Electrophoretic Deposition Mechanism of Zeolite Powder in N-Propanol under Constant Voltages

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Zeolite has been recognized as one of the materials used for inorganic membranes. To improve the reproducibility of preparation and high permselectivity, the seed technique has been applied to the zeolite membrane under hydrothermal synthesis. Here, electrophoretic deposition (EPD) mechanism of zeolite (A–4) powder, as with the fabrication of the separation membrane, has been investigated under constant applied voltages as one of seed crystal coating techniques. Zeolite–n-propanol suspension is used as the EPD bath. The potential gradient in the n-propanol depended on the distance between the electrodes and the applied voltages. The zeta potential of zeolite particles was −26.5 mV in n-propanol and the resistibility of the EPD bath decreased by dispersing zeolite powder. On the other hand, potential gradient in the bulk EPD bath was constant with the progress of EPD, and the actual working potential gradient decreased 35% against the applied potential and electrode distance. Moreover, current density was constant with the progress of EPD, and the deposition layer in the EPD bath had low resistivity. Therefore, the velocity of zeolite particles was constant in the progress of EPD and the amount of deposited zeolite powder increased linearly against the deposition time and applied voltage. In addition, EPD efficiency is approximately 80% up to the amount of deposit at 25 g/m². EPD is a useful technique for the coating of zeolite particles onto substrates because deposition can be easily controlled and it has high deposition efficiency.

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1. Introduction

In recent years, zeolite has been recognized as one of the materials used for inorganic membranes because of its high chemical and thermal stability as well as molecular sieving.1,2 We have also found that the zeolite membrane on a porous stainless steel support disk prepared under the hydrothermal synthesis condition exhibits very high andatherm permselectivity for ethanol aqueous solutions.3 However, micro and meso pores were present between crystal grains due to the polycrystalline membrane. In addition, the reproducibility of the preparation of zeolite membranes was very poor, resulting in unstable performance of the zeolite membranes. To improve the reproducibility, the seed technique has been applied to the zeolite membranes.4,5 We reported the preparation of zeolite membranes with the seed technique on the porous sintered stainless steel support disk under hydrothermal synthesis condition.6 The high potential of the seed technique has been highlighted.

Electrophoretic deposition (EPD) is a coating technique using an electrochemical driving force.7 EPD is gaining increasing interest as a ceramic processing technique for a variety of technical applications, e.g., electrodes, solid oxide fuel cells, fiber-reinforced and graded ceramic composites, nanostructured materials and coatings for electronic, biomedical, optical, catalytic and electrochemical applications.8 This EPD process is very simple; the dispersed and charged particles in a solvent migrate to an electrode substrate under some potential gradient with a DC power source. The EPD technique has some advantages compared with the other fabrication techniques especially on decreasing the fabrication costs, and the structural flexibility of substrates. We applied this fabrication technique to solid oxide fuel cells (SOFCs).9,10

We have already reported the technological feasibility of applying EPD technique to various kinds of zeolite as the seeding technique by using various kinds of solvents.11 Recently, experimental results of the EPD technique of several kinds of zeolite (e.g. FAU-, Y-, ZSM-5 and so on.) as a seeding technique have been reported.12–17 From these reports, the feasibility of seeding by the EPD technique was clearly confirmed. On the other hand, to enhance the EPD techniques as a seeding technique for the fabrication of zeolite membranes by using hydrothermal synthesis, detailed investigations of the fundamental characteristic of EPD were required.

Therefore, we have investigated the fundamental characteristic of EPD of zeolite–A under constant applied voltages for the fabrication of the zeolite membrane that showed high separation performance in the separation of an alcohol/water mixture. In this study, n-propanol was selected as an EPD bath because n-propanol could be adopted to various oxide materials.9,10,18 Here, we investigated the EPD behavior under applied constant voltages from the viewpoints of dispersion and deposition characteristic of zeolite in n-propanol using electrochemical analysis.

2. Experimental

A ground zeolite powder (Tosoh Corporation, Zeolite, Synthetic, A–4, Powder, ~4 means the pore size of zeolite 0.4 nm) by ball-milling was used commercially. Reagent grade n-propanol (Wako Pure Chemical Industries, Ltd) was used. Particle size distribution and the zeta potential of zeolite in n-propanol were measured at 25°C with an electrophoretic light scattering spectrophotometer (Otsuka electronics, ELS–8000). The EPD bath was prepared as follows. Zeolite powder was added to n-propanol. 5 g/L of n-propanol was used. The powder in the solution was dispersed by ultrasonic vibration for 10 min. The EPD for the fabrication of zeolite coating was operated using a cell configuration as shown in Fig. 1. The deposition substrate (anode) was made from stainless steel (SUS304) wire and the surface area was 0.5024 cm². The counter electrode (cathode) was made from stainless steel (SUS304) mesh or wire. The cathode surface areas were 0.5024 cm² (in case of measurement of current density, potential and resistibility) or approximately 94.2 cm² (in case of the fabrication of zeolite coating), respectively. The distance of
both electrodes was ca 10 mm. In the EPD process, DC voltages of 50 to 300 V were applied for 30 to 180 s using a regulated DC power supply (Advantest, R6552). For the measurement of current density, the DC power source and multi-meter were connected in series. In the case of potential measurement, one terminal of the multi-meter was connected to the deposition electrode for EPD and the other terminal was connected to the platinum (Pt) probe. This Pt probe was placed between both electrodes in the EPD bath. Figure 2 shows the case of two Pt probes set up. For the potential gradient measurement, one probe scans between both electrodes or two probes are fixed between both electrodes. EPD bath characteristic and deposit coating resistibility in the EPD bath were measured using an Impedance/Gain phase Analyzer (Solatron, SI-1260) and Electrochemical Interface (Solatron, SI-1287).

3. Results and discussion

3.1 Zeolite powder dispersion and the zeta potential in n-propanol

The dispersion characteristics and zeta potential of zeolite particles in n-propanol were examined respectively. A standardized zeolite particle before grinding is 200 mesh (75 µm). A standardized zeolite powder was ground by ball-milling with a zirconia ball and distilled water for 48 hours. Subsequently, the ground zeolite powder was dehydrated in a vacuum for 24 hours. The zeolite powder distribution in n-propanol after dispersed by using ultrasonic vibration is shown in Fig. 3. The average particle diameters of ground zeolite are approximately 1.0 µm. This zeolite/n-propanol suspension was relatively stable.

Next, zeta potential and electrophoretic mobility were measured. The velocity of the particles \( v \) [m/s] is expressed as:

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

where \( \varepsilon_0 \) is the relative dielectric constant, \( \varepsilon [F/m] \) is the dielectric constant in a vacuum, \( \zeta [V] \) is the zeta potential of particles, \( E [V/m] \) is the applied electrical field (potential gradient), and \( \eta [N\cdot s/m^2] \) is the viscosity of the solvents. Here, \( v/E [m^2/s\cdot V] \) is the electrophoretic mobility. Therefore, velocity of the particle is dependant on the applied electrical field. Table 1 shows the physical properties of n-propanol\(^9\), zeta potential and electrophoretic mobility of zeolite in n-propanol. The zeta potential shows −26.5 [mV]. This suspension was not observed as obvious sedimentation in the space of a few hours, and this zeta potential provides sufficient velocity from Eq. (1) in this study. Therefore, it is considered that the zeta potential is sufficient value for the suspension stability and to apply to the EPD technique. Moreover, the negative zeta potential means that the deposition can be obtained onto an anode substrate.

Table 1. Physical Properties of n-propanol and Electrophoretic Properties of Zeolite in n-propanol at 25°C

<table>
<thead>
<tr>
<th>n-Propanol (^9)</th>
<th>Zeta potential [mV]</th>
<th>Electrophoretic mobility [m²/s·V⁻¹]</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>−26.5</td>
<td>−2.5×10⁻⁹</td>
</tr>
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![Fig. 1. Cell configuration of EPD for the fabrication of zeolite coating.](image1)

![Fig. 2. Set up of EPD cell for the measurement of potential gradient using two probes.](image2)

![Fig. 3. Ground zeolite powder distributions in n-propanol.](image3)
On the other hand, the charging mechanism of zeolite particles can be considered as follows. The zeta potential of zeolite particles in n-propanol can be considered as the same as our previous report, in which we reported the zeta potential for various kinds of oxide particles in various alcohols including a small amount of H₂O.¹⁵ The commercial alcohols that we used in this study also included a small amount of H₂O. A small amount of H₂O in the alcohol generated H⁺ ions and OH⁻ ions by electrolytic dissociation. Here, zeolite is consisted of Al₂O₃ and SiO₂, and the lower SiO₂/Al₂O₃ ratio of zeolite shows low solid acidity.²⁰ The ratio of SiO₂/Al₂O₃ in Zeolite A-4 is 2. This indicates that the zeta potential may be influenced by the adsorption of OH⁻ ions onto the zeolite in n-propanol because the zeolite surface exhibits basic in n-propanol. Therefore, in the case of zeolite and n-propanol, it is considered that the generated OH⁻ ions are adsorbed onto the zeolite particles because the zeta potential is negative.

3.2 Characterization of n-propanol and EPD bath

Figure 4 shows the relationship between current density of zeolite powder free n-propanol and applied time as a function of applied DC voltages. It shows that the current density is comparably small to the applied high DC voltage to the n-propanol. The current densities are proportional to applied voltages and tend to be unstable with high applied DC voltages. It is considered that the unstable current density influences the formation of uniform deposition during EPD of zeolite powder. Therefore, it is suggested that the applied DC voltage should be less than 200 V in the case of n-propanol.

**Figure 5** shows the potential gradient between both electrodes when applied at 50, 100 and 200 V in zeolite powder free n-propanol. The electrode distance in Fig. 5(a-c) is 11 mm and 19.5 mm in Fig. 5(d-e). From the results in Figure 5, actual working voltage in bulk n-propanol is approximately 20% less than the applied voltage. For example, the applied voltage is 200 V and the actual working voltage in bulk n-propanol is ca 160 V as shown in Fig. 5(a). Moreover, the potential gradient and extrapolation intercept potential are proportional to the applied voltages, and the potential gradient is inversely proportional to the electrode distance, however, the extrapolation intercept potential does not change. Therefore, in the case where both the applied voltage and electrode distance are doubled, the potential gradient does not change, however, the extrapolation intercept potential doubles. Here, we do not discuss the effect of extrapolation intercept potential in the absence of fundamental data.

Next, the zeolite powder suspended n-propanol bath was investigated. Figure 6 shows the experimental results of the AC impedance analysis of zeolite powder free n-propanol and the zeolite powder dispersed n-propanol baths. In the case of powder free n-propanol, a semicircle is observed as shown in **Figure 6(a)**. The starting point of the semicircles is the origin of the coordinate axes and the semicircle is the only one. Therefore, this single resistance factor is caused by the electrode reaction. Here, we do not discuss the electrode reaction species in the absence of fundamental data. In this case, the observed resistance is about 1170 kΩ (anode and cathode: 0.5024 cm², electrodes distance: 1.0 cm) in zeolite powder free n-propanol. On the other hand, after the dispersion of zeolite powder, semicircle becomes smaller as shown in Figure 6(b-f). A decreasing semicircle means increasing electrode reaction quantity. A semicircle becomes smaller with an increase in the zeolite powder concentration, e.g., 1170 kΩ (0 g/L), 740 kΩ (1.0 g/L) and 450 kΩ (2.0 g/L). From this result, it is obvious that the dispersed particles become charged and the charged particles cause a migration of electric charge. Moreover, at a zeolite powder concentration over 3.0 g/L, the observed resistance for each suspension is not as different as for 390 kΩ (3.0 g/L), 375 kΩ (4.0 g/L) and 360 kΩ (5.0 g/L). This means that the electrode reaction resistance changes little for a zeolite powder concentration over 3.0 g/L. In other

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**Fig. 4.** Relationship between applied voltage and current density in n-propanol.

**Fig. 5.** Potential gradients as functions of electrode distance and applied voltages

Applied voltage and electrode distance: (a) 200 V, 11 mm, (b) 100 V, 11 mm, (c) 50 V, 11 mm, (d) 200 V, 19.5 mm, (e) 100 V, 19.5 mm and (f) 50 V, 19.5 mm.

**Fig. 6.** AC impedance diagrams of zeolite powder–n-propanol suspensions

(a) 0 g/L, (b) 1.0 g/L, (c) 2.0 g/L, (d) 3.0 g/L, (e) 4.0 g/L and (f) 5.0 g/L of zeolite powders in n-propanol. Anode and cathode: stainless steel wire (0.5024 cm²).
words, EPD bath resistance does not change with zeolite powder concentration over 3.0 g/L.

3.3 EPD properties

Next, EPD characteristics were investigated. Here, applied voltage at 100 V was selected because the current density was stable as shown in Fig. 4. **Figure 7** shows the current density under the progress of EPD applied at 100 V by using 5.0 g/L of zeolite/n-propanol bath. The current density slightly increased in the initial stages but reached an almost constant value. This current density was approximately 12 A/m² and that of the powder-free bath was approximately 19 A/m². It is considered that this decreasing current density was caused by the decrease in the actual anode surface area. The anode surface was immediately covered with zeolite particles in the progress of EPD. On the other hand, constant current density is caused by the deposited layer that acts as a conductive layer. Therefore, current density does not depend on the amount of deposit.

The relationship between potential gradient and deposition time between both electrodes was measured as shown in **Fig. 8**. The electrode distance was ca 11.5 mm. Two Pt probes were set up between both electrodes. One was set at 1.0 mm from the anode and the other was set at 9.5 mm from the anode. The applied voltage was 100 V (8.7 × 10⁴ V/m). The initial potential gradient was approximately 4.7 × 10⁵ V/m, however, the potential gradient was almost constant about 5.6 × 10⁴ V/m. It did not depend on the deposition time. This potential gradient decreased 35% from applied potential at 8.7 × 10⁴ V/m and this variation was larger than that of zeolite powder free n-propanol as shown in Figure 5. This was caused by the increasing of EPD bath conductivity by dispersion of zeolite particles. Moreover, constant potential gradient against deposition time means the deposition layer acts a conductive layer.

**Figure 9** shows the amount of deposit as a function of deposit time by using 5.0 g/L of zeolite/n-propanol bath. Here, the anode area and electrode distance are the same as in the above experiments (0.5024 cm² and 1.0 cm), however, the cathode area is approximately 94.2 cm² as shown in Figure 1. Zeolite powder was deposited onto the anode substrate because zeolite particles were negatively charged. The amount of deposit increased linearly till 120 s and 25 g/m². In the case of deposition time up to 120 s, deposition surfaces were almost flat. However, for a deposition time over 120 s, the deposited layer was partially detached. In general, the deposit rate was linear in the case of highly conductive particles and decreased in the case of low conductive particles. Zeolite particles themselves do not have high conductivity, however, it show high conductivity in water. In this study, zeolite powder was dispersed in n-propanol. Therefore, we investigated the EPD mechanism of zeolite powder in n-propanol by using AC impedance analysis.

**Figure 10** shows the experimental results of the AC impedance analysis between both electrodes of zeolite powder dispersed n-propanol bath with the deposition time at 100 V. Figure 10(a) is the zeolite powder free n-propanol, whose EPD bath condition is same as in Figure 6(a). However, EPD bath resistance is different because the cathode area is not 0.5024 cm², but 94.2 cm² as shown in Fig. 1. The AC impedance analysis of each deposition time is shown in Figure 10 (b-g). In each condition, there is only one semicircle, and the size is almost the same or a little bit smaller compared with the resistance of zeolite powder free n-propanol. This means that the electrode reaction is the only one factor, and the effect of the deposited layer is negligible because the deposited zeolite layer has high conductivity. In other words, the behavior of the EPD themselves do not change with the progress of EPD. This result indicates strong agreement with the constant current density and the constant potential gradient in the progress of EPD under applied constant voltage.

From these results, the EPD mechanism of zeolite powder
from n-propanol suspension can be simply explained as shown in Figure 11. Zeolite powder was negatively charged in n-propanol. Charged zeolite particles migrated onto the anode substrate by applied potential gradient. The resistivity of deposited zeolite layer was much lower than that of the EPD bath. Therefore, the potential gradient did not change and the deposition rate was constant. In this study, the initial zeolite powder concentration was 5.0 g/L. On the other hand, in the case of deposit at 100 V for 120 s onto 0.5024 cm² of anode, the amount of deposit was about 1.26 mg. Therefore, the variation in zeolite powder concentration is only 0.5%. This means the zeolite powder concentration \( N \) is approximately constant in the progress of EPD. The amount of deposit \( \omega \) can be estimated as:

\[
\omega = \alpha \int_0^t vN dt
\]

where \( \alpha \) is a coefficient of the efficiency of EPD. As velocity \( v \) and zeolite powder concentration \( N \) do not depend on the deposition time in this study, Equation (2) can be approximated as follows.

\[
\omega \approx \alpha vNt
\]

In one of the experimental condition, \( N \) is 5[g/L], the deposition time \( t \) is 120 s, the electrode distance is 1.0 cm, the applied voltage is 100 V, the electrophoretic mobility is \(-2.5 \times 10^{-5}[\text{cm}^2/\text{s} \cdot \text{V}]\) and the amount of deposit \( \omega \) is 1.26 mg. Apparent potential gradient is \( 1.0 \times 10^6[\text{V/m}] \), however, the actual working potential gradient decreased 35% from the result of Figure 8. Therefore, the actual potential gradient is estimated at \( 6.5 \times 10^5[\text{V/m}] \). Velocity \( v \) can be calculated from electrophoretic mobility and potential gradient, and is \( 1.625 \times 10^{-3}[\text{cm/s}] \). \( \alpha \) can be obtained by substituting \( v \), \( N \), \( t \) and \( \omega \) in Equation (3) to get approximately 1.28. Although this calculation is rough because it does not take into account the electrode configuration, the EPD efficiency is approximately 80%.

4. Conclusion

Electrophoretic Deposition (EPD) mechanism of zeolite (A-4) powder, as with the fabrication of separation membrane, has been investigated under constant applied voltages. Zeolite-n-propanol suspension is used as the EPD bath. The potential gradient in the n-propanol depended on the electrode distance and applied voltages. Zeolite particles were negatively charged in n-propanol and the resistivity of EPD bath decreased by dispersing zeolite powder. On the other hand, the potential gradient in the bulk EPD bath and current density were constant with the progress of EPD, and the deposition layer in the EPD bath had low resistivity. Therefore, the velocity of zeolite particles was constant in the progress of EPD and the amount of zeolite powder deposit increased linearly against deposition time and applied voltage. In addition, EPD efficiency was approximately 80%. EPD is a useful technique for the coating of zeolite particles onto substrates because deposition can be easily controlled and has high deposition efficiency.

References

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