Power efficiency of electrophoretic deposition of silica using nonflammable ethyl perfluorobutyl ether

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Electrophoretic deposition (EPD) has attracted attention as a coating technology for ceramic particles. Ethyl perfluorobutyl ether (EFE), a hydrofluoroether, can be used as a solvent for preparing silica particle suspensions for EPD. EFE is polar, nonflammable, and has a high density. In addition, the electrical insulation of EFE allows significant power savings over conventional EPD. In this study, the power consumption of EPD with EFE was compared with that of EPD with various common solvents. The silica particle suspension showed a high zeta potential in EFE. Power consumption per unit deposition amount in EFE at 10 V was 6.4 × 10⁻⁵% of that of water at 100 V. Similarly, it was 2.6 × 10⁻³% of that of acetone, 7.8 × 10⁻⁵% of that of ethanol, and 7.5 × 10⁻⁵% of that of ethanol at 100 V. Compared with the solvents used previously in EPD, EFE offers significant energy savings to the EPD process.

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1. Introduction

Electrophoretic deposition (EPD) is a powder assembling technology for ceramics. An electric field is established between the two electrodes immersed in a particle suspension, causing the charged particles to migrate to and accumulate on the oppositely charged electrode. EPD is especially appealing because of its low cost and ease of mass production. Almost any ceramic material can be deposited by EPD; therefore, it has been receiving increasing interest as a ceramic processing technique in fields such as energy, industrial technology, and biotechnology.

Electrophoresis is governed by the electrical double layer at the interface between the charged particles and their solvent. When the thickness of the electrical double layer (κ⁻¹) is sufficiently small relative to the particle diameter (a) or the particle diameter (a) is sufficiently large (κa > 1), the electrophoretic mobility \( u_e \) (m²·s⁻¹·V⁻¹) follows the Smoluchowski’s equation:

\[
u_e = \frac{v}{E} = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \quad (1)
\]

where \( v \) (m·s⁻¹) is the migration velocity, \( E \) (V·m⁻¹) is the applied electric field, \( \varepsilon_r \) (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 particles. Polar liquids such as organic solvents and aqueous solutions can be used in EPD to achieve high electrophoretic mobility, although each solvent has its own characteristics. EPD with nonpolar solvents such as hexane and toluene has also been reported.

In aqueous solution, EPD presents no fire hazard. However, the conductivity of the liquid is high and operating currents can be as large as 100 mA·cm⁻². When a high voltage is applied, electrolysis of water (abbreviated as Water) generates gas that will disturb the formation of the deposited layer. The dielectric constant of organic solvents such as alcohols and ketones is lower than that of Water; therefore, a high voltage can be used with organic solvents. However, many of these solvents are flammable. Moreover, in many cases, their conductivity is lower than that of Water, varying between \( \mu \)A·cm⁻² and mA·cm⁻².

It is generally assumed that the deposition follows a linear trend:

\[
\frac{m}{I} = \frac{u_e C_H}{\sigma} \quad (2)
\]

where \( m \) (g) is the deposited mass, \( S \) (m²) is the electrode surface area, \( C \) (g·m⁻³) is the particle concentration, \( \sigma \) (A·V⁻¹·m⁻¹) is the suspension electrical conductivity, \( I \) (A·m⁻²) is the current density, and \( t \) (s) is the deposition time. Equation (2) indicates that the ratio of conductivity and current is related to the deposited mass.

We have reported elsewhere that hydrofluoroether (HFE: an ether with alkyl and fluoroalkyl substituents) is a suitable solvent for EPD. HFE is a nonflammable and high-density polar organic solvent with a large electrical insulation resistance. Therefore, high voltages can be applied safely at lower currents than the above-mentioned solvents. In HFE, the settling velocity of the particles is slow as the density of the solution is high. An initial investigation into the power-saving benefits of EPD with ethyl perfluorobutyl ether (EFE) revealed that sedimentation of particles in EFE is low and the stability of the suspension is high. Therefore, a uniform EPD coating was obtained. However, the charging behavior of particles has not been evaluated yet. In addition, for conventional solvents and EFE, consideration of only power consumption of EPD is essential. In particular, a comparison of the power-saving rates of EFE and conventional solvents is necessary.

In this study, the power consumption and behavior of EPD were investigated by applying a constant voltage to silica powder in various solvents. For comparing the power consumption and
behavior of EPD with HFE, acetone (abbreviated as ACE), ethanol (EtOH), and isopropyl alcohol (IPA) were chosen as common solvents because they are flammable but high-voltage application is possible with these solvents. In addition, Water is also used for this comparison because high-voltage application is difficult with Water but it is nonflammable. The EPD behavior, zeta potential, current density, and deposition amount in various solvents were measured. In the respective solvent, the power consumption per unit area and per unit deposition amount was calculated; the advantage of the EFE was also investigated.

2. Experimental

Silica powder (density: 2.2 g·cm⁻³, Hipresica FQ N4N, Ube-Nitto Kasei Co., Tokyo, Japan) was used as the EPD deposition material. The EPD solvents were EFE (C₄F₉OC₂H₅, Novec HFE-7200, Sumitomo 3M Ltd.), Milli-Q water (resistance: 18 MΩ·cm⁻²; Merck Millipore Corporation), and special grade ACE, EtOH, and IPA (Wako Pure Chemical Industries). The physical properties of the solvents are shown in Table 1. The particle size distribution was measured at 25°C with an electrophoretic light scattering spectrometer (ELS-8000, Otsuka Electronics Co., Ltd., Osaka, Japan). The zeta potential and electrophoretic mobility of the silica particles were measured at 25°C by an electrophoretic light scattering spectrophotometer (Zetasizer-nano ZS, Malvern Instruments Ltd., Worcestershire, UK).

EPD experiments were performed as previously reported.²) The experiment is briefly described as follows. Each EPD suspension was prepared as follows: First, silica powder was dried at 120°C for 3 h; then, it was allowed to cool to room temperature under a dry atmosphere achieved by using a silica gel in a desiccator. A molecular sieves. The volume of the solution in the EPD cell was 3 g·L⁻¹. Then, it was allowed to cool to room temperature under a slow. The high zeta potential of silica in the EFE suspension and precipitation of silica particles in EFE is 7 mL. A platinum wire (length: 25 mm, diameter: 0.8 mm, deposition area: 0.628 cm²) was used as both the deposition and counter electrodes. The distance between the two 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. Power consumption W (Wh) was calculated as follows using the applied voltage V (V), current I (A), and EPD time t (h):

$$W = I \cdot V \cdot t.$$  (3)

The deposit amount and the electrode area are necessary for calculating the power consumption.

3. Results and discussion

3.1 Zeta potential and electrophoretic mobility

In EPD, the physical properties of solvents in Table 1 have following implication. Boiling point affects the ease of drying the EPD coating. Drying of the EPD layer is easy in the EPD solvents used. Density of the solvent affects the sedimentation rate of the dispersed particles. Dielectric constant and viscosity affect the electrophoresis. Their relationship is shown in Eq. (1). Presence or absence of flammability affects the equipment of EPD and safety of operation. EPD requires charged particles and an electric field. The zeta potential and electrophoretic mobility of silica powder in various solvents are shown in Table 2.

The charging mechanism of the particles used in this study has not yet been determined because of the difficulty in elucidating the mechanism of charged particles in nonaqueous solvents. Therefore, the thickness of the electric double layer is unknown. However, the silica particle size in EFE was 420 nm,³ 604 nm in ethanol, 793 nm in IPA, 782 nm in acetone, and 1163 nm in water. Therefore, in this study, the zeta potential can be calculated by assuming that the particle diameter is larger than the thickness of the electric double layer [Eq. (1)]. Silica particles are negatively charged in all solvents. The zeta potential values of the silica particles in EtOH, IPA, ACE, and Water are −50, −51, −60, and −64 mV, respectively. These potentials are large enough for EPD, although their respective differences are small. The electrophoretic mobility is affected by the dielectric constant and viscosity of the solvent [Eq. (1)]. The mobility of silica particles was in the order Water > ACE > EtOH > IPA. The zeta potential of the silica particles in EFE was −83 mV, which is the highest potential among all the solvents investigated. A high potential is advantageous because dispersion stability increases with zeta potential, making particle agglomeration rare. The densities of EtOH, IPA, ACE, and Water are 0.785, 0.781, 0.788, and 0.997 g·cm⁻³, respectively; however, the density of EFE is significantly higher at 1.43 g·cm⁻³. Therefore, precipitation of silica particles in EFE is slow. The high zeta potential of silica in the EFE suspension and the large density of EFE support the observed high dispersion stabilization of the silica powder in EFE.²)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Zeta potential [mV]</th>
<th>Electrophoretic mobility [m²·s⁻¹·V⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>−64</td>
<td>−5.0 × 10⁻⁸</td>
</tr>
<tr>
<td>ACE</td>
<td>−60</td>
<td>−2.9 × 10⁻⁸</td>
</tr>
<tr>
<td>EtOH</td>
<td>−51</td>
<td>−1.0 × 10⁻⁸</td>
</tr>
<tr>
<td>IPA</td>
<td>−50</td>
<td>−3.5 × 10⁻⁹</td>
</tr>
<tr>
<td>EFE</td>
<td>−83</td>
<td>−9.5 × 10⁻⁹</td>
</tr>
</tbody>
</table>

Table 2. Zeta potential and electrophoretic mobility of silica particles in various solvents at 25°C

All the values except that of the boiling point were obtained at 25°C.

Table 1. Abbreviation, physical properties and flammability of solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Abbreviation</th>
<th>Boiling point [°C]</th>
<th>Density [g·cm⁻³]</th>
<th>Viscosity [mPa·s]</th>
<th>Relative dielectric constant</th>
<th>Flammability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Water</td>
<td>100</td>
<td>0.997</td>
<td>0.89</td>
<td>7.3</td>
<td>nil</td>
</tr>
<tr>
<td>Acetone</td>
<td>ACE</td>
<td>56.3</td>
<td>0.788</td>
<td>0.303</td>
<td>20.7</td>
<td>high</td>
</tr>
<tr>
<td>Ethanol</td>
<td>EtOH</td>
<td>78.4</td>
<td>0.785</td>
<td>1.096</td>
<td>24.5</td>
<td>high</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>IPA</td>
<td>82.4</td>
<td>0.781</td>
<td>1.96</td>
<td>18.3</td>
<td>high</td>
</tr>
<tr>
<td>Ethylperfluorobutyl ether²¹)</td>
<td>EFE</td>
<td>76.0</td>
<td>1.43</td>
<td>0.57</td>
<td>7.35</td>
<td>nil</td>
</tr>
</tbody>
</table>

All the values except that of the boiling point were obtained at 25°C.
In addition, as described later, the electrical insulation of EFE is higher than that of either alcohol or ACE. Therefore, the electric double layer in EFE may be quite thick, allowing the surface potential and the zeta potential to be approximately equal. In such cases, the Hückel equation or Henry’s equation applies and the zeta potential obtained is 1.5 times the maximum value obtained from the Smoluchowski’s equation. This means that the zeta potential in the EFE is high. On the other hand, the electrophoretic mobility is dependent on the dielectric constant and viscosity of EFE. The viscosity of EFE lies between the values of ACE and EtOH (Table 1). The relative dielectric constant of EFE is low compared to the other solvents (e.g., it 1/3rd of that of Water and 1/3rd of that of ACE). Nevertheless, the electrophoretic mobility of EFE is almost equal to EtOH at

\[ \frac{1}{3} \text{rd of that of Water} \]

Thus, silica particles in EFE have a high zeta potential and an electrophoretic mobility sufficient for EPD.

3.2 EPD in various solvents

EPD of silica powder was performed in each of the chosen solvents at 100 V for 5 min. Figure 1 shows the photographs of the deposited samples. In Water, silica particles were deposited on the electrode but the coating was thicker toward the end of the electrode. In ACE and EtOH, silica particles were deposited but most particles accumulated at the lower end of the substrate. Almost no silica particles were deposited with IPA. In EFE, however, the substrate was uniformly coated with silica particles. The difference in the morphology could be due to the larger secondary silica particle size in Water, ACE, EtOH, and IPA than that in EFE. Figure 2 shows the deposition amount in each solvent. Water showed the best EPD, depositing 11.6 \( \text{mg cm}^{-2} \) of silica powder; while 7.6 \( \text{mg cm}^{-2} \) was deposited with ACE and 6.4 \( \text{mg cm}^{-2} \) with EFE. The alcohols deposited significantly less silica, 3.2 \( \text{mg cm}^{-2} \) for EtOH and 0.2 \( \text{mg cm}^{-2} \) for IPA. However, the use of zeta potential and mobility could not help explain why EtOH and, in particular IPA, performed so poorly. It was observed that during EPD the particles do not always accumulate on an electrode. This phenomenon is under investigation. Although the deposition amount is high when Water is used as the EPD solvent, the coating is affected by the gas generated by the electrolysis of Water. Therefore, EFE and ACE are suitable EPD solvents. It has already been reported that the time dependence and voltage dependence of the deposition amount of EFE are similar to those of the general EPD. The EPD charging mechanism in EFE has not been fully elucidated for the silica particles described above which makes it difficult to determine the reason for the high coating homogeneity obtained with EFE. The deposition behavior depends on many factors: charging of particles, mobility of particles, and coagulation of particles at the electrode. In the absence of supporting data, we will not discuss the details of the deposition mechanism. However, the ease of silica particles deposition in EFE may be because the silica particles are small, have a larger zeta potential, and show good dispersibility unless an external force is applied. The affinity between hydrophilic silica particles and hydrophobic EFE will be quite low. Therefore, as silica particles approach the electrode under the influence of the electric field, they are stabilized by coagulation, which assists coating formation.

Current density during EPD was measured for each solvent (Fig. 3). The results for ACE and EFE are quoted from the previous report. The observed current is the sum of the charge transferred by the deposition of charged particles and the current flowing through the solvent. For Water, the current density was around 1 mA cm\(^{-2}\). Compared to Water, the current density of EtOH was one order of magnitude lower, and those of IPA and ACE were two orders of magnitude lower. This is because the conductivity of organic solvents is lower than that of Water. EtOH and IPA are organic solvents that hydrogen bond; however, the hydrophobicity of EtOH is higher than that of IPA. Because ACE is a molecular organic solvent, it does not show much interaction with electrical conductors. The current density of EFE is five orders of magnitude lower than that of Water and three orders of magnitude lower than those of ACE and IPA. This is probably because EFE is highly hydrophobic. The solution resistance is inversely proportional to the current. In Eq. (2), the deposition amount is proportional to the current and inversely proportional to the conductivity of the solvent. Therefore,
although current density may be low during EPD because of high solvent resistance, the deposition of silica powder is still efficient. The electrophoresis of charged particles is dependent on the electric field, not the current [Eq. (1)].

Power consumption during EPD (Fig. 4) was calculated from the applied voltage, deposited amount, and current density. For Water, the power consumption per unit electrode area was \(\sim 10\) mWh\(\cdot\)cm\(^{-2}\), because the deposition amount is not taken into account, power consumption per unit area is proportional to the average current density. Therefore, because EtOH shows low deposition amount, power consumption is increased when EtOH is used. In the case of ACE, power consumption per unit electrode area was of the order of 0.1 mWh\(\cdot\)cm\(^{-2}\). In contrast, using EFE as the EPD solvent achieved a power consumption of \(\sim 100\) nWh\(\cdot\)cm\(^{-2}\), orders which is a considerable power saving compared to the other solvents. However, these results do not take into account the amount deposited. The power consumption per unit deposition amount in Water, ACE, and EFE are 1.3 Wh\(\cdot\)g\(^{-1}\), 31 mWh\(\cdot\)g\(^{-1}\), and 39 \(\mu\)Wh\(\cdot\)g\(^{-1}\), respectively. Power consumption in EtOH and IPA was almost equivalent to that in Water. Compared to Water, EFE consumes only 3.0 \(\times\) 10\(^{-3}\)% of the power required to achieve the same deposition amount. Similarly, it was 0.125% compared with that in ACE. Thus, the energy efficiency of the EFE is very high compared to Water and other conventional organic solvents.

3.3 EPD in EFE

The relationship between power consumption and applied voltage for EFE was studied (Fig. 5). The profile at 100 V in Fig. 5 corresponds to the profile of EFE in Fig. 3. The current density was dependent on the applied voltage. At 100 V, the current density was 30–50 nA\(\cdot\)cm\(^{-2}\) and 1 nA\(\cdot\)cm\(^{-2}\) at 10 V.

Although the current density is low, the EPD behavior was the same as the conventional organic solvent EPD. Here, when the applied voltage was 1/10, the current was also approximately 1/10. Because power consumption is the product of voltage and current, when the applied voltage was 1/10, the power consumption becomes approximately 1/100. Figure 6(A) shows the applied voltage dependence of power consumption per electrode area. At 100 V, the power consumption was 247 nWh\(\cdot\)cm\(^{-2}\), and at 10 V, it was 0.66 nWh\(\cdot\)cm\(^{-2}\). When the applied voltage was decreased by one order of magnitude, the power consumption per unit area decreased by more two orders of magnitude. Figure 6(B) shows the applied voltage dependence of power consumption per deposition amount of silica powder. At 100 V, the power consumption was 39 \(\mu\)Wh\(\cdot\)g\(^{-1}\), the same result as in Fig. 4(B). As described above, the amount deposited during EPD is proportional to the applied voltage.\(^2\) At 10 V, the power

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**Fig. 4.** Power consumption of (A) per unit area and (B) per unit deposit amount in various solvents. EPD: at 100 V for 5 min. Suspension: 3 g\(\cdot\)L\(^{-1}\) silica in solvents. Here, the amount of the deposition and current density in Figs. 2 and 3 was used to calculate the power consumption.

**Fig. 5.** Current density during the progression of EPD for 5 min. Suspension: 3 g\(\cdot\)L\(^{-1}\) silica in EFE.

**Fig. 6.** Power consumptions of (A) per unit area and (B) per unit deposit amount with respect to the applied voltage for 5 min. Suspension: 3 g\(\cdot\)L\(^{-1}\) silica in EFE.
consumption per unit deposition amount was 0.82 μWh·g⁻¹. Therefore, lowering the applied voltage by an order of magnitude decreases the power consumption per unit area and per unit deposition amount by more than an order of magnitude. During EPD the current remains relatively stable, and is almost proportional to the applied voltage. The deposition amount is also proportional to the voltage. Therefore, when the applied voltage is low, the power consumption per unit deposition amount also reduced.

EPD power consumption in EFE at 10 V is only 6.4 × 10⁻⁵% of that of Water at 100 V. Similarly, it is only 2.6 × 10⁻⁵% of that of ACE, 7.8 × 10⁻⁵% of that of EtOH, and 7.5 × 10⁻⁵% of that of EOH at 100 V. Further investigation into the relationship between the quality of the deposited coating and the applied voltage is required. Compared with common EPD solvents, EFE can contribute to drastic energy savings in the EPD process.

4. Conclusion

Conventional solvents used in EPD were compared to EFE. EFE is a nonflammable high-density organic solvent with a small dielectric constant. Using EFE, the power consumption during EPD was reduced because the conductivity of EFE is low. Silica particles showed a large zeta potential in the EFE suspension. Under the same EPD conditions, the amount of silica deposited from EFE was similar to that of ACE and Water. Significantly, the power consumption required to obtain the same amount of deposition in EFE, the power consumption was 3.0 × 10⁻⁵% compared with Water and 0.125% compared with ACE. Furthermore, the power consumption per unit deposition amount could be further reduced if a low voltage was applied. Power consumption per unit deposition amount in the EFE at 10 V is only 6.4 × 10⁻⁵% of that of Water at 100 V and only 2.6 × 10⁻⁵% of that of ACE at 100 V. This study shows that EFE is a safe solvent that offers significant energy savings to the EPD process.

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References

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