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Critical particle concentration in electrophoretic deposition

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Abstract

The role of particle concentration in electrophoretic deposition (EPD) was investigated with two different suspension systems. The first system consisted of positively charged TiO_2 nanoparticles dispersed in isopropanol with 1 vol% water. The second system consisted of negatively charged polystyrene (PS) microbeads dispersed in isopropanol. Constant voltage EPD was performed using suspensions with variable particle concentration (0.013–0.43 vol% TiO_2 and 0.06–11.4 vol% PS). Threshold concentration values were identified for both systems after EPD at 100 V (250 V cm^{-1}) for 1 min. Below these values the deposited mass deviated from the trend dictated by Hamaker's equation. Higher applied voltages and longer deposition times were tested and the results suggested that the threshold concentration did not depend on those parameters. A phenomenological model of particle deposition was proposed, which accounts for the local electrochemical conditions close to the substrate in relation to particle size.

Keywords: Suspensions; Electrochemistry; Diffusion; TiO_2

1. Introduction

Electrophoretic deposition (EPD) is an electrochemical coating technique involving two steps: the migration of charged particles suspended in a liquid medium under the effect of an electric field and the deposition of those particles on the oppositely charged electrode. The yield of deposition during EPD with planar electrodes is described by Hamaker's equation[1]:

$$Y = \sigma C \iint \frac{\mathrm{d}V}{\mathrm{d}n} \mathrm{d}S\, \mathrm{d}t \quad (1)$$

where Y is the deposition yield (g); C is the particle concentration (g cm^{-3}); $\mathrm{d}V/\mathrm{d}n$ is the electric field (V cm^{-1}) perpendicular to the surface S (cm^2); $\mathrm{d}t$ is the deposition time (s); and σ(cm^2 V^{-1} s^{-1}) is a constant which depends on the chemical composition of the suspensions but not on the physical conditions of the experiments. The constant 'σ' is equal to the electrophoretic velocity when every particle reaching the electrode actually takes part in the formation of the deposit.[1] The equation of Hamaker consists of a balance of mass, where the amount of electrophoretically deposited mass is proportional to the time, the surface area of the electrode, the electric field and the particle concentration.

Hamaker derived his equation on the base of experiments carried out with suspensions of $BaCO_3$, $BaSr(CO_3)_2$, a mixed crystal of $BaCO_3$ and $SrCO_3$, MgO, $MgCO_3$, Al_2O_3 and CaF_2 in methanol, ethanol, acetone or mixtures there of. Hamaker observed deviations from his equation in terms of an excessive decrease of electrophoretic mobility in three cases: at low voltages, short deposition times and low particle concentrations. The author explained these deviations on the base of convection currents acting against particle deposition. The case of deviation due to low concentration was stated to be more complicated than the others. In this case, electrolytic current was claimed to increase with respect to particle transport, causing a change in the conditions under which electrodeposition took place. Our experience with EPD at constant voltage with isopropanol based suspensions of nanosized TiO_2 particles and of polystyrene microsized particles functionalized with TiO_2 nanoparticles confirmed the occurrence of a lower threshold concentration observed by Hamaker.[2,3] No other reports about deviations from Hamaker's equation at low particle concentrations with constant voltage EPD have been found in the literature.

The role of particle concentration in EPD mechanisms including the explanation for a lower threshold concentration is still unclear. This is confirmed by the recent review by Besra and

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Liu,[4] where the issue of particle concentration is treated in a short section focused on multi-component EPD.

For a better understanding of the role of particle concentration in relation to EPD mechanisms, we carried out systematic experiments at constant applied voltage and variable particle concentration with nanosized TiO_2 and microsized polystyrene (PS) in isopropanol based suspensions. Most of the results regarding the TiO_2 system have been recently published.[2] The results of the PS system are presented here. The experiments conducted with TiO_2 suspensions demonstrated a threshold concentration of 0.1 vol% TiO_2. Below this threshold concentration, no EPD coating was formed despite the increase of the applied voltage and deposition time. Above this threshold concentration, the deposit yield was in agreement with Hamaker's equation. A further analysis of the results from the TiO_2 system is presented here. This analysis facilitates a comparison with the results from the PS system and supports the development of a general phenomenological model relating to a threshold concentration in EPD. In particular, this model provides an explanation for different threshold concentrations found for different suspension systems in relation to particle size.

2. Materials and methods

2.1. Preparation of suspensions

The titanium dioxide (TiO_2) and polystyrene (PS) suspensions used in this study are described in Table 1. Zeta potential measurements were performed using a light scattering based device (ZetaSizer Nano Z, Malvern Instruments Ltd.); a standard pH meter (PHM 210 MeterLab) was used for the determination of the pH.

The TiO_2 particles, produced in house by a flame-synthesis process, showed a particle size distribution with $d_{10} = 107$ nm; $d_{50} = 129$ nm; $d_{90} = 155$ nm. The TiO_2 particles used in this study assumed an acid behavior when dispersed in isopropanol with 1 vol% deionized water. The measured pH of the medium without particles was in the range 4.5–4.7 and the measured pH of the suspensions decreased from pH 4.2 with 0.01 vol% TiO_2 to pH 3.6 with 0.4 vol% TiO_2, as reported in Table 1. Consequently, the equilibrium reaction between adsorbed and free protons regarding each amphoteric group on the surface of each TiO_2 particle depended on particle concentration. In the time frame applied in this study (EPD within 2 days after preparation of the stock suspension), the above mentioned equilibrium reaction was at acid pH values considerably lower than the IEP of TiO_2, assumed to be 5–6. This implies that a sufficient amount of protons was adsorbed on particles surface generating a global positive charge on particles. Since the pH tended to slightly increase with decreasing particle concentration from 3.6 to 4.0, the charge of particles at lower concentrations is expected to be accordingly lower. This is in agreement with the results of the zeta potential measurements on supernatants after centrifugation of the suspensions at variable particle concentration (see Table 1). The zeta potential measurements nevertheless confirmed that TiO_2 particles suspended at lower concentration values were characterized by a relatively high and positive surface charge. In fact, no sedimentation was observed with decreasing particle concentration.

A volume of 15 ml of a 0.4 vol% TiO_2 suspension was prepared by slow addition of TiO_2 powder into isopropanol with 1 vol% H_2O. We observed that the addition of water yielded better reproducibility of the electrophoretic current and of the overall deposition process. The obtained suspension was sonicated during 15 min, stirred overnight with a magnetic stirrer bead and sonicated again for 15 min the next day. Suspensions with variable particle concentration were then obtained by dilution of the 0.4 vol% TiO_2 suspension, referred to as a 'stock suspension'.[2]

Carboxylate-modified polystyrene (PS) beads of 4.6 μm in diameter with coefficient of variation <2% were purchased from Duke Scientific Corporation. The PS beads were delivered in 4 wt% (3.8 vol%) water suspensions. The carboxyl microspheres had negatively charged surface carboxyl groups and were stable above pH 5, which is the approximate pK_a of the carboxyl group. Pure isopropanol (p.a., Fluka) was chosen as suspension medium. A dedicated procedure was developed in order to transfer the PS beads from the original aqueous suspension to isopropanol with different final particle concentrations. It aimed to maximize the zeta potential (absolute value) in a reproducible manner for anodic EPD. The steps of this procedure are described in Table 2. The final suspension consisted in ~5 ml of ~11.4 vol% (3 × 3.8 vol%) negatively charged PS in isopropanol.

2.2. EPD experiments

EPD experiments were performed at constant voltage applied by a Xantrex XDC 300-20 Digital DC Power Supply. The current was indirectly measured by means of a voltage drop over a resistance of 10 kΩ. After each dilution and before EPD, suspensions were sonicated for 1–2 min. Table 3 summarizes the series of EPD experiments carried out with variable particle concentration under different EPD conditions. For each system, a different particle concentration range was established. Concentration values in each range are multiple of each other. Referring to Table 3, column 4 reports how many tests were performed for each concentration and under the given EPD conditions; column 5 reports which series of experiments were independent from each other concerning the stock suspension used. Suspensions with variable particle concentration diluted from different stock suspensions may differ because of minor non-systematic experimental errors in the preparation of the suspension, in particular in the case of the PS system (more elaborated preparation procedure).

A dedicated electrochemical cell was constructed in our laboratory for a controlled withdrawal of the sample from the suspension (see Fig. 1). The volume capacity of the cell was 5–6 ml. The substrate-electrode (1) was mounted on the external wall of the cell having a conic shaped hole (2) with a diameter of 4 mm. This diameter determined the exposed area of the substrate-electrode (0.126 cm^2). An O-ring (3) ensured a tight seal. The substrate-electrode was held by a screwed plate (4) with electric contact (5). The counter-electrode was fixed inside

Table 1
Overview of the suspensions used for EPD experiments with variable particle concentration (ρ = density; ε_r = relative permittivity; η = dynamic viscosity; and ζ = zeta potential). The properties reported in this table refer to a temperature of 20 °C; zeta potential values were calculated from the Henry's equation with the Hückel's approximation. For the zeta potential measurements: the supernatants after centrifugation (2 h, 4000 rpm) of the suspensions at variable particle concentration (indicated in vol%) were used in the case of the TiO_2 system; diluted samples of two independent stock suspensions were used in the case of the PS suspensions (11.4 vol% PS diluted of a factor 1000).

Particles		Medium		Particle concentr., vol%	ζ, mV	pH	Suspension preparation, remarks
Nature	Size	Nature	ε_r/η, kg/(s m)[a]				
TiO_2	129 nm (d_{50})	2-Propanol, 1 vol% H_2O	$20.78/2.03 \times 10^{-3}$		$0.426 + 50.5 \pm 4.8$	3.6	Powder added to medium while mixing
					$0.213 + 50.0 \pm 1.2$	3.7	
					$0.107 + 45.2 \pm 5.6$	3.8	
					$0.053 + 52.0 \pm 2.6$	3.9	
					$0.027 + 36.0 \pm 8.7$	4.0	
					$0.013 + 29.3 \pm 3.3$	4.2	
PS	4.6 μm	2-Propanol	$20.18/2.04 \times 10^{-3}$	11.4	-57.2 ± 4.8; -60.0 ± 2.9	–	Original suspension diluted and centrifuged in more steps

[a] The values of ε_r and η were calculated proportionally to the vol% composition of the medium, using the original values given by the CRC Handbook of Chemistry and Physics (D.R. Lide (Ed.), 86th edition, 2005–2006) for water ($\varepsilon_r = 80.10$; $\eta = 0.890$ cP) and 2-propanol ($\varepsilon_r = 20.18$; $\eta = 2.04$ cP) at 20 °C.

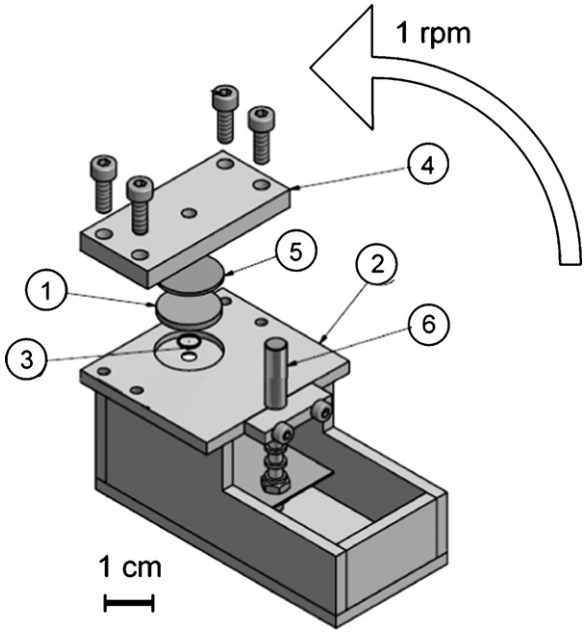

Fig. 1. A drawing of the electrochemical cell used for EPD, with indication of: substrate (1); wall of the cell with conic aperture defining the exposed area of the working electrode (2); O-ring (3); screwed plate (4); electric contact (5); and contact to counter-electrode (6). The arrow indicates the rotation direction to the vertical position, at which the EPD experiment can be started.

the cell at a set distance of 4 mm from the substrate-electrode (6). The substrate-electrode was mounted with the cell lying horizontally and already containing the suspension. Before starting the EPD, the cell was rotated to the vertical position so that the electrodes were immersed in the suspension. During the last 10 s of EPD, the cell was turned back to the horizontal position so that the substrate-electrode was gradually removed from the suspension. The rotation of the cell was controlled by means of an electric motor with a constant angular velocity of approximately 1 rpm (under load). All experiments were conducted at 22 °C ± 1 °C and a relative humidity of 32% ± 1%.

The substrate-electrodes were made of Ti_6Al_4V. The surface roughness (measured by white light profilometry, Cotec Altisurf) was $R_a = 0.074 \pm 0.005$ μm in the case of the TiO_2 experiments and $R_a = 0.22 \pm 0.02$ μm in the case of the PS experiments. Substrate-electrodes were cleaned in ultrasonic bath with acetone, ethanol and deionized water before storage. Just before EPD they were sonicated in piranha solution ($H_2SO_4/H_2O_2 = 3/1$ in volume) for 30 s, rinsed with H_2O and isopropanol and dried with an argon jet. As counter-electrode, a stainless steel (316 L) plate with an exposed area of ~0.4 cm^2 was used.

The EPD samples were characterized by mass difference before and after EPD (Mettler AT261 Delta Range®) and

Table 2
Steps of the procedure for the preparation of the polystyrene (PS) suspensions with variable particle concentration for anodic EPD. Centrifugation was carried out at 2500 rpm (equivalent to 3250 × g) for 15 min using a Hermle Z 300 Universal Centrifuge.

Step 1	A volume of 15 ml of the original 3.8 vol% PS aqueous suspension was divided into three parts and each part (5 ml) was diluted in 42.5 ml of deionized water (18.2 MΩ cm, Milli-Q).
Step 2	The dilution of each part was completed with addition of 2.5 ml of a 0.1 wt% NH_3 solution, obtaining a final dilution factor of 10 in 3 mM NH_3.
Step 3	The three volumes (50 ml each) were centrifuged; the supernatant of each volume was replaced with 4 ml isopropanol and the sediment was dispersed again in the new medium by shaking. This step was repeated 3 times.
Step 4	The three volumes (~4 ml each) were mixed.
Step 5	The total volume (~12 ml) was centrifuged; the supernatant was replaced with 5 ml isopropanol; the sediment was dispersed again by shaking.

Table 3
Overview of the series EPD experiments at variable particle concentration and different EPD conditions with the TiO_2 and PS suspensions. The indicated EPD time includes the final 10 s of sample removal. The distance between the electrodes was 4 mm in all cases.

Susp.	Concentration, vol%	EPD conditions	Nr. of series	Stock susp.	Substrate polarization
TiO_2	0.013–0.426[a]	100 V/60 s	2	A, B	Cathode (−)
	0.027–0.426	200 V/60 s	1	C	
	0.107	300 V/60 s	1	C	
	0.426	25 V/60 s	1	C	
	0.003	100 V/30 min	1	B	
PS	0.06–11.40[b]	100 V/60 s	2	A, B	Anode (+)
	0.12–0.95	200 V/60 s	1	C	
	0.06	100 V/30 min	1	B	

[a] Intermediate concentration values (vol% TiO_2): 0.027; 0.053; 0.107; and 0.213.
[b] Intermediate concentration values (vol% PS): 0.12; 0.24; 0.48; 0.95; 1.90; 3.80; and 7.60.

scanning electron microscopy (SEM Hitachi S-4800 and Zeiss DSM 962). The balance sensitivity was limited to 10^{-5} g and the last significant digit was not fully reproducible.

3. Results

Fig. 2 illustrates the results in terms of deposited mass and morphology of deposited particles relative to one series of anodic EPD at 100 V for 60 s with PS suspensions at variable particle concentration. An increasing number of deposited particles with increasing particle concentration is observed on the SEM micrographs. The PS particles did not fully cover the substrate for concentrations ≤0.48 vol% (5.0×10^{-3} g cm^{-3}) PS, generating partial two-dimensional (2D) deposits. Above this concentration value, a three-dimensional (3D) coating was formed. The deposited mass was 1.89 g at 3.8 vol% PS, 4.32 g at 7.6 vol% PS and 8.55 at 11.4 vol% PS. Digital images of the side view of some samples (not shown) provided an estimation of the coating thickness obtained from concentrated suspensions. For example, the deposited mass of 4.32 g (from the 7.6 vol% PS suspension) corresponded to a coating thickness of 0.8 mm and the deposited mass of 1.89 g (3.8 vol% PS suspension) corresponded to a coating thickness of 0.4 mm. Similar results were obtained also for the other independent series of EPD experiments at variable particle concentration. However, in the other series particles did not fully cover the substrate up to 0.24 vol% PS instead of 0.48 vol% PS.

The 30-min long experiment at low particle concentration (0.059 vol% PS, refer to Table 3) resulted in no coating formation. A 2D partial deposit revealed by the SEM analysis (not shown) corresponded to a deposited mass below the balance detection limit ($\Delta w = 0.00$ mg).

SEM micrographs relative to the cathodic EPD experiments with the TiO_2 suspensions at variable particle concentration are given in Fig. 3. In the case of the TiO_2 system, particles did not fully cover the substrate on samples obtained at concentrations ≤0.11 vol% (4.5×10^{-3} g cm^{-3}) TiO_2. The average thickness of the deposit corresponding to the 0.21 vol% TiO_2 suspension was 18 μm, while at 0.11 vol% TiO_2 no profilometric height difference was detected.[2] Additionally a transition from a 2D partial deposit to no deposit was observed with decreasing particle concentration (below 0.027 vol% TiO_2).

The results in terms of deposited mass of both series deposited under 100 V for 60 s EPD are summarized in Fig. 4, together with the results in terms of deposited mass of the additional series of EPD under 200 V (60 s).

Typical currents measured during the EPD experiments at 100 V for 60 s and variable particle concentration in both TiO_2 and PS suspension systems are illustrated in Fig. 5.

4. Discussion

4.1. Experimental results

When considering the deposit yield after EPD experiments at 100 V for 60 s with both the TiO_2 and PS suspension systems, a threshold value in terms of a critical minimal concentration (called 'C_{min}') was observed. At this threshold concentration and below it ($C \leq C_{min}$), no deposited mass could be detected and the proportionality between concentration and deposited mass did not follow Hamaker's equation. This situation corresponded to samples where particles did not fully coat the substrate (SEM micrographs of Figs. 2 and 3).

The longer EPD experiments showed that below C_{min} a deposited mass could still not be obtained as expected from Hamaker's equation. This was clear when comparing the deposited mass of 0.21 mg obtained with the 0.95 vol% PS suspension for 1 min to the deposited mass of 0.00 mg obtained with 0.059 vol% (16 times less than 0.95 vol%) for 30 min (30 times longer than 1 min). From the proportionality dictated by Hamaker's equation, a double deposited mass (≈0.4 mg) was expected on this sample, while no deposited mass (0.00 mg) was detected. The same trend was observed also in the TiO_2 system, where a negligible deposited mass (0.01 mg) was measured after a 30-min long EPD experiment with a 0.003 vol% TiO_2 suspension, instead of a deposited mass of 0.2 mg predicted by Hamaker's equation.[2] These results suggest that the occurrence of C_{min} is not time dependent.

An increase of applied voltage also did not affect the C_{min}. As can be observed in Fig. 4a, in the TiO_2 system the value of $C_{min} = 0.11$ vol% TiO_2 was found to be independent of the applied voltage (100 or 200 V). In the PS system, the value of C_{min} could not be strictly reproduced by the two independent series of experiments (see Fig. 4b). It resulted $C_{min,1} = 0.24$ vol%

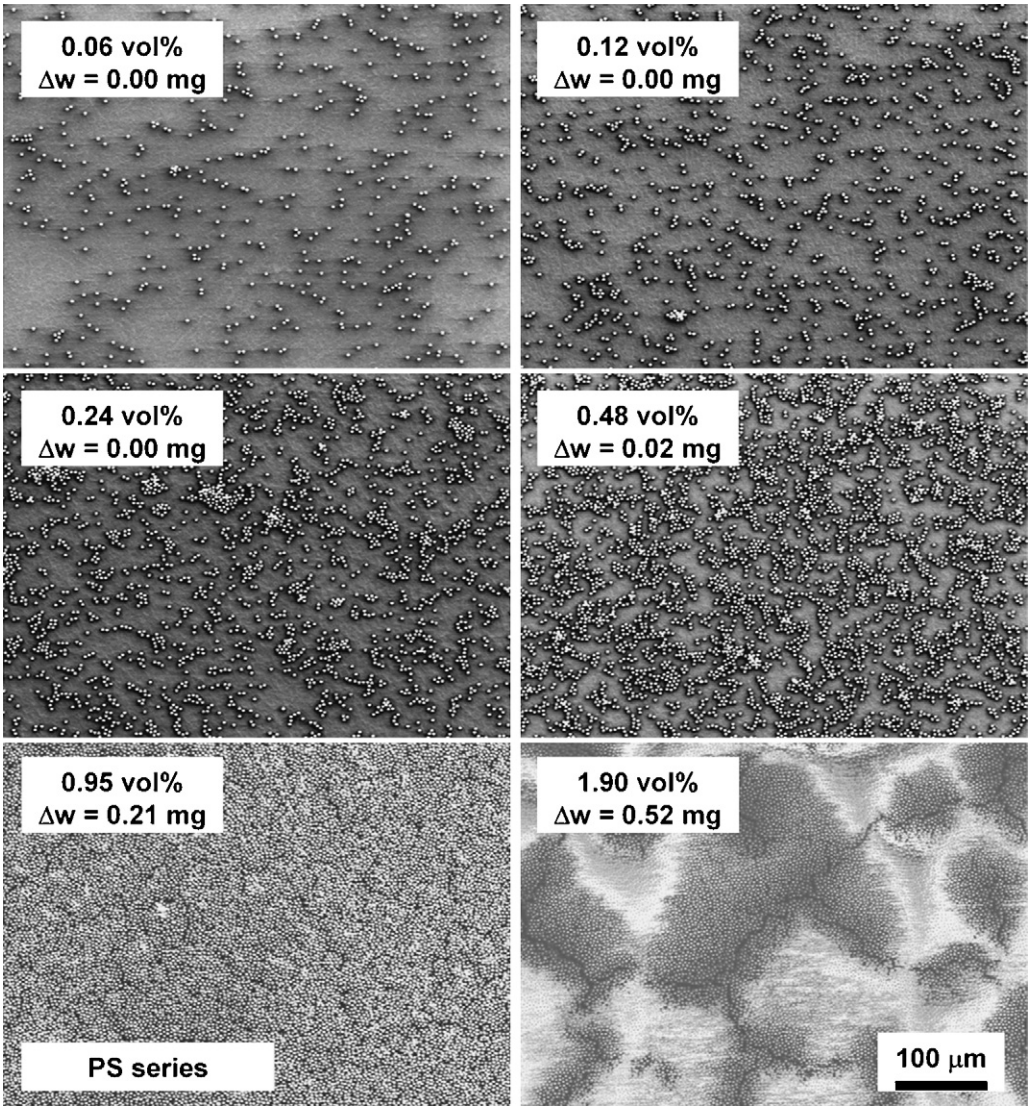

Fig. 2. SEM micrographs from one series of EPD experiments with polystyrene (PS) suspensions and variable particle concentration (100 V, 60 s, series 2). The deposited mass is also indicated. The images refer to the centre of the sample. On the sample obtained from the concentration 1.9 vol% electron charging caused imaging artefacts.

PS and $C_{min,2} = 0.48$ vol% PS for series 1 and 2, respectively. The value of $C_{min,2} = 0.48$ vol% PS was also found in the series at 200 V. For the sake of discussion, we state $C_{min} = 0.48$ vol% for the PS system.

4.2. Electrochemical aspects (TiO_2 system)

The current curves obtained during the EPD experiments at 100 V for 60 s at low TiO_2 concentrations (Fig. 5a) were useful to investigate the electrochemical behavior of the TiO_2 suspension system. The reduction of hydrogen (Eq. (2)) is the cathodic electrode reaction.

$$H^+ + e^- \leftrightarrow \tfrac{1}{2}H_2 \quad (2)$$

A plot of the current density versus the inverse square root of time showed a trend of linear relationship for three concentration values below $C_{min} = 0.11$ vol% TiO_2 (see Fig. 6). This linear relationship is in agreement with a diffusion limited reaction governed by Cottrell's equation[5]:

$$i(t) = nF(c_{bulk} - c_{electr})\left(\frac{D}{\pi t}\right)^{1/2} = Kt^{-1/2} \quad (3)$$

where *i(t)* is the diffusion current density (A cm^{-2}) as a function of the time t (s); n is the number of electrons required to reduce one protons in this case ($n = 1$); F is the Faraday constant (C mol^{-1}); c_{bulk} and c_{electr} are the molar concentrations of the reacting species (of protons in this case), respectively, in the bulk electrolyte and at the electrode surface (mol cm^{-3}); and D is the diffusion coefficient for the reacting species (protons) (cm^2 s^{-1}). The constant K can be calculated from the slope of the curves "current density versus inverse square root of time", as given in the Fig. 6. From these values of K, the diffusion coefficient D can be derived from Cottrell's equation (Eq. (3)).

Values for the diffusion coefficient D in the order of magnitude of 10^{-5} cm^2 s^{-1} were calculated by assuming c_{electr} equal to zero (protons immediately consumed at the electrode).

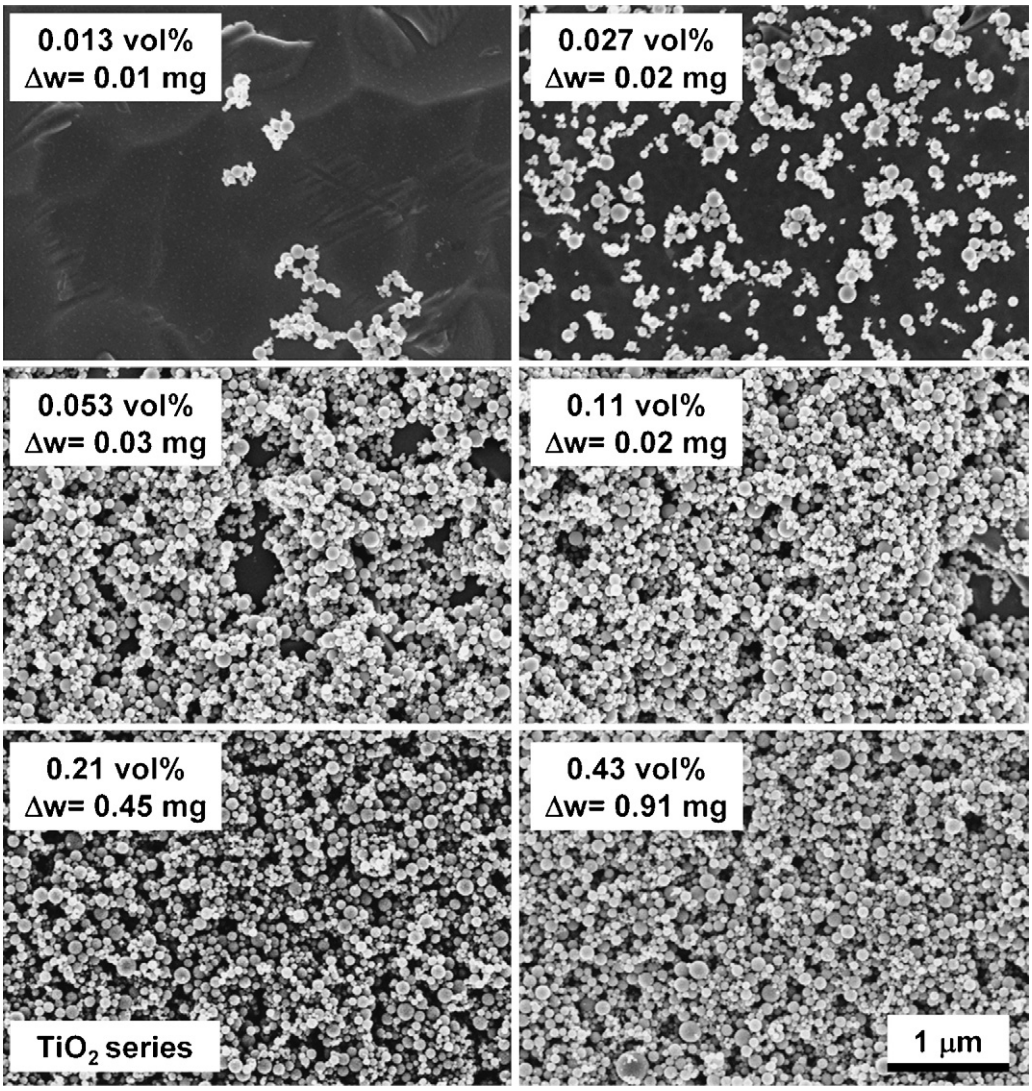

Fig. 3. SEM micrographs from one of the series of EPD experiments with titanium dioxide (TiO_2) suspensions and variable particle concentration (EPD 100 V, 60 s, series 2). The deposited mass is also indicated. The images refer to the centre of the sample.

Values for c_{bulk} were derived from the measured pH values ($c_{bulk} = 10^{-pH}\,mol\,l^{-1} = 10^{-(pH+3)}\,mol\,cm^{-3}$) and were in the order of magnitude of $10^{-7}\,mol\,cm^{-3}$. The calculated order of magnitude of D is the same as for the diffusion coefficient of H^+ ions in dilute aqueous solution ($D = 9.311 \times 10^{-5}\,cm^2\,l^{-1}$ from the CRC Handbook of Chemistry and Physics).

The thickness of the diffusion layer δ was estimated using Eq. (4).[5] The result was approximately 200 μm after 2 s and 400 μm

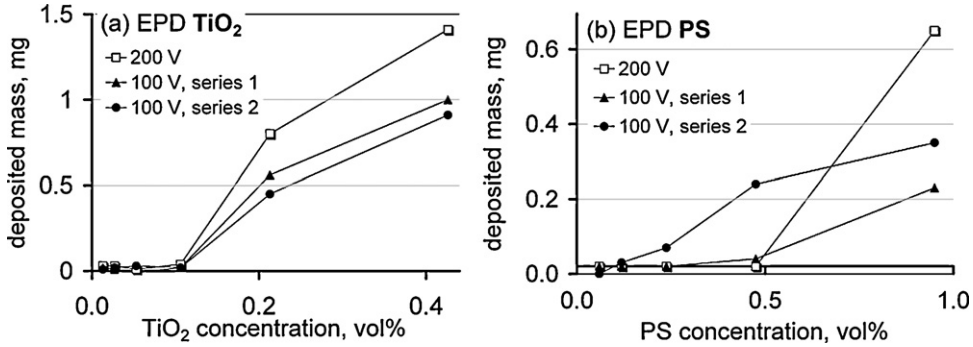

Fig. 4. Deposited mass weighted after the EPD experiments performed at 100 and 200 V with TiO_2 suspensions in the concentration range 0.01–0.43 vol% (a) and with PS suspensions in the concentration range 0.06–0.9 vol% (b).

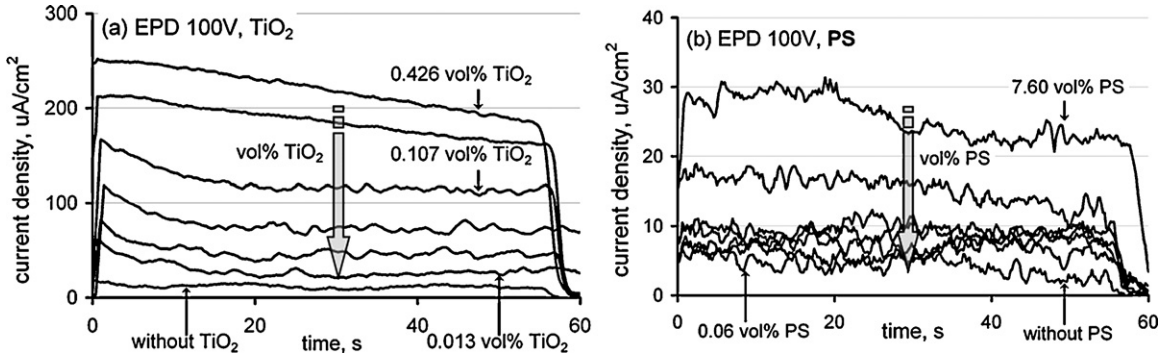

Fig. 5. Typical current evolutions measured during the EPD experiments at constant applied voltage (100 V for 60 s, distance between electrodes = 4 mm) and variable particle concentration: (a) cathodic EPD of TiO_2 nanoparticles dispersed in isopropanol with 1 vol% H_2O, particle concentrations 0.013; 0.027; 0.053; 0.107; 0.213; and 0.426 vol% and (b) anodic EPD of PS microparticles dispersed in isopropanol, particle concentrations 0.06; 0.12; 0.24; 0.48; 0.95; 1.90; 3.80; and 7.60 vol%.

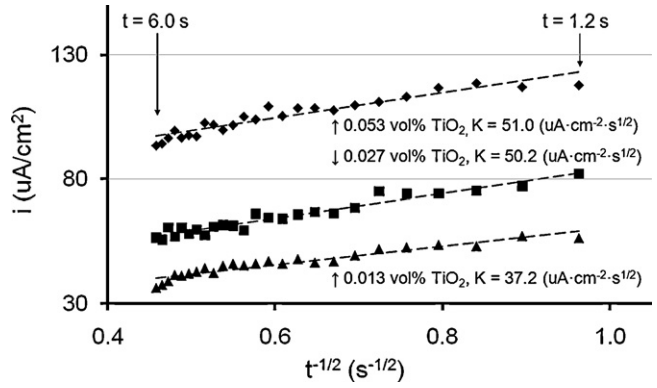

Fig. 6. Relationship between the inverse square root of time and the measured current density in the interval $1.2 < t < 6.0$ s during EPD experiments (100 V, 60 s) with TiO_2 suspensions at to low concentration values (0.013–0.053 vol% TiO_2, series 1). No deposited mass was detected for these concentration values.

after 6 s.

$$\delta(t) = (\pi D t)^{1/2} \quad (4)$$

4.3. Phenomenological model

A qualitative model for the interpretation of the threshold concentration was developed. This model refers to constant voltage cathodic and anodic EPD. The model is theoretically valid for any suspension system, and not only for the TiO_2 and PS systems investigated here. As an illustrative example, the TiO_2 system used for cathodic EPD is considered in more details next. The following three hypotheses are at the base of the model.

First, protons are charge determining ions for the TiO_2 particles according to Eqs. (5) and (6), where IEP is the isoelectric point of the particle material (pH range of global neutral charge). Fig. 7 (top row) illustrates three levels of charge which can be assumed by the TiO_2 particles depending on the pH of the surrounding medium in relation to the IEP. The charge levels of PS particles are also shown in Fig. 7 (bottom row) in relation to the pK_a of the carboxyl group and will be discussed later.

$$\text{Ti–OH}_2^+ \leftrightarrow \text{Ti–OH} + \text{H}^+ \quad (\text{pH} < \text{IEP}) \quad (5)$$

$$\text{Ti–OH} + \text{OH}^- \leftrightarrow \text{Ti–O}^- + \text{H}_2\text{O} \quad (\text{pH} > \text{IEP}) \quad (6)$$

Second, a gradient of concentration of protons in the medium $[H^+]$ is generated in front of the electrode (perpendicularly to the surface) when the EPD potential is applied; this gradient is due to a limit in mass transport of protons and it is time dependent. The gradient of $[H^+]$ is extended to a certain distance from the electrode, called here the diffusion layer (δ). The evolution of $[H^+]$ as a function of time and distance from the electrode surface after a step potential is qualitatively illustrated in Fig. 8. The thickness of the diffusion layer δ increases with time and is therefore also called 'non-stationary diffusion layer'. In the absence of convection, the non-stationary diffusion layer thickness increases over an indefinite time. In the presence of convection, a steady state is reached when the thickness of the non-stationary diffusion layer equals the thickness of the stationary diffusion layer defined by hydrodynamic parameters of the convection system.[5] The hypothesis of a local change of pH close to the cathode reaching alkaline pH values is supported by the recent work by Stapper et al.[6] By adding cresol red in the EPD of alumina nanoparticles suspended in ethanol it was observed that the deposited particles adjacent to the electrode meet local basic conditions.

Third, the thickness of the diffusion layer depends on particle concentration and tends to increase with decreasing particle concentration. This hypothesis is based on the equilibrium between particle amphoretic groups and H^+ ions in the medium (Eqs. (5) and (6)).

During EPD particles migrating to the electrode enter the diffusion layer δ and release H^+ ions adsorbed on the particle surface according to Eq. (5) (pH increase but still below the IEP). Two limit cases occur depending on particle concentration (refer to Fig. 9):

- For $C > C_{min}$ (formation of a 3D deposit, see Fig. 9a), particle accumulation and local electrochemical conditions yield a deposit formation according to Hamaker's equation. The thickness of the double layer δ is such that the pH condition of particle IEP is reached at a distance λ from the electrode, which is smaller than or in the same order of magnitude of the particle size ($\lambda \leq \varnothing$, refer also to Eq. (5)). The same mechanism of particle neutralization and accumulation takes place at the new interface and the coating continues to grow. The

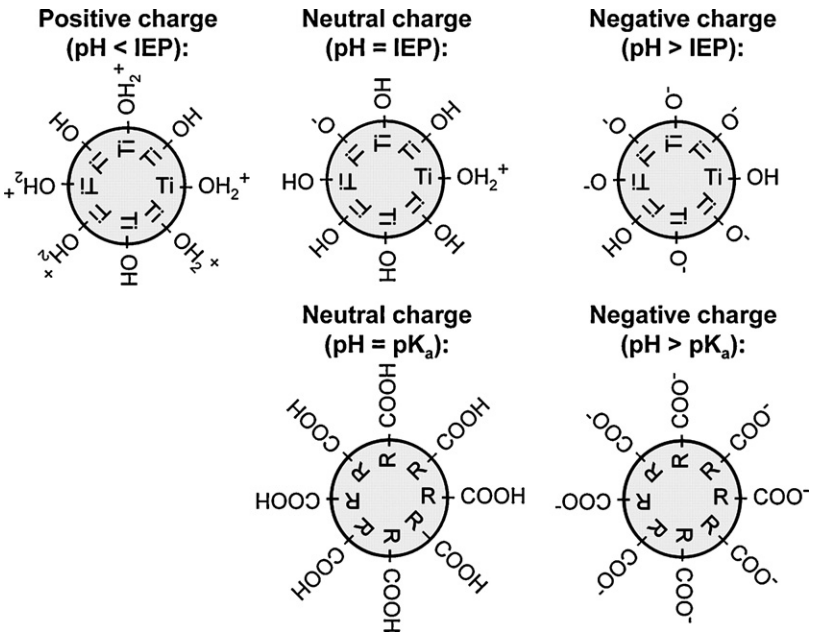

Fig. 7. Levels of particle charge of the TiO_2 (top row) and PS (bottom row) particles in suspension depending on the pH of the medium.

gradient of $[H^+]$ in front of the electrode eventually decreases due to the presence of the already deposited particles (dotted lines). This phenomenon depends on the green density of the coating and was already investigated in the literature.[7]

- For $C < C_{min}$ (no deposit formation, see Fig. 9b), particles do not accumulate and the growth of a 3D coating does not take place. The decreased particle concentration has two consequences: a lower probability of particle accumulation and a thicker diffusion layer δ extending perpendicularly from the electrode surface. Particles reaching the electrode find themselves in a neutral charge state already at a distance from the electrode, which is larger than the particle size ($\lambda > \varnothing$). In these conditions, the influence of convection flows acting against deposition becomes more important. In addition, the extension of diffusion layer may be so large ($\lambda \gg \varnothing$), that particles approaching the electrode enter pH conditions corresponding to a negative charge and tend to release protons from their amphoretic groups according to Eq. (6). Particles may be then driven back to the bulk suspension by the electric field. Under these conditions, no deposit is likely to form despite an increase of deposition time or applied voltage. The influence of time and applied voltage is discussed later.

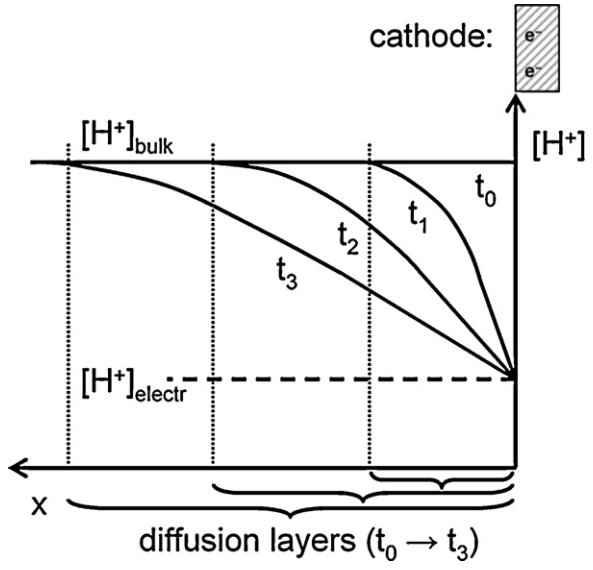

Fig. 8. Illustration of concentration profiles of $[H^+]$ close to the cathode at different times after application of a constant voltage.

The thickness of the diffusion layer estimated above neglecting the presence of particles supports the new model presented here. In fact, already after 2 s of EPD the thickness of the diffusion layer ($\delta \approx 200\ \mu m$) is three orders of magnitude higher than the diameter of the TiO_2 nanoparticles ($\varnothing = 0.13\ \mu m$).

The model presented in Fig. 9 is modified in the case of the PS system as follows: electrons are consumed at the anode in the oxidation reaction of OH^- ions instead of being provided by the cathode for the reduction reaction of H^+ ions; a gradient of $[OH^-]$ replaces the gradient of $[H^+]$ close to the electrode surface; the charge level goes from negative to neutral instead of from positive to neutral (negative). In the PS system, only two particle charge levels are possible: negative and neutral, as illustrated in Fig. 7 (bottom row).

An increase of deposition times has two contrasting effects: first, a larger number of particles reaches the electrode (coating growth following Hamaker's equation in the case of $C > C_{min}$). However, as already observed in Fig. 8 the thickness of the double layer increases with time, extending the distance from the electrode surface where particle neutralization and eventually charge inversion take place. The time effect enables us to explain the formation of 2D coatings (not full coverage of the substrate by particles), experimentally observed both in the TiO_2 and PS systems (Figs. 2 and 3). An initial deposition process is

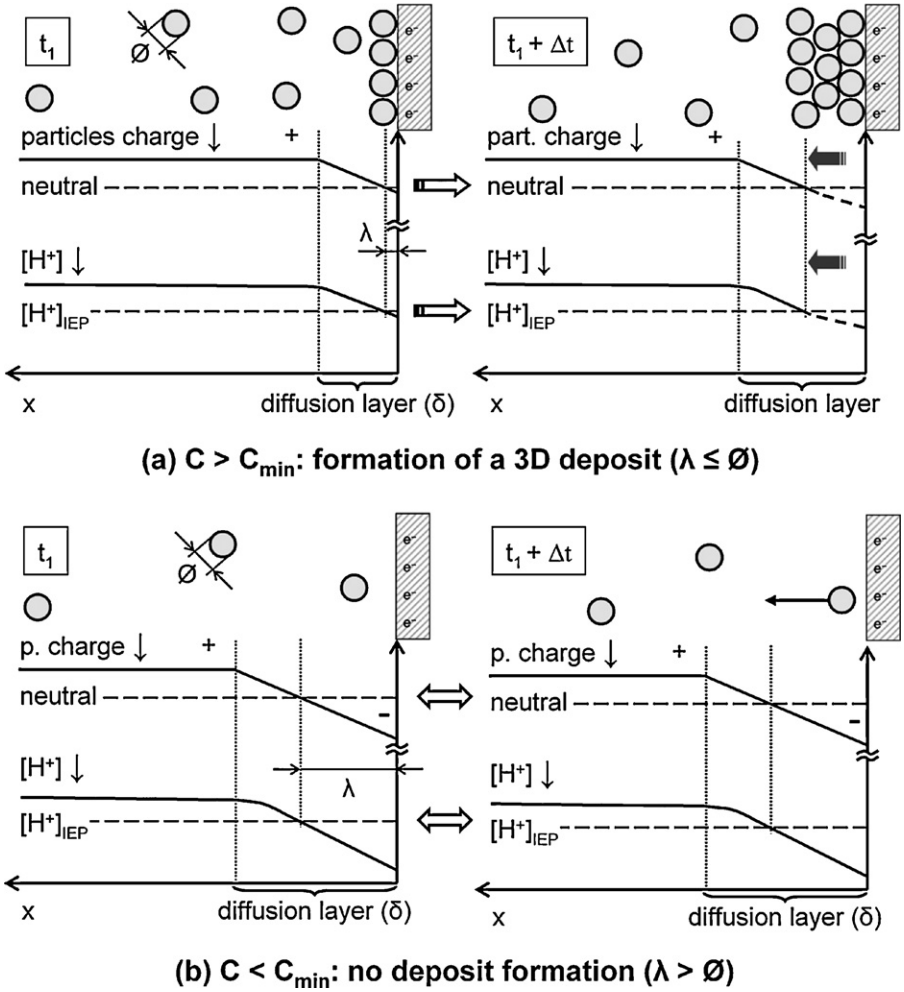

Fig. 9. Two cases of the EPD mechanism depending on particle concentration: (a) deposit formation yielded by particle accumulation and (b) no deposit formation hindered by local electrochemical conditions.

stopped by the local electrochemical conditions and the contrasting action of convection flows.

Similarly to an increase in deposition time, an increase in applied voltage has two contrasting effects: an enhancement of particle electrophoretic transport; a drop of proton concentration [H^+] at the electrode. In the case of $C > C_{min}$, the faster electrophoretic transport is the dominant effect, Hamaker's equation applies and the deposit yield increases proportionally to the applied voltage. In the case of $C < C_{min}$, the enhanced particle transport promotes accumulation while the decrease of [H^+] at the electrode extends the zone close to the electrode with pH > IEP, where particle neutralization and charge inversion may take place. It is concluded, that the effect of a voltage increase depends on the system. For example, in the case of the TiO_2 system, the two contrasting effects were balanced, so that C_{min} did not change by increasing the applied voltage. This conclusion can be assumed also for the PS system, although the voltage influence was uncertain due to the scattering observed on the experimental values relating to C_{min}.

The model presented here is able to provide an explanation for the difficulty of obtaining EPD deposits in relation to particle size, for organic suspension systems similar to the ones considered here. No reports on EPD of bare PS microbeads on substrates without any kind of pre-pattern could be found in the literature.

The proposed qualitative model requires further investigation. There is still need of theoretical and modelling work on the mechanism of EPD, as highlighted in the very recent review on EPD by Corni et al.[8] It would be interesting to develop a quantitative model for any suspension system. A dedicated electrochemical setup for *in situ* observation of EPD with particles in the nano- and micro-size range for further investigation of the occurrence of C_{min} would be useful.

5. Conclusions

- A threshold concentration was found after constant voltage EPD experiments at variable particle concentration using two different organic suspensions systems (nanosized TiO_2 and microsized PS particles in isopropanol based suspensions). Below the threshold concentration, no deposit growth occurred independently from the applied voltage and the deposition time.
- The investigation on the role of particle concentration in EPD led to the development of a phenomenological model related to the mechanism of particle deposition.

- According to the model, a minimal critical value of particle concentration (C_{min}) is defined, below which no deposit growth takes place and the deposit yield does not follow the linear trend dictated by Hamaker's equation.
- The model has three hypotheses: the charge determining ion of particles takes part in the electrode reaction (typically oxide particles and reduction of H^+ at the cathode); a concentration gradient of the charge determining ion is generated in front of the electrode serving as substrate and this gradient dictates the charge level of particles approaching the electrode by electrophoresis; the extension of this gradient into the bulk suspension is inversely related to particle concentration.
- In the model, the size of the particles is compared to the distance from the electrode, at which particles enter conditions of charge neutrality (pH around the IEP) and eventually of charge inversion (pH beyond IEP). Consequently, the threshold concentration C_{min} depends on particle size, decreasing as larger particles are considered.
- The model provided an explanation for the three different behaviors observed experimentally in constant voltage EPD experiments at variable particle concentration: no deposit formation; partial 2D deposit formation; 3D coating formation.

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