Ultra-low-electric power electrophoretic deposition by using non-flammable hydrofluoroether

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A relative dielectric constant of a solvent is important for the electrophoretic deposition (EPD) suspension, and when the electrical resistance of the solvent is high, a large quantity of material is expected to be deposited. In this study, ethylperfluorobutylether (EFE), which is a kind of hydrofluoroether, was applied as the solvent for preparing a particle suspension for the EPD. EFE has the advantages of being polar, non-flammable, and having high electrical insulation properties. Silica powder was selected as the deposition material. When EFE is used, unlike when acetone-based EPD suspension was used, the amount deposited remains the same, but power consumption is 1/2,000 or less. Depending on conditions, power consumption is reducible even to 1/200,000. Thus, highly efficient EPD with ultra power saving ability was achieved. In addition, this process is extremely safe as EFE is non-flammable, removing the hazard of ignition. As the specific gravity of EFE is large, sedimentation of inorganic particles is slow; therefore, the dispersibility is excellent, and highly uniform coatings can be obtained. Unlike water-based EPD suspensions, the application of a high voltage is possible. In the present study, the deposition behavior was no different from that for conventional EPD, being controllable by varying the applied voltage, deposition time, and particle concentration.

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1. Introduction

In recent years, coating technology has been advanced by the ability to arrange fine particles in two or three dimensions, providing additive properties.1,2) Wet-process fabrication is especially attractive because of its low cost and ease of mass production. Electrophoretic deposition (EPD) is an example of such a process, and involves ceramic powder assembling technology. In the EPD process, an electric field is established between two electrodes immersed in a particle suspension, causing the electrically charged particles to migrate to and accumulate on the oppositely charged electrode.3) The electrophoretic mobility, \( u_e \) (m²·s⁻¹·V⁻¹), follows Smoluchowski’s equation:4)

\[
u_e = \frac{v}{E} = \frac{\varepsilon_0 \varepsilon R_{\zeta}}{\eta}
\]

where \( v \) (m·s⁻¹) is the migration velocity, \( E \) (V·m⁻¹) is the applied electrical field, \( \varepsilon \) (dimensionless) is the relative dielectric constant of the solution, \( \varepsilon_0 \) (F·m⁻¹) is the dielectric constant in vacuum, \( \eta \) (Pa·s) is the viscosity of the solution, and \( \zeta \) (V) is the zeta potential of the oxide particles. Virtually any type of ceramic material can be deposited by EPD; therefore, it has been gaining increasing interest as a ceramic processing technique for providing technical materials such as water adsorption/desorption materials,5) solid oxide fuel cells (SOFCs),6) hydroxypatite,7) photocatalysts,8) catalytic coatings,9) carbon nanotubes,10) solar cells,11) bio-glass,12) and separation membranes.13,14)

Owing to the basic principles of electrophoresis, as indicated in Eq. (1), a solvent with a high relative dielectric constant is necessary for use in the EPD bath. Generally, the dielectric constant of water is higher than most organic solvents; however, large currents of 1–100 mA·cm⁻² can be formed in EPD suspensions based on water.15) If a high voltage is applied to water, gas is generated through electrolysis. On the other hand, a high voltage can be applied to polar organic solvents such as alcohols and ketones, with currents only on the order of \( \mu \)A·cm⁻² to mA·cm⁻² in many cases.16-21) It is generally assumed that the growth of deposits follows a linear trend according to Hamaker’s equation:18,22)

\[
\frac{m}{S} = \frac{\mu C H}{\sigma}
\]

where \( m \) (g) is the deposited mass, \( S \) (m²) is the electrode surface area, \( C \) (g·m⁻³) is the concentration of particles, \( \sigma \) (A·V⁻¹·m⁻²) is the suspension conductivity, \( I \) (A·m⁻²) is the current density, and \( t \) (s) is the deposition time. For constant voltage EPD, power consumption is dependent on the current \( (W = I·V) \); therefore, carrying out EPD in a water-free suspension would save power. From Eq. (2), when the electrical resistance of the solvent is high, a large quantity of material is expected to be deposited. In general, industrial manufacturers aim to avoid the use of flammable organic solvents in their production processes. Therefore, the use of a non-flammable polar organic solvent for EPD would improve both power efficiency and safety. We have previously reported the possibility of achieving this aim by employing a hydrofluoroether to prepare the EPD suspension;23) however, the dependence of the level of deposition on the current has not yet been evaluated.

In the present study, the technological feasibility of preparing silica coatings using high voltage EPD in a non-flammable polar organic solvent was investigated. Ethylperfluorobutylether

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(EFE), which is a kind of hydrofluoroether, was applied as the solvent for preparing the EPD suspension. The two main purposes of this study were to realize high voltage EPD without the hazard of ignition by using non-flammable, polar, EFE, and to form energy efficient coatings by exploiting the electrical insulation properties that are known to be excellent in this solvent.

2. Experimental

Silica powder (Hyprecica FQ N4N) was obtained from Ube-Nitto Kasei Co., Tokyo, Japan. EFE (Novec HFE-7200, Sumitomo 3M Ltd.) was used as the EPD solvent (see Table 1 for physical properties). The EPD suspension was prepared as follows: First, silica powder was heat-treated at 120°C for 3 h in order to dry it, and then allowed to cool to room temperature. A predefined quantity of silica powder and an appropriate amount of molecular sieves (3A, 1/16, Junsei Chemical Co., Tokyo, Japan) were added to EFE and it was stirred for 10 min using a magnetic stirrer. After 24 h, the molecular sieves were removed from the solution and ultrasonic vibration of the solution was carried out for 10 min.

The EPD was performed using the cell configuration shown in Fig. 1. The volume of the solution was 7 mL. A platinum wire (length: 25 mm, diameter: 0.8 mm) was used as the deposition electrode, and two stainless steel plates (length: 50 mm, width: 5 mm, thickness: 0.5 mm) were used as the counter electrodes. The distance between the deposition electrode and counter electrodes was set at 10 mm. A DC voltage was applied using a DC voltage/current source/monitor (R6243; Advantest Corporation, Tokyo, Japan). The resolution of the current was 100 pA. The aggregation and sedimentation properties of the particles were evaluated using a Turbiscan Lab Thermo (Formulaction, France). This analyzes the behavior of the dispersion particles in a glass vial by transmission light. The transmission light intensity in each height of the suspension was measured at constant intervals. The profile of the transmission light intensity vs time shows the behavior of the cohesion and sedimentation in a suspension. If particles cohesion, the transmission light intensity will increase. Also, if the particles sediment, the transmission light intensity of the upper part of the glass vial will increase. When the stable dispersion condition is being maintained, the transmission light intensity is steady with time. The cross-sectional morphology of the coating was observed using a confocal laser scanning microscope (VK9500; Keyence Corporation, Osaka, Japan)

3. Results and discussion

3.1 Suspension properties

The silica powder was monodispersed in the EFE, with a relatively uniform particle size of average diameter 420 nm, as shown in Fig. 2. The decentralized stabilization of the suspension is shown in Fig. 3. The intensity of transmitted light intensity was measured every 10 min for 1 h, with few differences evident during this time. This can be seen more clearly in the magnified section of the measurements taken at the 10 mm position in the cell (inset, Fig. 3). The intensity increased slightly over time, but was only 1.5% higher after 1 h. In addition, no sedimentation can be observed in Fig. 3. These results indicate that there was only a very low level of particle cohesion during the first hour after formation of the suspension in the EFE, demonstrating the high stability of the system. The majority of EPD experiments conducted by this study were carried out for less than 5 min.

3.2 Silica coating by EPD

No silica powder was found to deposit on the electrode in the absence of an applied electric field. For all of the EPD experiments, the silica was deposited onto the anode, demonstrating
that it was negatively charged within the suspension. The exact mechanism by which the particles acquired this charge has not yet been elucidated. This is because fundamental data regarding the charging of silica particles in EFE, such as zeta potential, does not provide enough information. Therefore, the charging behavior of silica powder in EFE is not discussed in the present study.

**Figure 4** shows the dependence of the amount of material deposited with deposition time for the EPD bath with a 3 g·L⁻¹ concentration of silica, at an applied DC voltage of 100 V. The rate of deposition can be seen to decrease with time. During the initial stages, the amount of material deposited increased steadily; however, after approximately 7 min, the rate of deposition gradually decreased. This was attributed to the reduction in silica particle concentration within the EPD bath as the deposition onto the substrate proceeded. For example, about 7 mg of silica was deposited in 10 min on an electrode area of 0.628 cm². This is equivalent to approximately 1/3 of the total quantity of powder in the suspension being deposited (initial concentration was 21 mg in 7 mL EFE). In addition, the electric field in the EPD bath may decrease with the formation of an insulating silica layer.

**Figure 5** shows the relationship between deposition amount and applied voltage. It can be seen that the amount of deposited material increased with increasing voltage. This result is the same as the behavior generally observed, independent of particle concentration.

**Figure 6** shows the relationship between the deposition amount after 5 min, and silica concentration. A photograph of the coated electrode and a representative 3D image of a fractured cross section of the silica coating is shown in **Figure 7**. From the image in **Fig. 7(a)**, the silica can be seen to be uniformly coated on the electrode, with no unevenness observed. As the specific gravity of EFE is large, particle sedimentation is slow. This is considered to be one of the reasons for the formation of the smooth, uniform coating. From the 3D image of the fractured cross section of the silica coating on the substrate, the thickness was measured to be approximately 58 µm. The lower level (bright area) is the substrate and the upper level (dark area) is the surface of the deposited silica coating. The quantity of deposited material for the sample imaged in **Fig. 7** was 8 mg·cm⁻², as calculated from **Fig. 6**. This translates to a mass of 5 mg, taking into account the actual electrode area. The volume of the coating calculated from the thickness and the electrode area was 3.64 × 10⁻³ cm³. Therefore, the specific weight of the coating was 1.37 g·cm⁻³, and the porosity was 38%. This demonstrates that the coating was quite dense.

### 3.3 Current density of EPD

The above-mentioned deposition phenomena are commonly observed for EPD systems. However, the data obtained regarding current density differ greatly from conventional studies. The current densities when acetone and EFE were used for the EPD are shown in **Fig. 8**. The amounts of deposited material were 4.8 mg (7.6 mg·cm⁻²) from acetone containing 1 wt% of water, 0.1
mg (0.16 mg·cm⁻²) from dehydrated acetone, and 5.0 mg (8.0 mg·cm⁻²) from EFE. Only low quantities of silica were deposited from dehydrated acetone, in comparison to both that containing water and the EFE, which was attributed to the low zeta potential in this solvent. On the one hand, when acetone containing 1 wt% of water was used, an almost comparable amount of deposit was obtained as in the case of EFE. The energy efficiency of the deposition from these two solvents was calculated from the quantities of silica deposited and the current densities. In the case of acetone containing 1 wt% water, the amount of deposit was 4.8 mg after 5 min of EPD. With an average current density of 100 μA·cm⁻² (from Fig. 8), and an electrode area of 0.628 cm², the average current was 6.28 × 10⁻⁵ A, and the power consumption was calculated to be 6.28 mW (=6.28 × 10⁻⁵ A × 100 V). Although 100 V were applied, the deposition from acetone containing 1 wt% of water was relatively efficient. When EFE was used, the amount of deposit was found to be 5.0 mg after 5 min EPD. With an average current density of 50 nA·cm⁻², the average current was 3.14 × 10⁻⁸ A. Compared to the acetone containing 1 wt% water, almost the same amount of deposit was obtained for only approximately 1/2000 the amount of electricity, with a power consumption of only 3.14 μW (=3.14 × 10⁻⁸ A × 100 V).

The current densities when the applied voltage was lowered to 10 V are shown in Fig. 9. In this experiment, the measured current is very small, and very close to the detection limit of the DC voltage/current source/monitor. Therefore, in Fig. 9, the results are shown in the form of curve fitting. The quantities of material deposited were found to be 0.8 mg (1.3 mg ·cm⁻²), 0.9 mg (1.4 mg ·cm⁻²), and 0.9 mg (1.4 mg ·cm⁻²) for silica concentrations of 3, 4, and 5 g·L⁻¹, respectively. The amount of deposit was approximately 1/6 of the values achieved at 100 V, and the current was around 1/60 lower. In addition, the power consumption was only 5.0 nW (=0.50 nA × 10 V). For the same amount of deposit, the deposition efficiency was 100 times greater than when the EPD was carried out at 100 V. This demonstrates ultra power saving ability, reducing the electric power to 1/200,000 of the amount used to achieve the same quantity of deposit as for the acetone containing 1 wt% water.

4. Conclusion

Ultra power saving EPD was here investigated. The polar and non-flammable EFE, which has high electrical insulation properties, was applied as the solvent in which the suspension was formed. EPD of silica was carried out, with highly uniform coatings obtained. For the same amount of deposit, in comparison with acetone-based EPD, the EFE was significantly more energy efficient, with power consumption being 1/2,000 or less. Depending on the EPD conditions, the power consumption could be reduced to even 1/200,000. Thus, highly efficient EPD with ultra power saving ability was achieved. In addition, as the non-flammable EFE was used as the solvent, this process is safe, as there is no hazard of ignition. Unlike water-based EPD suspensions, the application of a high voltage is possible. As the specific gravity of EFE is large, sedimentation of inorganic particles is slow; therefore, the dispersibility is excellent, and highly uniform coatings can be obtained. In the present study, the deposition behavior was no different from that for conventional EPD, being controllable by varying the applied voltage, deposition time, and particle concentration.

References

1) A. R. Boccaccini and I. Zhitomirsky, *Curr. Opin. Solid State Mater. Sci.*, 6, 251–260 (2002).
2) T. Uchikoshi, T. S. Suzuki, H. Okuyama, Y. Sakka and P. S. Nicholson, *J. Eur. Ceram. Soc.*, 24, 225–229 (2004).
3) C. Baldisserri, D. Gardini and C. Galassi, *J. Colloid Interface Sci.*, 347, 102–111 (2010).
4) R. M. Rock, P. J. Sides and D. C. Prieve, *J. Colloid Interface Sci.*, 383, 306–313 (2013).
5) H. Negishi, A. Endo, T. Ohmori and K. Sakaki, *Ind. Eng. Chem. Res.*, 47, 7236–7241 (2008).
6) H. Negishi, N. Sakai, K. Yamaji, T. Horita and H. Yokokawa, *J. Electrochem. Soc.*, 147, 1682–1687 (2000).
7) T. M. Sriridhar, U. K. Mudali and M. Subbaiyan, *Corros. Sci.*, 45, 237–252 (2003).
8) S. Yanagida, A. Nakajima, Y. Kameshima, N. Yoshida, T. Watanabe and K. Okada, *Mater. Res. Bull.*, 40, 1335–1344 (2005).
9) K. S. Yang, Z. D. Jiang and J. S. Chung, *Surf. Coat. Tech.*, 168, 103–110 (2003).
10) X. Li and I. Zhitomirsky, *J. Power Sources*, 221, 49–56 (2013).
11) J. Akilavasan, K. Wijeratne, H. Moutinho, M. A. Jassim, A. R. M. Almoud, R. M. G. Rajapakse and J. Bandara, *J. Mat. Chem. A*, 1, 5377–5385 (2013).
12) M. Mehdipour, A. Afsheer and M. Mohabdi, *Appl. Surf. Sci.*, 258, 9832–9839 (2012).
13) B. Onokhanond and M. E. Mullins, *J. Membr. Sci.*, 194, 3–13 (2001).
14) H. Negishi, M. Okamoto, T. Imura, D. Kitamoto, T. Ikegami, Y. Yidemoto, N. Koura, T. Sano and H. Yanagishita, *J. Am. Ceram. Soc.*, 89, 124–130 (2006).
15) Z. Wang, J. Shenilt and P. Xiao, *Scr. Mater.*, 42, 653–659 (2000).
16) B. Ferrari, A. J. Sanchez-Herencia and R. Moreno, *J. Eur.
17) T. Uchikoshi, K. Ozawa, B. D. Hatton and Y. Sakka, J. Mater. Res., 16, 321–324 (2001).
18) B. Ferrari and R. Moreno, J. Electrochem. Soc., 147, 2987–2992 (2000).
19) H. Negishi, N. Koura and Y. Idemoto, J. Ceram. Soc. Japan, 105, 351–355 (1997).
20) H. Negishi, A. Endo, A. Miyamoto, K. Sakaki and T. Ohmori, Key Eng. Mater., 412, 171–176 (2009).
21) K. Miyazaki, K. Shima, T. Aoki and K. Kamiya, J. Ceram. Soc. Japan, 106, 1129–1134 (1998).
22) H. C. Hamaker, Trans. Faraday Soc., 36, 279–286 (1940).
23) H. Negishi, A. Miyamoto, A. Endo, K. Sakaki, H. Yanagishita and K. Watanabe, Advanced Ceramic Coatings and Interfaces V: Ceramic Engineering and Science Proceedings, 31(3), Jan. 24–29, Florida, USA (2010) pp. 177–185.
24) http://www.mmm.co.jp/cmsd/fluorine/products/novec7000.html.
25) H. Negishi, T. Tsuru, K. Nouzaki, T. Kitazato, K. Sakaki and H. Yanagishita, Desalin. Water Treat., 17, 99–105 (2010).
26) H. Negishi, A. Miyamoto, K. Sakaki and A. Endo, J. Ceram. Soc. Japan, 119, 168–172 (2011).
27) Y. Takayama, H. Negishi, S. Nakamura, N. Koura, T. Idemoto and F. Yamaguchi, J. Ceram. Soc. Japan, 107, 119–122 (1999).