.% PVB, the deposited layers were not dense (Fig. 5(a) and (c)). This is because the viscosities of the suspensions were not high enough to form dense layers on porous substrates. The sprayed suspensions with 5 and 10 wt.% PVB were absorbed into the porous NiO-YSZ substrates because of low viscosity and relatively small particle size. Thus, it is difficult to find the interface between the deposited layer and the NiO-YSZ anode substrate in Fig. 5(b) and (d). On the other hand, the deposited film for the 15 wt.% PVB suspension was dense (Fig. 5(e) and (f)) and its thickness reached to about 5 μm. The higher viscosity and relatively larger particle size prevent the sprayed suspension droplets from being absorbed into the substrate pores. Therefore, the interfaces of the deposited film become

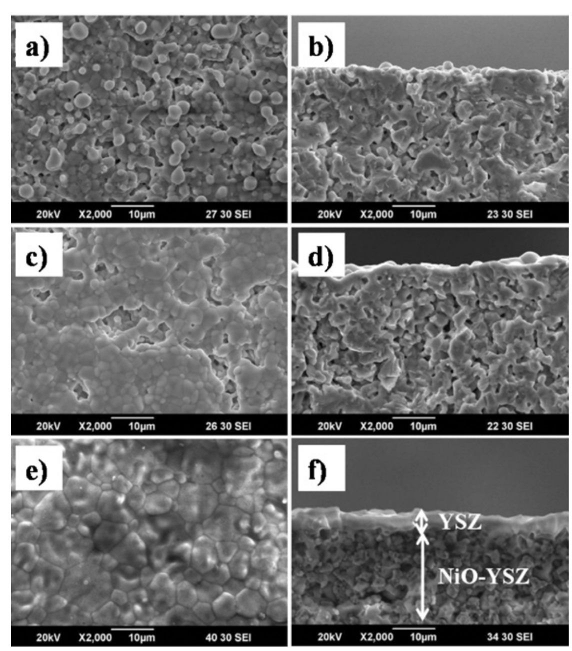

Fig. 5. SEM images of YSZ films deposited by ESD with different PVB contents. Left column is for surface and right column is for cross-sectional images; (a) and (b) with 5 wt.%, (c) and (d) with 10 wt.%, and (e) and (f) with 15 wt.%. All suspensions were sprayed for 20 min at a cone-jet mode with the applied voltage of 10 kV, flow-rate of 5 mL/h, and nozzle to substrate distance of 5 cm. After deposition, all specimens were sintered at 1400 °C for 5 h.

clearly distinguishable from the substrate as shown in Fig. 5 (e) and (f). However, if the viscosity of the suspension is excessively high, the suspension cannot be sprayed in the ESD system because the applied voltage cannot atomize the suspension to fine droplets.

4. Conclusions

The influence of PVB contents on the dispersion of the YSZ suspension and the effect of the suspension containing various PVB concentrations on the morphology of films deposited by the electrostatic spray deposition (ESD) were investigated. The PVB addition reduced the agglomerated particle size from 1920 nm for the suspension without PVB to 580 nm with 5 wt.% and the particle size increased again to 830 nm, and 910 nm with 10 wt.% and 15 wt.% PVB, respectively. The PVB addition improved the dispersion of YSZ powder in nonaqueous suspensions by the steric stabilization mechanism. It is confirmed that the PVB played a role as a dispersant for the suspension at relatively lower PVB contents ($<$5 wt.%) and as a binder at a higher PVB ($>$5 wt.%). The dense YSZ film of about 5 μm thickness was obtained from 15 wt.% PVB suspension, and this was due to the optimized viscosity and the agglomerated particle size of the suspension. The control of suspension viscosity and particle aggregation are critical factors if one considers obtaining a dense film by ESD process.

Acknowledgements

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