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Thin Film Structure of Titania Nanoparticles Prepared by Electrophoretic Deposition

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Electrophoretic deposition (EPD) is advantageous in preparing thin films, consisting of nanoparticles (NPs), with homogeneous microstructure on a conductive substrate of little restriction to its geometry. This film-preparation technique could play a significant role in improving, by properly structuring the film in terms of its thickness and porosity, the performance of electrode of dye-sensitized solar cells (DSSCs). In this study, we attempted to prepare thin films of titania NPs by applying EPD from non-aqueous suspensions and discussed the effects of water content of suspension, particle size, particle shape and the type of solvent on the structure of thin film. When the commercial product (P-25, Evonik, 21-nm primary particle size) was used, the deposition weight of particles from the ethanol suspension linearly increased with applied EPD time, and was found to be estimated by the Hamaker equation. The water content in the suspension did not affect the structure of the thin film characterized by its weight, thickness and porosity. When the particle size was controlled by applying a milling operation, the porosity of deposition layer increased with particle size over a certain thickness range of deposition layer, although the deposition rate did not depend on the particle size. When the rod-like NPs (HPW-18NR, JGC C&C, 20-nm primary particle size) were used instead of round P-25 NPs, the deposition rate of HPW-18NR NPs became lower than that of P-25 NPs, as in the case of the porosity of the deposition layer of HPW-18NR NPs. When P-25 NPs suspended in a mixture solvent of ethanol and t-butyl alcohol (2-methyl-2-propanol) were tested for EPD, the structure of the deposited thin film depended on the mixture composition ratio.

1. Introduction

Electrophoretic deposition (EPD) is one of the promising processes for the thin film preparation with homogeneous microstructure on a conductive substrate (Cabanas-Polo and Boccaccini, 2016). A major advantage is that there is little restriction to the substrate geometry, as well as that low viscosity and low concentration of particle suspension can be used, comparing with dip and/or spin coating methods (Radice et al., 2010). Also advantageous, the weight of the particle layer deposited by EPD can sometimes be estimated by a simple calculation using such as Hamaker equation. Moreover, it is highly possible to control the structure of the deposition layer by adjusting electric operating conditions. Liou et al. (2011) and Shao et al. (2014) used titania nanoparticle (NP) films prepared by EPD for electrodes of dye-sensitized solar cells (DSSCs), and reported that such EPD-deposited titania films were useful for low-temperature DSSCs. In improving device performance of DSSCs, the thin film structure of NPs plays an important role where the thickness and the porosity of the NP film relate to the amount of dye adsorbed, transport speed of electrons, light transmissibility and the diffusion rate of electrolyte ions (Saito et al., 2004; Liang et al. 2006; Ni et al., 2006). Ofir et al. (2008) pointed out the dependence of electron diffusion on the porosity of the deposition layer of titania NPs, by applying compaction to the deposition layer after its preparation through EPD operation.

We attempted in this study to prepare the thus-desired thin film of titania NPs by EPD from non-aqueous suspension and to elucidate the effects of water content of suspension, particle size, particle shape and solvent type on the structure of thin film of titania NPs, characterized by such factors as the weight, thickness

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and porosity of the particle layer deposited by EPD, which are all important in improving the power conversion efficiency of DSSCs.

2. Experimental

2.1 Particles

The commercially available spherical P-25 NPs (Evonic) or rod-like HPW-18NR NPs (JGC Catalysts and Chemicals) were used as the titania NPs for EPD. SEM images of these NPs are shown in Figure 1. The P-25 particle powder was added into dehydrated-ethanol with acetylacetone; the particle concentration in the resulting suspension was 10 wt% while acetylacetone was added in 0.32 mmol per 1 g-titania. After 24-h mixing with a magnetic stirrer, 8.5 g of the P-25 NPs suspension was poured into a 20-mL polyethylene container with 40 g of alumina beads (0.1 mm and 0.5 mm in diameter), and then rotated at 150 rpm for a certain period (10 min to 10 h). After this rotating/milling operation, a sample suspension for EPD was prepared by dilution with the supernatant ethanol solution of the suspension, which was obtained by centrifugation. The particle concentration of the EPD sample suspension was fixed at 1.0 wt%.

The HPW-18NR NPs, supplied as 21-wt% suspension in water, were separated by a centrifuge (10,000 rpm for 20 min), and then dispersed in dehydrated-ethanol at 8.0-wt% particle concentration. After mixing in the presence of dehydrated-ethanol with acetylacetone in an ultrasonic bath for 90 min, the EPD sample suspension of 1.0-wt% particle concentration was obtained.

The particle size and size distribution of EPD sample suspension were measured using a dynamic light scattering apparatus (MCLS-1000, Otsuka Electronics). The electrophoretic mobility of particles was measured with ELS-8000 (Otsuka Electronics). The electrical conductivity of EPD sample suspension was measured with a conductivity meter (ES-71, Horiba), which was specified along with the applied electrical current and the measured voltage at the beginning of each EPD experiment (Farrokhi-Rad and Shahrabi, 2012). The water content in EPD sample suspension was measured with a Karl Fischer moisture titrator (MKC-610, Kyoto Electronics Manufacturing).

2.2 Electrophoretic deposition

The fluorine-doped tin oxide (FTO, Nippon Sheet Glass) with 15-Ω sheet resistance was used as the conductive glass substrate for a cathode electrode of EPD. The counter anode electrode used was a stainless steel plate. All the EPD experiments were carried out under DC constant current maintained by a potentiostat (AMEL 7050). The EPD electrodes were staged on a polyvinyl chloride plate of 15-mm thickness with a 7-mm rectangular hole or a 10-mm round hole; the area of electrode was then 49 mm^2 for the rectangular hole, or 78.5 mm^2 for the round hole, and the distance between electrodes was 15 mm.

The film thickness was measured with a surface profile meter (DEKTAK 150, Veeco) and estimated as an average value of the height profiles obtained along four scanning lines. The titania NPs having deposited on the FTO substrate was dissolved in a sulfuric solution and the concentration of titanium complex with hydrogen peroxide in the solution was measured at 410-nm wavelength with a spectrophotometer (UV-2400, Shimadzu) to determine the weight of the deposited NPs. The porosity of the thin film of particle deposition was calculated from the measured weight and thickness of film with the known density of anatase-type titania.

3. Results and discussion

3.1 Hamaker equation

The weight of particles deposited by EPD, m, can be expressed by the following equation, the so-called Hamaker equation, ignoring the contribution of any electrochemical reaction to consume the current in EPD (Ferrari and Moreno, 2010):

$$m = C\,S\,\mu_\mathrm{p}\,E\,t = C\,I\,\mu_\mathrm{p}\,t \big/ \sigma_\mathrm{s}\ , \tag{1}$$

where μ_p is the electrophoretic mobility of particles, S is the deposition area, C is the mass concentration of particles, E is the electric field, and t is the EPD operation time. E is expressed in terms of the applied current, I, and the electrical conductivity of suspension, σ_s.

Figure 2 shows the weight of the particle layer deposited under 35-μA constant current EPD operation from the suspension of 1-wt% mass concentration of P-25 NPs. When the EPD operation time was short, the particle weight increased in proportion to the EPD operation time. In considering the suspension properties of a given C, μ_p and σ_s maintained constant during EPD operation, the deposition weight should be proportional to the EPD operation time as predicted by Equation (1). It is noted that the broken straight line in Figure 2 corresponds to the calculated result of Equation (1) based on the average values of four sets of measurements for μ_p and σ_s, which supports the validity of Equation (1) if ethanol with low water content (< 1 wt%) is used as the solvent.

3.2 Water content

When suspensions with different water contents, w, were used in the EPD experiment, the deposition weight increased with EPD operation time, with apparently no dependency on the water content, as shown in Figure 2. This experimental finding could be predicted by Equation (1), if the measured electrical values of μ_p and σ_s did not change when water was added into the suspension after the preparation of the sample suspension. To confirm this water-content insensitivity of particle deposition phenomena, the EPD sample suspension was prepared at low water content, followed by the addition of a varying amount of water. Table 1 gives the measured particle size, μ_p and σ_s, indicating clearly that these values did not depend on the water content in the suspension. This confirmed trend signifies that the EPD phenomena are irrelevant to water content, in line with Equation (1) being applied. Table 2 provides the weight, thickness and porosity of the particle layer deposited on the substrate from various water-content suspensions by EPD operation for 60 s at constant current of 35 μA. The weight and the thickness of the deposition layer did not change appreciably when the water content in the suspension was changed from 0.155 to 0.722 wt%, leading to essentially invariant values of the porosity of the particle deposition layer. We can then conclude that such a low water content (less than 1 wt%) in ethanol suspension does not affect the deposition behaver of titania NPs by EPD.

3.3 Particle size

P-25 particle size in EPD sample solution decreased significantly as the milling operation period was extended, as expected. With decreasing particle size in suspension thus attained, the measured values of μ_p and σ_s increased, in ethanol with almost constant water content (w = 0.2 – 0.35 wt%), as shown in Figure 3.

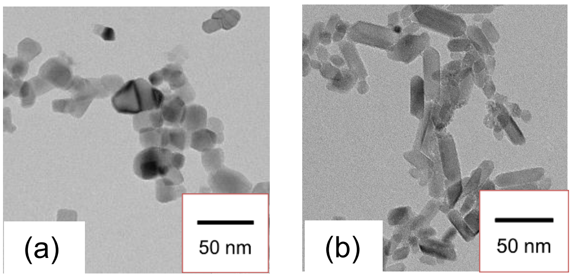

Figure 1. SEM images of (a) P-25 NPs and (b) HPW-18NR NPs.

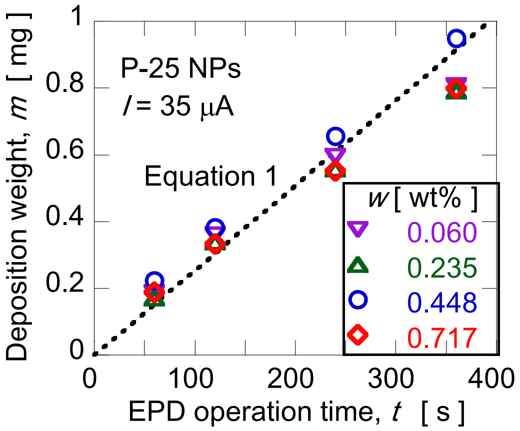

Figure 2. Effect of water content on particle weight deposited by EPD and calculated by Equation (1).

Table 1: Effect of water addition in P-25 suspension on particle size, mobility of particles, and suspension conductivity

Water content [wt%]	Particle size [μm]	Mobility [10^{-5} $cm^2/(V\ s)$]	Conductivity [μS/cm]
0.056	92.6	10.7	5.77
0.313	92.7	9.6	5.90
0.826	92.1	12.1	5.93

Table 2: Weight, thickness, and porosity of P-25 particle layer deposited by 35-μA constant current EPD for 60 s from various water-content suspensions

Water content [wt%]	Weight [mg]	Thickness [μm]	Porosity [%]
0.155	0.401	5.09	58.8
0.350	0.414	5.08	59.3
0.507	0.391	5.23	60.1
0.722	0.397	5.29	59.4

These trends could be explained as follows: As aggregates of P-25 NPs were disintegrated during the milling operation, the surface charge of P-25 NPs increased due to the separation of ions from titania surface to the solution at the same time. As a longer milling period rendered the particles acquiring smaller sizes, smaller-sized particles had larger surface charge, leading to more ions existing in the suspension. As a consequence, the electrophoretic mobility of particles and the electrical conductivity of suspension increased with decreasing particle size (see Figure 3). It is worthwhile, however, to note that the ratio μ_p/σ_s was almost constant (μ_p/σ_s = 1.90 – 1.97×10^{-5} m^3/C) under the conditions prevalent in Figure 3. This trend signifies that the particle deposition rate, i.e. m/t in Equation (1), could be constant even if the particle size in EPD sample suspension was changed.

Figure 4 shows the particle weight deposited on the substrate during EPD operation as a function of It; the dashed lines in the figure represent the calculated results from Equation (1) with the average of measured values of μ_p/σ_s. The experimental results tended to deviate from the calculation line as the EPD operation time increased. Since the volume of the sample suspension in our experimental apparatus was small, the particle concentration of the suspension could have been reduced appreciably in the course of EPD operation at larger times. Once this particle-concentration reduction is incorporated into the Hamaker equation, the following relation can be used as proposed by Ferrari and Moreno (2010):

$$m = C_0\, V\left\{1-\exp\left[-\left(f\, I\, \mu_p\, t\right)/\left(\sigma_s\, V\right)\right]\right\}, \tag{2}$$

where V is the volume of EPD sample suspension, C_0 is the initial mass concentration of particles, and f is an efficiency factor, which was introduced by Sarkar and Nicholson (1996). Note that $0 < f < 1$, that is, some part of the current during EPD operation is consumed by electrochemical reaction and/or some part of particles moved near the electrode did not deposited on it. The solid lines given in Figure 4 signify the calculation based on Equation (2) with $f = 1$, which indeed predicts the experimental results better than Equation (1) does when using P-25 NPs.

While the thickness of the particle deposition layer also increased with the product of the applied current and the EPD operation time, It, as shown in Figure 5, it depended on the particle size in the suspension as well. A conventional titania electrode for DSSCs usually requires a thickness of 10 – 20 μm; in this respect, the present results given in Figure 5 should justify that the EPD could easily control the thickness of deposition layer provided the particle shape is round (i.e., for P-25 NPs). The same particle shape provides a trend that the growth rate of deposition-layer thickness increased with particle size in the suspension. This result suggests that the porosity of deposition layer must have increased with particle size, because the weight-deposition rate was almost constant irrespective of particle size (see Figure 4).

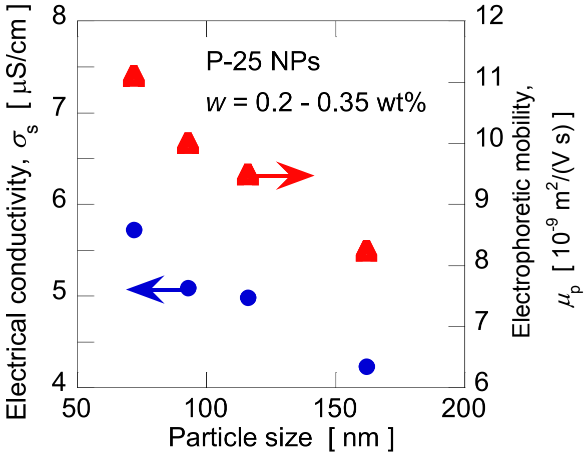

Figure 3. Effect of particle size in EPD sample suspension on electrical conductivity of suspension and electrophoretic mobility of particles.

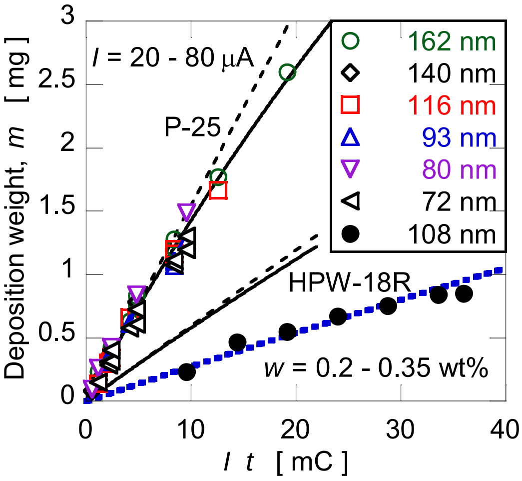

Figure 4. Particle weight deposited by EPD from suspensions with various particle sizes.

The porosity of the particle deposition layer calculated from the weight and the thickness was shown in Figure 6. As can be seen in the figure, the porosity increased slightly with the thickness. Dor et al. (2009) reported a similar result that the apparent density of the deposition layer decreased with increasing layer thickness, although they carried out constant-voltage EPD. An important implication to be noted in Figure 6 is that a wide range of the porosity could be realized by varying the particle size in the suspension, so that we will be able to test which combination of particle size and porosity is suitable for having proper power conversion efficiency.

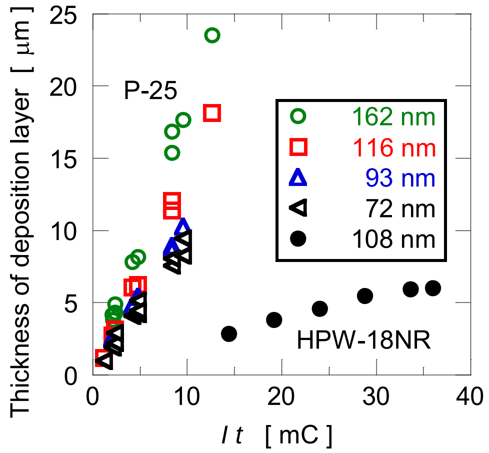

Figure 5. Thickness of particle deposition layer prepared by EPD from suspensions with various particle sizes.

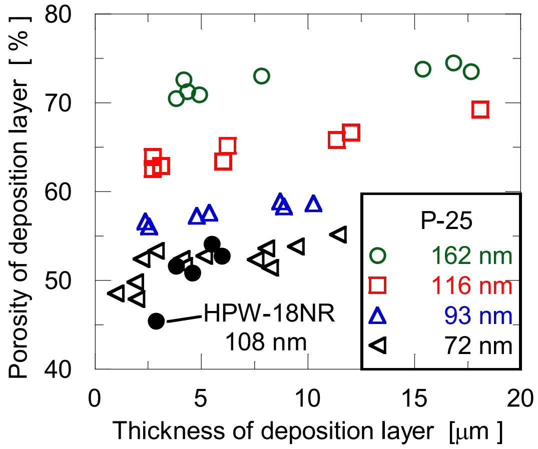

Figure 6. Effect of particle size on porosity of particle deposition layer.

3.4 Particle shape

When using the rod-like HPW-18NR NPs, the experimental results differed in the weight, thickness and porosity of deposition layer quantitatively from those for the round P-25 NPs, as compared in Figures 4, 5 and 6, respectively. The weight of HPW-18NR NPs deposition increased with It, but did not follow Equations (1) and (2); both the calculated results suggest that the weight deposition rate for HPW-18NR NPs was half the rate for P-25 NPs. This difference is believed to stem mainly from σ_s, implying that the ions in the HPW-18NR NPs suspension were present more profoundly than those in the P-25 NPs suspension. However, the calculated results even considering high σ_s of HPW-18NR NPs suspension was about double rate of the experimental results, that is, the thick dotted line in Figure 4 is the calculation line obtained from Equation (2) with f = 0.47, exhibiting good agreement with the experimental data. We might conclude that a half of particles moved near electrode did not deposit due to the repulsion of particles toward the electrode. A much slower increase in the thickness of deposition layer of HPW-18NR NPs, shown in Figure 5, than that of P-25 NPs is indeed in line with the said quantitative difference in the rate of weight deposition.

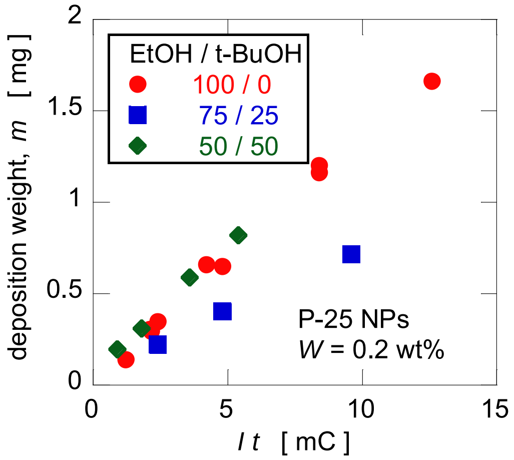

Figure 7. Particle weight deposited by EPD from P-25 NPs in mixture solvents.

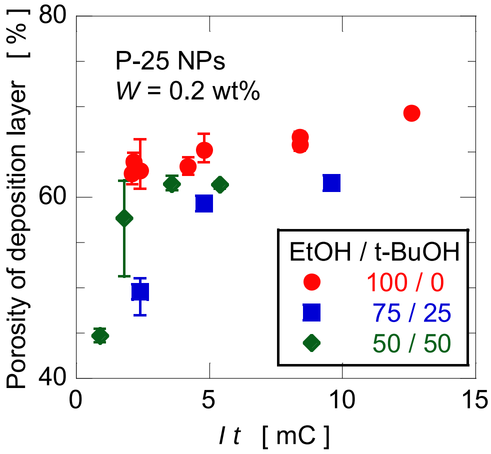

Figure 8. Porosity of particle deposition layer prepared by EPD from P-25 NPs in mixture solvents.

The porosity of deposition layer of HPW-18NR NPs was almost the same as that of P-25 NPs with 72-nm particle size. In reference to the profound effect of particle size on the porosity for P-25 NPs discussed above with a technical implication in Figure 6, the porosity for HPW-18NR NPs is regarded to be very low, considering the particle size of HPW-18NR NPs suspension being 108 nm. It is presumed here that the HPW-18NR NPs could deposit closely when their rod-like particle shape helps aligning effectively.

3.5 t-butyl alcohol (2-methyl-2-propanol)

The effects of suspending solvent on the EPD phenomena were examined when the P-25 NPs were suspended in mixture solvents of ethanol and t-butyl alcohol (2-methyl-2-propanol) in different compositions. Figures 7 and 8 show the weight and the porosity, respectively, of the deposition layer. While an increase in the fraction of t-butyl alcohol in the mixture solvent led to increasing particle size, decreasing electrical conductivity of the suspension and decreasing electrophoretic mobility of particles, no clear trends in the deposition weight and the porosity with respect to the mixture ratio of solvents were found, as indicated in the figures; it can only be stated at this stage that there should be some complex influences of the mixture ratio on the prevailing EPD film structure, warranting further research for elucidation.

4. Conclusions

An attempt made in this study to prepare thin films of titania NPs by applying EPD from non-aqueous suspensions of different particle shapes led to the following findings: The deposition weight of round particles, P-25 NPs, from the ethanol suspension linearly increased with EPD operation time; the trend was fairly predicted by the Hamaker equation and even better with an efficiency factor taken into account. The water content in the suspension, though limited in its range less than 1 wt%, had minimal effects on the thin film characteristics including the film weight, thickness and porosity. The size of round P-25 NPs, controlled by milling action, had a significant influence such that the porosity of deposition layer increased with particle size, while the deposition rate did not depend on the particle size. When the rod-like NPs, HPW-18NR, were used instead of round P-25 NPs, the former deposition rate became lower than the latter, as in the case of the porosity of the deposition layer. When the P-25 NPs suspended in a mixture solvent of ethanol and t-butyl alcohol (2-methyl-2-propanol) were tested for EPD, the structure of the deposited thin film depended on the mixture composition ratio.

Acknowledgments

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