

Short communication

The mathematical expression for kinetics of electrophoretic deposition and the effects of applied voltage

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Abstract

Electrophoretic deposition (EPD) is a ceramic process. Although the kinetics for EPD have been established. However, there are still some ambiguities. In present study, a modified kinetic model was applied to describe the completely different behavior of EPD at -10 and -40 V respectively. The variation of the concentration profile during electrophoretic deposition at -10 and -40 V was simulated to explain what affected the EPD process. Based on the simulation, the depletion of colloidal particles near the electrode may be responsible for the EPD kinetic behaviors.

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1. Introduction

Electrophoretic deposition (EPD) is a two-step process: First, the charged colloidal particles in the suspension migrate to the electrodes under an external electric field. This migration step involves the bulk properties of the colloidal suspension, such as conductivity, viscosity, particle concentration and dispersion, and the surface-charge density and the local field strength in the bath [1,2]. Secondly, the deposition step involves a complex combination of electrochemical and aggregation phenomena. Producing a dense and coherent deposition layer requires that the particles release their surface charge at the electrode [3]. Although several efforts have been devoted to study this process, there are still many parameters that must be considered to control the formation of EPD, leading to a highly nonlinear relationship between those parameters [4]. In the present study, a correction which describes the potential variation during electrophoretic deposition [5] was introduced into the proposed kinetic expression of EPD [6]. The kinetic behavior of EPD was explored using this modified kinetic model. Furthermore, different applied voltages were used to investigate their influence on EPD kinetics.

2. Theoretical background

2.1. The factors affecting EPD

The mechanisms of EPD include charged colloidal particles in solution moving under an applied external voltage, and a deposition of particles onto an electrode where charge transfer takes place. Two groups of parameters determine the characteristics of this process: (a) the specifics of suspensions and (b) the physico-chemical parameters of the electrochemical cells.

For the EPD of particles, part of the current carries either the charged particles or free ions in the solution, so the number of deposited particles is not only relative to current. It is believed that the accumulated ions at the electrodes restrict subsequent deposition [7]. However, the number of free ions is generally small in organic suspensions, such as in ethanol. In this sense, the influence of the accumulation of ions is negligible in the initial period.

The first attempt to correlate the number of particle with the affecting parameters of EPD was made by Hamaker and Avgustnik et al. [8]. The Hamaker law can be expressed as

$$w = \int_{t_2}^{t_1} f\mu EAC dt \quad (1)$$

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It relates to the deposited weight (w) to the electrical field strength (E), the electrophoretic mobility (μ), and the particle concentration in suspension (C) and f is a factor between 0 and 1 that takes into account the fact that not all powders brought to the electrode are incorporated in the deposit.

Ishihara et al. [9] and Chen and Liu [6] used an expression based on the assumption that if all particles in a suspension are spherical, the mobility of particles could be approximated by Henry's equation [10], and Eq. (1) can be re-written as

$$w = f \frac{2}{3} C \varepsilon_0 \varepsilon_r \zeta \left(\frac{1}{\eta} \right) \left(\frac{E}{L} \right) t \quad (2)$$

where ε_0 is the permittivity of a vacuum, ε_r the relative permittivity of the solvent, ζ the zeta potential of suspension particle, η the viscosity of solvent, and L is the distance from the cathode to the anode.

However, the applied voltage must be modified because it is influenced by the increase of deposited layer thickness. Anné et al. [5] proposed a model, which was developed to explain the origin of the potential drop over the deposit during EPD. The magnitude of the potential drop over the deposit is explained in terms of the ion transport through the deposit. More details can be found in [5]. The following expression was used to describe the voltage variation:

$$V_{\text{real}} = V_{\text{total}} \left(1 - \frac{d_{\text{deposit}}}{d_{\text{deposit}} + (d - d_{\text{deposit}})Y} \right),$$

$$Y = \frac{r_{\text{suspension}}}{r_{\text{deposit}}} \quad (3)$$

where r_{deposit} is the deposit resistance, $r_{\text{suspension}}$ the suspension resistance, d_{deposit} the thickness of the deposit, d the thickness between the cathode and the anode, and V_{total} is the applied voltage. Eq. (3) was introduced to modify Eq. (2). Therefore, the modified equation takes the form:

$$w = f \frac{2}{3} C \varepsilon_0 \varepsilon_r \zeta \left(\frac{1}{\eta} \right) \left(\frac{V_{\text{real}}}{d - d_{\text{deposit}}} \right) t \quad (4)$$

This equation has to be numerically solved to calculate the yield. From all of the parameters in this equation, the f factor is still unknown and has to be fitted in EPD experiment.

3. Experimental procedure

3.1. Preparation of the LaSrMnO₃ substrate

The precursors of LaSrMnO₃ (LSM) powders were prepared using La₂O₃ (Alfa), MnO₂ (Aldrich), and Sr(NO₃)₂ (Aldrich). The stoichiometrical amount of these precursors was mixed with ethanol (99.8% Kanto Chemicals, Tokyo, Japan). Afterward, the powders were milled, sieved, and calcined at 1200 °C. The calcined powders were then pressed into the shape of a disk, and sintered at 1400 °C. The diameter of an LSM-disk after heat treatment was about 1 cm.

3.2. Suspension for EPD

Ytria-stabilized zirconia suspension (YSZ) (TZ-8Y, Tosho) was prepared in solvents of ethanol (99.8% Kanto Chemicals, Tokyo, Japan). The powder was dispersed in the suspension using an ultrasonic horn (DC400H, Delta) for 30 min, with the pH (TDK-5721S) value adjusted to 4.03 using acetic acid (Fluka).

3.3. The apparatus and geometry of EPD

A two-probe electrochemical cell and the associated apparatus were applied in the EPD process. A carbon electrode was used as the anode, and the prepared LSM disk was used as the cathode, which was connected to a balance (Mettler 6900). The electrodes were set parallel to each other with a separation distance of 1 cm, and immersed into the YSZ suspension, which was kept at a constant temperature of 25 °C. A pH meter (TDK-5721S) was used to measure the pH variation during the whole process. A dc power supply (Agilent 3617A) was used as the source of electrical energy. The variation of current data was logged by a multi-meter (HP-4392A). A personal computer controlled the whole integrated system and recorded the data.

3.4. The EPD process

In this experiment, YSZ coatings were deposited at constant voltages of −10, −12.5, −15, −30, −40, and −50 V respectively. The deposition time was 5–15 min. During the electrophoretic deposition, the deposited weight on the cathode, the pH value, the working temperature, the current density through the EPD cell, the deposition time, and the applied potential were logged on the PC.

4. Results and discussions

The black lines in Fig. 1(a) and (b) illustrate the deposited YSZ weight using EPD at −10 and −40 V, respectively. In addition, the theoretical predictions calculated using Eq. (4) for each condition is shown as dotted lines. There was a linear relationship between deposited weight and deposition time at −10 V, implying that the hypothesis in this model was suitable for this condition. However, the kinetic behavior of YSZ deposited weight at the higher applied voltage of −40 V changed from linear to an exponential decay. This interesting transformation can be attributed to the depletion of YSZ concentration near the electrode, which is explained in the following section. In brief, the modified model failed to describe the kinetics of EPD.

The weight of YSZ electrophoretically deposited on the LSM substrate from −10 to −50 V for 200 s is shown in Fig. 2. The deposited weight is linearly dependent on the external applied voltage in the region below −15 V. The linear dependence of the weight of the deposited YSZ on the deposition period and applied voltage implies that the shield effect of the deposited YSZ layer on the concentration of the suspension and the resistance of the electrochemical cell was negligibly small. However, when the applied voltage was higher than −15 V, the kinetic

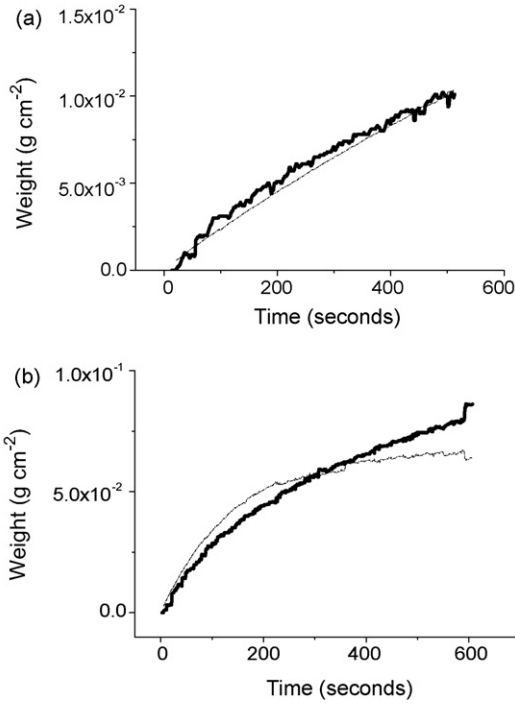


Fig. 1. The actually deposited weight of YSZ and the theoretical predictions for EPD at (a) -10 V and (b) -40 V. The solid line shows experimental data, and the dotted line shows the predictions.

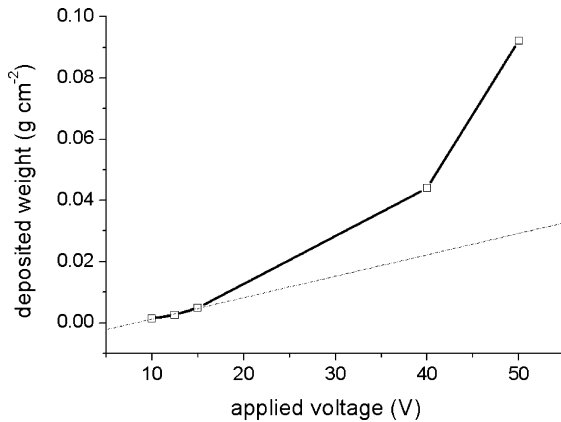


Fig. 2. The deposited weight of YSZ for 200 s at different potentials. The squares and solid line show experimental data, and the dashed line represents the linear region in this curve.

behavior no longer followed a linear relationship. To investigate the cause of this distinct kinetic behavior, the simulation was applied here.

5. Simulation for the colloidal particle concentration profile

In this calculation, the finite element method [11–15] in the MATLAB 7.0 pde tool box was applied. The geometry, which includes the domain and boundaries, is shown in Fig. 3a $1\text{ cm} \times 1\text{ cm}$ square. The governing equations and the boundary condition were introduced below.

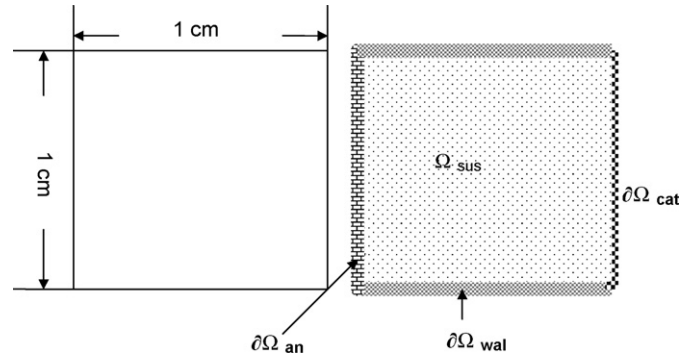


Fig. 3. Schematic drawing of the deposited layer geometry for the model. Ω_{sus} represents the domain of the suspension, $\partial\Omega_{\text{p}}$ is the boundary for deposited particles, $\partial\Omega_{\text{cat}}$ is the boundary for the cathode, $\partial\Omega_{\text{an}}$ is the boundary for the anode, and $\partial\Omega_{\text{con}}$ denotes the wall of the container.

5.1. Governing equations

Because the current was attributed to the flux of ionic species in the suspension, CH_3COO^- (called Ac^- in the present research), the free protons not adsorbed on the YSZ surface, the charged colloidal particles consisting of YSZ, and adsorbed ionic species were taken into account. The thickness of the deposit was too small to be significant. Mass balance and energy conservation were applied to simply describe the profile of the YSZ concentration in the cell during EPD.

5.2. Mass balance

The Nernst–Planck equation that describes the conservation of ion species in suspension is written in the form:

$$\frac{\partial C_i}{\partial t} + \nabla \cdot (-D_i \nabla C_i - z_i \mu_i F C_i \nabla \Phi) = 0 \quad (5)$$

where C_i represents the concentration of species i , the proton H, Ac^- , YSZ, etc.; and D_i is the diffusivity of species i in ethanol. For YSZ colloidal particles, C_i is obtained from the calculation of the Hückel equation; $D_{\text{YSZ}} = \zeta_p / 1.5\eta$ where z_i is the valance of each species. For YSZ colloidal particles, the valance values represent the number of charges the colloidal particle carry. In addition, the values of z_{YSZ} can be calculated from the zeta potential of YSZ colloidal particles; μ_i is the mobility of species i ; F the Faraday's constant; and Φ is the applied potential.

5.3. Energy balance

The current density is given by Faraday's law:

$$i = -F \sum z_i^2 \mu_i F C_i \nabla \Phi \quad (6)$$

Eq. (4) can be simply Ohm's law for ionic current transport and can be simplified to the current below:

$$i = -\kappa \nabla \Phi \quad (7)$$

where κ is the conductivity of the electrolyte. A current balance gives the current and potential density in the cell:

$$\nabla \cdot i = \nabla \cdot (-\kappa \nabla \Phi) = 0 \quad (8)$$

Table 1
A summary of the initial condition of each parameter

Description	Notation	Unit	Value
Diffusion coefficient of a proton	D_H	$\text{m}^2 \text{s}^{-1}$	9.31×10^{-9}
Diffusion coefficient of Ac^-	D_{Ac^-}	$\text{m}^2 \text{s}^{-1}$	1.23×10^{-9}
Diffusion coefficient of YSZ	D_{YSZ}	$\text{m}^2 \text{s}^{-1}$	5.31×10^{-9}
Mobility of a proton in ethanol	μ_H	$\text{m}^2 \text{J}^{-1} \text{s}^{-1}$	3.78×10^{-12}
Mobility of Ac^- in ethanol	μ_{Ac^-}	$\text{m}^2 \text{J}^{-1} \text{s}^{-1}$	4.84×10^{-13}
Mobility of YSZ in ethanol	μ_{YSZ}	$\text{m}^2 \text{J}^{-1} \text{s}^{-1}$	2.14×10^{-12}
Valance charge of a proton	Z_H	NaN	1
Valance charge of Ac^-	Z_{Ac^-}	NaN	-1
Valance charge of YSZ	Z_{YSZ}	NaN	50
Initial conductivity of suspension	κ_0	S m^{-1}	3.3×10^{-4}
Initial concentration of protons	C_H^*	M	9.33×10^{-5}
Initial concentration of YSZ	$C_{\text{Ac}^-}^*$	M	9.33×10^{-5}
Initial concentration of YSZ	C_{YSZ}^*	M	3.96×10^{-9}

where the κ is the function of proton concentration:

$$\kappa = F \sum_i |z_i| \mu_i C_i \quad (9)$$

5.4. Boundary conditions and initial condition

The Ω_{sus} shown in Fig. 3 represents the domain of the deposited layer where governing equations worked. $\partial\Omega_{\text{an}}$ is the boundary for the anode, which takes the form:

$$\begin{aligned} \text{mass balance : } & j_H = f(C_H, V_{\text{real}}); \quad C_{\text{YSZ}} = C_{\text{YSZ}}(t); \\ & C_{\text{Ac}^-} = C_{\text{Ac}^-}(t); \\ \text{energy balance : } & \Phi = V_{\text{real}} \end{aligned} \quad (10)$$

$\partial\Omega_{\text{cat}}$ represents the boundary for the cathode, which takes the form:

$$\begin{aligned} \text{mass balance : } & j_H = -f(C_H, V_{\text{real}}); \\ & j_{\text{YSZ}} = -f(C_{\text{YSZ}}, V_{\text{real}}); \\ & C_{\text{Ac}^-} = C_{\text{Ac}^-}(t); \\ \text{energy balance : } & \Phi = 0 \end{aligned} \quad (11)$$

$\partial\Omega_{\text{wal}}$ is the boundary for the two sides of the container, which takes the form:

$$\begin{aligned} \text{mass balance : } & n \cdot j_i = 0; \quad i = \text{H, YSZ, Ac}^-; \\ \text{energy balance : } & n \cdot \nabla\Phi = 0 \end{aligned} \quad (12)$$

The initial conditions are listed in Table 1.

6. Results and discussion

Figs. 4 and 5 show the calculations of YSZ concentration distribution profiles during EPD at -10 and -40 V, respectively. Fig. 4 illustrates the conditions after electrophoretic deposition for 1, 3, and 100 s at -10 V. The increase of YSZ concentration in the suspension near the cathode can be attributed to the fact that the migration velocity of YSZ particles was faster than the deposition rate; thus, the accumulation of YSZ became more

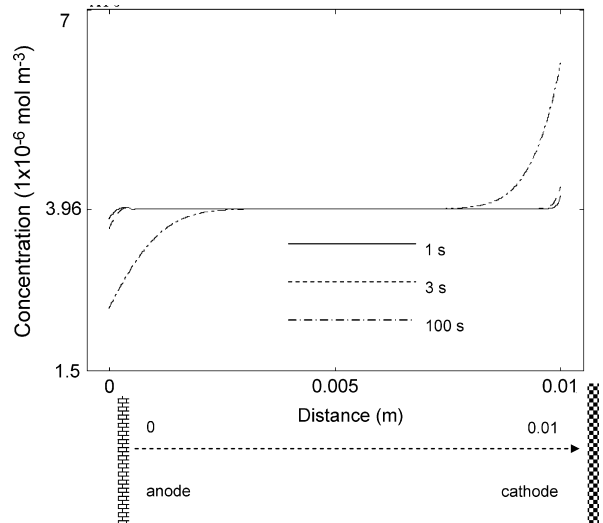


Fig. 4. The concentration distribution profile between the electrodes during EPD at -10 V for 0, 1, 3, and 100 s. The initial value of YSZ concentration is $3.96 \times 10^{-6} \text{ mol m}^{-3}$.

obvious as time passed. When the deposition time was 100 s, the values of YSZ suspension concentration increased to about $6 \times 10^{-6} \text{ mol m}^{-3}$. The EPD process at -10 V can be considered a deposition-rate-controlled reaction. On the contrary, the YSZ concentration in the suspension near cathode decreased when EPD was carried out at -40 V. This was because the deposition of YSZ particles was faster than EPD at -10 V, which resulted in a deposition rate that is faster than the migration velocity even though both increased with increasing applied voltage. Thus, the rate-determining step changed from being deposition-rate-controlled to being diffusion-controlled. In conclusion, different applied voltages led to the increase or decrease of YSZ concentration in suspension near the cathode, affecting the kinetic behavior of the weight deposition curve.

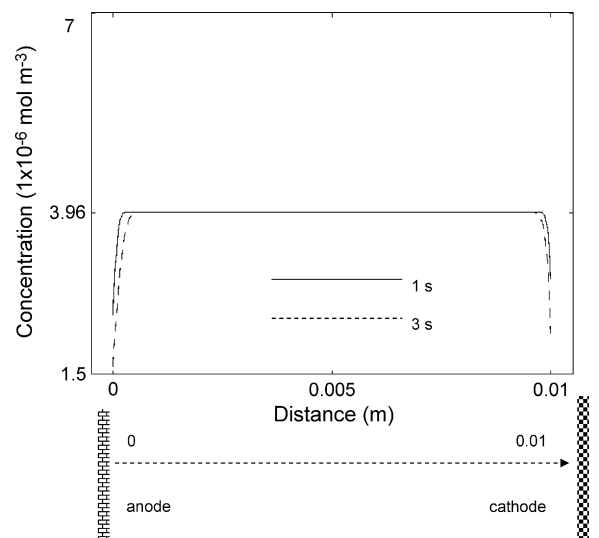


Fig. 5. The concentration distribution profile between the electrodes during EPD at -40 V for 0, 1, and 3 s. The initial value of YSZ concentration is $3.96 \times 10^{-6} \text{ mol m}^{-3}$.

7. Conclusion

In this study, the modified kinetic expression for electrophoretic deposition at constant voltages works when the applied voltage is below -15 V. However, it fails if the applied voltage is high enough, such as beyond -40 V. This divergence is caused by the variation of the YSZ concentration near the cathodes. When the applied voltage was small, the rate-determining step was the deposition rate, resulting in the increase of YSZ concentration in the suspension near the cathode. The rate-determining step became diffusion-controlled at -40 V, resulting in the decrease of YSZ concentration near in the suspension near the cathode.

References

- [1] H.C. Hamaker, *Trans. Faraday Soc.* 35 (1940) 186–191.
- [2] H.C. Hamaker, E.J.W. Verwey, *Trans. Faraday Soc.* 35 (1940) 180–185.
- [3] E. de Beer, J. Duval, E.A. Meulenkaamp, *J. Colloid Interface Sci.* 222 (2000) 117–124.
- [4] G. Anné, K. Vanmeensel, J. Vleugels, O. van der Biest, *J. Am. Ceram. Soc.* 88 (2005) 2036–2039.
- [5] G. Anné, B. Neirinck, K. Vanmeensel, O. van der Biest, J. Vleugels, *J. Am. Ceram. Soc.* 89 (2006) 823–828.
- [6] F. Chen, M. Liu, *J. Eur. Ceram. Soc.* 21 (2001) 127–134.
- [7] L. Besra, M. Liu, *Mater. Sci.* 52 (1) (2007) 1–61.
- [8] A.I. Augustinik, V.S. Vigdergauz, G.I. Zharavlev, *J. Appl. Chem.* 35 (1962) 2175–2180.
- [9] T. Ishihara, K. Shimose, T. Kudo, H. Nishiguchi, T. Akbay, Y. Takita, *J. Am. Ceram. Soc.* 83 (8) (2000) 1921–1927.
- [10] R.J. Hunter, *Foundations of Colloid Science*, vol. 1, 1st ed., Clarendon Press, Oxford, UK, 1987, pp. 198–203.
- [11] P. Zhou, C.W. Wu, G.J. Ma, *J. Power Sources* 163 (2007) 874–881.
- [12] G.H. Guvelioglu, H.G. Stenger, *J. Power Sources* 163 (2007) 882–891.
- [13] K.H. Kwon, C.B. Shin, T.H. Kang, C.S. Kim, *J. Power Sources* 163 (2006) 151–157.
- [14] A. Kusoglu, A.M. Karlsson, M.H. Santare, S. Cleghorn, W.B. Johnson, *J. Power Sources* 161 (2006) 987–996.
- [15] S. Yang, W. Yang, G. Sun, H. Knickle, *J. Power Sources* 161 (2006) 1412–1419.