Electrophoretic deposition of lead zirconate titanate (PZT) powder from ethanol suspension prepared with phosphate ester

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Abstract
The formation of thick PZT films via electrophoretic deposition (EPD) was studied. The colloidal suspension of a nano-sized PZT powder dispersed in ethanol was prepared using a phosphate ester (PE) as a dispersant. The amount of PE addition on the stability of the PZT suspension has been investigated by measuring the pH and conductivity of the suspension, deposition weight and the relative density of the PZT green compacts. The effect of the applied voltage on the relative green density was also determined as a function of the wt% PE. The composition and microstructure of the sintered PZT ceramics were characterized by XRD and SEM. The electrical properties of the PZT ceramics were also investigated.
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1. Introduction

Lead zirconate titanate (PZT) is a ferroelectric ceramic material used in many advanced applications such as sensors, actuators, ultrasonic motors, and piezoelectric transformers [1–4]. PZT thick films have been fabricated by sol–gel [5–8], sputtering [9–12] and hydrothermal synthesis [13–16]. However, PZT films prepared by these methods are usually thinner than 10 μm, a thickness not required for actuation devices in microelectromechanical systems, and besides, these films are liable to crack and the fabrication process takes a relatively longer time. Electrophoretic deposition (EPD) is one of the enabling processing techniques capable of preparing thick ceramic films due to the simple apparatus required, and it is fast, low cost and versatile [17–20]. Therefore, the application of the EPD processing for fabricating thick PZT films has been promising [21–25]. EPD is a combination of two processes: electrophoresis and deposition. Electrophoresis is the motion of charged particles in a suspension under the influence of an electric field. Deposition is the coagulation of particles into a dense mass [26].

For the EPD processing, optimization of the colloidal suspension is very important [27–33]. A successful EPD processing is closely related to the choice of solvents and additives. It is essential that the colloidal particles in a solvent should be electrostatically stabilized for the electrophoresis. The addition of binders sometimes helps to increase the adherence and strength of the deposit and prevent cracking during the subsequent drying. Phosphate ester (PE) is an effective electrostatic stabilizer which positively charges the particles in organic solvents by donating protons to the surface. It has been used as a dispersant in tape casting technology [34,35]. Recently, it has been reported that the use of PE as a dispersant in non-aqueous solvents offers several advantages for EPD processing [36–38]. However, the study of PE on the EPD processing is still limited.

In this study, we investigated the effect of PE on the characteristics of the suspension stability and the following electrophoretic deposition. The electrical property of a thick PZT film prepared by EPD was also investigated.
2. Experimental procedure

The PZT powder used in this study was commercial PbZr0.53Ti0.47O3 powder (PZT, Sakai Chemical Co., Japan) with major impurities of Fe2O3 (0.006 wt%), SiO2 (0.006 wt%) and Na2O (0.001 wt%). A scanning electron micrograph of the powder is shown in Fig. 1. Each particle has similar granular shape and particle size. The average particle size calculated from the BET specific surface area was 0.19 μm. This particle size is fairly consistent with that estimated from the SEM photograph in Fig. 1. Reagent grade ethanol (>99.5%) was used as the dispersant. The poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB) with an average Mw of 50,000–80,000 (Sigma-Aldrich Corp., USA) and polyethyleneimine (PEI) with an average Mw of 10,000 (Wako Pure Chem. Ind. Ltd, Japan) were used as a binder and a dispersant, respectively.

The mixture of 10 g of PZT powder per 100 ml of ethanol was dispersed with PE. Suspensions of 0–2.18 wt% PE additions versus the weight of the powder were prepared. The suspensions were ultrasonicated (Model USP-600, Shimadzu, Inc.) at a frequency of 20 kHz and a power of 160 W for 5 min to break the agglomeration [39], and then were stirred for at least 30 min. A pH meter (Model HM-14P, TOA Electronic, Ltd, Japan) and an electric conductivity meter (Model ES-12, Horiba, Ltd, Japan) were used to characterize the PZT suspensions. The zeta-potential of the PZT suspension was measured by an acoustic and electroacoustic spectrometer (Model DT-1200, Dispersion Technology, Inc., USA).

It must be noted that the ‘operational pH’ measured using a pH meter calibrated for aqueous solvent differs from the real pαH in a non-aqueous solvent; i.e. [26,40],

\[
\text{pH} - \text{pαH} = \frac{\Delta E_j}{0.05916} \quad (at \ 25^\circ C)
\]

or

\[
\text{pH} - \text{pαH} = \frac{\Delta E_j}{0.05916}
\]

where pαH (= −log aH) is the negative logarithm of the proton activity in a non-aqueous solvent, \(\Delta E_j\) is the residual liquid-junction potential encountered in the standardization and testing step of a standard pH meter. For the ethanol suspension, \(\Delta E_j/0.05916 = -1.23\) as calculated by Wang et al. [40]. In this paper, the uncorrected pH was used for convenience.

The electrophoretic deposition was carried out at a constant voltage condition using a DC power supply (Model 2410, Keithley Instruments, Inc., USA) from the PZT suspensions prepared with different amounts of PE addition. The applied voltage was fixed at 50, 100 or 200 V. Stainless steel sheets with a working area of 20×20 mm² were used as the electrodes. The distance between the cathode and anode was fixed at 20 mm. The deposited weights were measured by weighing the stainless steel substrates before and after deposition and drying in air at room temperature. Most of the experiments to characterize the suspension and the following deposition properties were conducted using the suspensions prepared with PE only as an additive so as to simplify the chemical reaction between the PE and the powder surfaces.

Some deposition procedures were conducted for a couple of hours to prepare self-standing thick films or bulk materials. The PVB and PEI were also added to the suspensions to make thick, crackless PZT compacts for the electrical property measurements. The samples were dried in air after the deposition and then separated from the substrate. The PZT compacts were sintered in a covered, cement sealed alumina crucible with coarse PZT powder to prevent the evaporation of Pb during the sintering. The sintering was conducted at 1100 or 1250 °C for 2 h.

The green and sintered densities of the PZT deposits were measured by Archimedes’ method in kerosene. The microstructures of the sintered bodies were observed by a scanning electron microscope (SEM) (Model JSM 6500F, JEOL, Ltd, Japan) using polished and thermally etched surfaces.

The electrical measurements of the polished sample with Au electrodes were performed at room temperature in silicone oil. Leakage currents were measured using a femtoampere meter (Model 6417A, Keithley Instruments, Inc., USA) with a voltage increment of 50 s. After the voltage was applied to the samples, the current half a minute later was considered to be the leakage current. To avoid the influence of absorption charge of the samples [41,42], the current half a minute later was set to the leakage current after a voltage was applied to the samples [43].

3. Results and discussion

3.1. Suspension characterization

The operational pH and conductivity as a function of amount of phosphate ester (PE) are shown in Fig. 2. As the amount of PE increased, the pH dropped and the electrical conductivity increased. The characteristics of the suspension
can be classified into two stages with the PE amount: Stage I (PE ≤ 0.41 wt%)—rapid increase in conductivity and rapid drop in pH; stage II (PE > 0.41 wt%)—slight increase in conductivity and slight decrease in pH. The zeta-potential as a function of the amount of PE is shown in Fig. 3. The maximum zeta-potential was achieved with the 0.41 wt% PE addition. This value was consistent with the PE addition which showed the change in the slopes in Fig. 2.

The butyl acid phosphate used in this study was a mixture of the mono- and di-esters. They dissociate in an organic solvent and the protons (or hydronium ions) liberated from PE adsorb onto the powder and make the powder surface positively-charged. Therefore, the zeta-potential of PZT increases as shown in Fig. 3. When the amount of PE is increased, the amount of adsorbed protons becomes gradually saturated and the dissociation of PE reaches the equilibrium state. As a result, the dissociation of PE stops and excess PE molecules exist in the neutral state in the suspension. That is why the decrease in pH and the increase in the electric conductivity gradually show the gentle slopes, as shown in Fig. 2. The excessive addition of PE also caused a decrease in the zeta-potential.

### 3.2. Electrophoretic deposition of the PZT suspension

The PZT deposit yield for various amounts of PE under a constant voltage deposition at 100 V for 4 min is shown in Fig. 4. No deposition was observed from the suspension prepared with no PE addition. When a small amount of PE was added to the suspension, the deposit yield remarkably increased and showed the first maximum at the 0.41 wt% PE. Thereafter, the deposit yield decreased until 0.95 wt% PE and then increased again with continuous the PE addition. The over-addition of PE caused a decreased zeta-potential as shown in Fig. 3, but an increased adhesion of the deposit to the metal substrate. It was getting harder to wipe off the deposited powder from the stainless steel substrate after the experiment.

The relation of the deposit yield versus the deposition time at different applied voltages is shown in Fig. 5. The additional amount of PE was fixed at 0.41 wt% (Fig. 5(a)) and 0.82 wt% (Fig. 5(b)). These values are saturated amounts of PE adsorption and overaddition amount of PE, respectively. The relation between the deposit weight and the deposition time was non-linear and the deposition rate gradually slowed down with time. It is noted that in constant voltage deposition, the potential-induced electrophoresis decreases with increasing deposition on the electrode. This voltage drop across the electrodes hence results in the decrease in current density, and, hence, the deposition rate [18]. This was probably due to the sedimentation of the particles during the EPD; however, this phenomenon was not observed when the DC was not applied to the suspension. This problem was improved by slightly stirring the suspension using a magnetic stirrer during the deposition. A larger amount of deposit was obtained at higher applied voltages and longer deposition times. The total amount of deposit from the 0.82 wt% PE-added suspension was higher than that from the 0.41 wt% PE-added one. Thicker deposits with smooth surfaces were obtained from the excess added suspension. In the field of analytical chemistry, PE is often used as an extraction agent of metal ions from solutions by liquid–liquid extraction since it easily forms...
complexes with metal ions. It is likely that PE has strong chemical bonds with the substrate’s metal ions.

The relation of the relative green density of the PZT deposits versus the applied voltage is shown in Fig. 6. The green density slightly decreased with the increase in voltage. A similar tendency has been reported by Ma et al. [18] and Kang et al. [21] for the EPD of PZT powder. It seems that the EPD at higher voltages is unfavorable for particle packing though the deposition rate can be significantly raised with an increase in the voltage. In this study, the highest green density of 55.2% was observed for the compact deposited at 50 V from the suspension of 0.41 wt% PE addition, the amount of PE which gave the maximum zeta-potential as shown in Fig. 3.

The PZT thick film compacts deposited from the suspensions prepared with only PE addition tended to crack during drying. This tendency was suppressed by adding PVB and PEI. Quite thick, crackless bulk deposits with a thickness of 1–3 mm could be obtained from the suspension prepared with PE, PVB and PEI. The green and sintered densities of the PZT compacts prepared from the suspension with PE, PVB (1.11 wt%) and PEI (0.03 wt%) are shown in Fig. 7. The EPD was conducted at a constant voltage of 50 V. The relative green densities of the compacts prepared from 0.41, 0.82 and 1.63 wt% PE were, 48.2, 47.3 and 48% of the theoretical density, respectively. These values are a little lower than those of the green compacts deposited from the suspension prepared with only PE as shown in Fig. 6. The supplemental addition of PVB and PEI caused a slight decrease in the green densities, but produced thick, crackless PZT ceramics. Sintered densities at 1100 °C of all the PZT samples reached >99% of the theoretical density regardless of the PE concentration.

3.3. Characterization of the sintered PZT ceramics

The microstructures of the PZT ceramics sintered at 1100 and 1250 °C are shown in Fig. 8. The samples were prepared from the suspension with PE (0.41 wt%), PVB (1.11 wt%) and PEI (0.03 wt%). The average grain sizes of these PZT ceramics were 0.41 and 23.9 μm, respectively. The surface of the sintered PZT ceramics was smooth with no visible pores or cracks. The relative densities of both sintered PZT samples were >99% of the theoretical density.
The X-ray diffraction (XRD) pattern of the PZT ceramic sintered at 1250 °C is shown in Fig. 9. The XRD pattern of the as-received PZT powder is also shown in this figure. These data showed no unusual diffraction peaks except those from the standard PZT phase.

The polarization versus electric field (P–E) hysteresis loop of the PZT ceramic sintered at 1250 °C is shown in Fig. 10. The remnant polarization $P_r$ and the coercive field $E_c$ are 38 μC/cm$^2$ and 20 kV/cm, respectively. These values are similar to those of PZT thick films fabricated using various methods. The leak current of the PZT ceramic sintered at 1250 °C is shown in Fig. 11. It was confirmed that the insulation resistance of the PZT sample is sufficiently high.

4. Conclusions

The phosphate ester provided a good dispersion and surface charging of the PZT particles in an ethanol solvent. The pH and conductivity measurements indicate the adsorption saturation of the phosphate ester on the PZT surface. The highest zeta potential was observed at the saturated amount of the PE adsorption. The overaddition of PE caused a decreased zeta-potential but increased adhesion of the deposits to a metal substrate during EPD. Thick deposits with smooth surfaces were obtained from the suspension with the over-added PE. The supplemental addition of PVB and PEI caused a slight decrease in the green density, but enabled to fabricate thick, crackless sintered PZT ceramics. The PZT ceramics prepared by EPD showed a good polarization hysteresis and high insulation resistance.
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