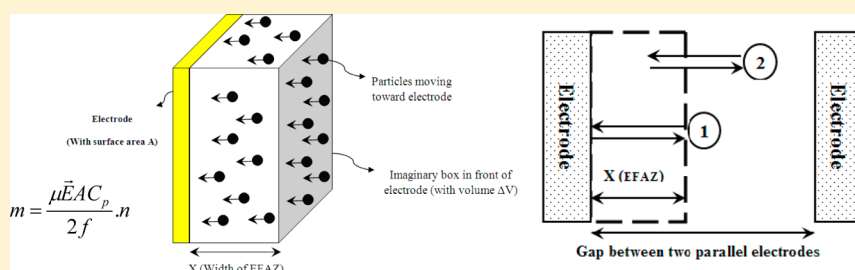# Role of the Electric Field Affected Zone (EFAZ) on the Electrophoretic Deposition of TiO$_2$ Nanoparticles under Symmetric Low-Frequency AC Electric Fields

J. Esmaeilzadeh, S. Ghashghaie, B. Raissi Dehkordi,* and R. Riahifar

Materials and Energy Research Center, P.O. Box 14155-4777, Tehran, Iran

ABSTRACT: In the present study, electrophoretic deposition (EPD) of TiO$_2$ nanoparticles under the application of symmetric AC fields was investigated. In the first step, EPD of TiO$_2$ nanoparticles under a DC field at 50 V resulted in the particles' deposition on one electrode, consistent with conventional EPD principles. However, no deposits were formed on any of the electrode surfaces for symmetric sinusoidal waves at 1 Hz. In this case, enhancing the electric field strength through the application of higher potentials was considered to extend the electric field affected zone (EFAZ) in front of the electrode, increasing the particles' opportunity to deposit. A kinetic model was then derived based on the Hamaker approach to calculate the deposited mass under an AC electric field. Although this model was found to be in agreement with experimental results at 1 Hz above 200 V, some deviation was detected at lower voltages. This trend shows that there is a threshold field strength below which EFAZ is not wide enough to let particles deposit under an AC electric field.

INTRODUCTION

The electrophoretic deposition (EPD) technique with a wide range of novel applications in the processing of ceramic materials has been extensively employed to form coatings from submicrometer- and nanometer-sized particles. Cost-effectiveness, a simple apparatus, and relatively short deposition durations are among the main advantages of EPD.

In the EPD process, an electric field is applied between two electrodes, and charged particles suspended in a suitable liquid medium move toward the oppositely charged electrode, creating a relatively compact and homogeneous film. Although the EPD process has been dominantly carried out using uniform DC fields, the idea of employing other forms of electric fields such as pulsed DC and AC asymmetric fields has been taken into consideration. Naim et al.[1] used pulsed DC fields to deposit TiO$_2$ particles. Their results showed that under this condition, the particles will be deposited according to their size. In another study, Van der Biest et al.[2] used asymmetric alternating electric fields for deposition in aqueous suspensions. They finally showed that for α-alumina particles, the quality of the layer obtained under asymmetric AC fields is better in comparison with layers formed under conventional DC fields. The two formerly mentioned methods also eliminate the water electrolysis reaction in aqueous suspensions, limiting the bubbling within the suspension during deposition.

Although the application of pulsed DC and asymmetric AC fields was found to have desirable consequences in the EPD process, there are no major interests in using symmetric fields for deposition. The main belief among research in this case is that the net movement of a particle in one cycle is zero when symmetric waves are applied. Hirata et al. investigated the deposition of alumina particles under symmetric AC fields in aqueous media, where the deposition rate was extremely low, being controlled by the diffusion of alumina in the suspension. On the basis of their findings, they concluded that no net electrophoresis occurs under the influence of symmetric AC fields.[3]

In our previous studies, we showed that the application of symmetric waves to coplanar gold electrodes will result in the particles' deposition on both electrodes as well as the interelectrode gap.[4] Although the assembly of suspended particles under nonuniform AC electric fields is mostly attributed to a polarization effect and dielectrophoresis force, we successfully showed that deposition would take place even at frequencies as low as 0.1−1 Hz, where the electrophoresis force is still dominant.[5]

In the present study, the possibility of applying symmetric fields to deposit ceramic nanoparticles on parallel planar electrodes has been studied using square waves. We tried to control the symmetric electric field frequency as well as the applied voltage to obtain optimum conditions to have particles deposited on both electrodes. A quantitative comparison was finally conducted between experimental and theoretical (based on the Hamaker relation) values of the deposition weight.

■ EXPERIMENTAL SECTION

TiO$_2$ nanopowder (with a particle size of about 100 nm) purchased from Merck Company was used as a common ceramic material in electrophoretic deposition studies. The 2 g/L suspensions of TiO$_2$ in acetone were prepared by ultrasonic agitation of the TiO$_2$/acetone system for 15 min. Symmetric wave-assisted EPD was carried out using a relay and a high-voltage power supply (Philips PE4839). The electrodes employed in deposition tests were fabricated on a borosilicate glass using commercial gold paste (Degussa Inc., GZ117), dried, and stabilized by firing at 610 °C. Deposition durations for AC-EPD on parallel planar electrodes were 1 and 10 min, and the obtained layers were dried in air. The distance between the electrodes was set to be 1 cm. We tried to control the symmetric electric field frequency as well as the applied voltage to obtain optimum conditions to have particles deposited on both electrodes. A schematic presentation of the experimental setup is shown in Figure 1a.

■ RESULTS AND DISCUSSION

In the first step, electrophoretic deposition of TiO$_2$ nanoparticles under a DC electric field was carried out at 50 V. In this case, deposition occurred on one electrode, which is consistent with classical EPD principles. Under the DC field, charged suspended particles are forced toward the electrode of the opposite potential and deposited there to form a thick layer of TiO$_2$. The possible deposition mechanisms have been discussed in the literature.[6]

In order to investigate the deposition pattern of the layer obtained under AC fields, EPD was carried out under a symmetric (rectangular) AC field at 1 Hz and 50 V. As depicted by Figure 1b, the TiO$_2$ film has not been formed on any of the electrodes. This is in agreement with conventional beliefs on EPD under the application of symmetric waves where the net movement of a given particle is considered to be zero. However, it must be remembered that the effective force pushing a particle toward the opposite electrode is the Coulomb force exerted on surface charge. Thus, it is expected that by increasing the electric field strength, we would be able to increase the distance that a particle travels in one cycle and, consequently, its chance for approaching the electrode and deposition.

To study the effect of an electric field on AC electrophoretic deposition on planar parallel electrodes, deposition was carried out at 200, 300, and 500 V for 10 min. The image of the electrodes after deposition, which is illustrated by Figure 2a−c, respectively, shows that deposition of TiO$_2$ nanoparticles has occurred on both electrodes. In other words, by increasing the applied voltage of the uniform AC field, a fraction of suspended ceramic particles have been able to reach the electrode of the opposite charge and deposit.

This result (Figure 2) is in contrast with the common belief that no deposit will form under symmetric AC electric fields.
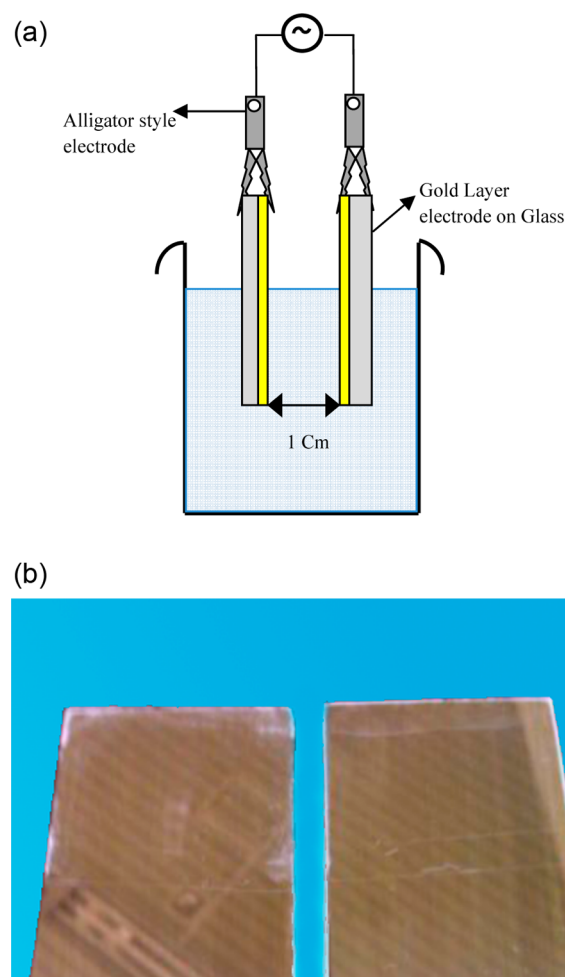

Figure 1. (a) A schematic presentation of the setup. (b) Electrophoretic deposition of TiO$_2$ nanoparticles at 1 Hz and 50 V.
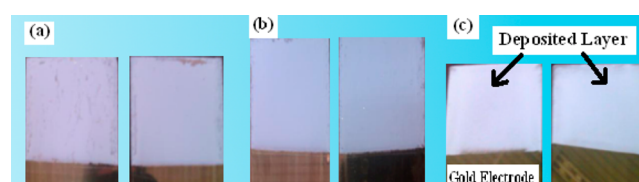

Figure 2. AC electrophoretic deposition pattern of TiO$_2$ nanoparticles at 1 Hz and (a) 200, (b) 300, and (c) 500 V.

Actually, when an AC electric field is applied, it is assumed that each particle starts to oscillate around a fixed point. The amplitude of these oscillations is directly proportional to the applied voltage while inversely depending on the frequency of the electric field. Hence, only particles neighboring the electrode would have the chance to reach the surface. As illustrated by the schematic design of Figure 3, particle 1 has the chance to reach the electrode surface in a half cycle, while particle 2 is not expected to behave like this because its net movement is zero. In other words, it is strongly possible for particle 1 to deposit in one cycle. However, in the Hamaker relation modified for uniform DC fields (eq 1),[7] the f_H coefficient explains that just a fraction of particles reaching the electrode surface are expected to deposit while the remaining will go back to the liquid medium.
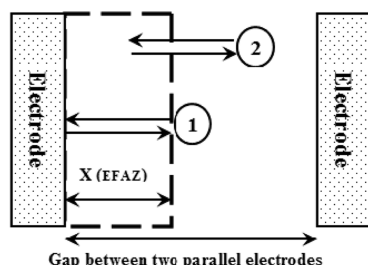
Figure 3. A Schematic design of the electric field affected zone (EFAZ).

$$\frac{dY}{dt} = f_H \mu C_p \vec{E} S \tag{1}$$

In this equation, dY/dt is the deposition rate, μ is the mobility of the particle, C_p is the concentration of particle in suspension, and $\vec{E}$ and S are the electric field and the area under deposition, respectively.

The region in front of the electrode where particles have the chance to reach the surface and deposit can be called the electric field affected zone (EFAZ). It is possible to estimate the dimension of EFAZ by considering the effective forces exerted on a particle under the influence of an AC electric field.

For particle sizes ranging 50 nm to 5 μm, Coulomb and drag forces could be considered as the main forces affecting the particles' movement across the liquid. In this particle size interval, the Brownian motion, regarded as strongly affecting particles below 50 nm, and the gravity force, considered to be dominant for particles above 5 μm in diameter, can possibly be ignored. Thus, for a spherical particle of radius r

$$F_{Drag} = (6\pi r\eta)\vec{v} \tag{2}$$

where η is the fluid viscosity and $\vec{v}$ is the relative velocity of the particle and fluid. The Coulomb force exerted on this particle within the electric field $\vec{E}$ is

$$F_{Coulomb} = E \cdot q \tag{3}$$

Also, in a nonaqueous medium, q (surface charge) can be obtained by[8]

$$q = 4\pi r\varepsilon_r\varepsilon_0\xi \tag{4}$$

where ξ is the zeta potential of the powder, $\varepsilon_0 = 8.85 \times 10^{-12}(F/m)$ is the permittivity of free space, and ε_r is the dielectric constant of the medium. Hence, the velocity of a particle in such conditions would be obtained by eqs 2 and 3. Considering eq 4

$$\vec{v} = \frac{2\vec{E}\varepsilon_r\varepsilon_0\xi}{3\eta} \tag{5}$$

Assuming the particle's velocity in one cycle to be constant ($\vec{v} = X/t$)

$$X = \frac{2\vec{E}\varepsilon_0\varepsilon_r\xi}{3\eta} \cdot t = \frac{2V_0\varepsilon_0\varepsilon_r\xi}{3d_e\eta} \cdot t \tag{6}$$

where V_0 and d_e are the applied voltage and the distance between electrodes, respectively.

Applied frequency can be regarded in eq 6 by considering t in a half cycle ($2t = 1/f$).

$$X = \frac{V_0\varepsilon_0\varepsilon_r\xi}{3d_e\eta f} \tag{7}$$

According to eq 7, displacement of a particle in a half cycle is directly proportional to the applied voltage that determines the strength of the electric field. In other words, at high electric field strengths, the width of EFAZ is increased, and more particles have the opportunity to reach the electrode surface and deposit. As shown in Figure 2, as the applied voltage is increased, an observable TiO_2 layer is formed, which is attributed to the extension of EFAZ at higher field strengths (eq 7).

In order to complete our discussion, it is necessary to derive a kinetic formula for EPD under an AC electric field. By applying mass balance, Hamaker derived eq 1 to relate the amount of particles deposited during EPD to the parameters of the process. In the same way, it is possible to relate the deposited mass in an AC electric field to parameters affecting EPD. For this purpose, the concept of EFAZ is employed (eq 7) to derive a kinetic equation. Figure 4 represents a schematic illustration of this zone where particles are shown to be traveling with constant velocity toward the opposite electrode.
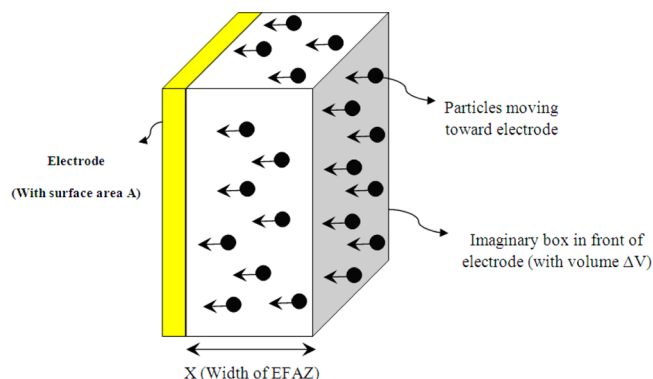

Figure 4. A 3D schematic presentation of the electrode, EFAZ, and particles in this zone having the chance to reach the electrode surface and deposit in one-half of a cycle under an AC electric field.

Assuming ΔV as the volume of EFAZ in front of the suspension in which particles are prone to deposit

$$\Delta V = X \cdot A \tag{8}$$

where X and A are the width of EFAZ and the area of the electrode where deposition can be observed, respectively. Using eq 7

$$\Delta V = \frac{V_0\varepsilon_0\varepsilon_r\xi}{3d_e\eta f} \cdot A \tag{9}$$

On the other hand, the ΔV volume of a C_p (g/L) ceramic suspension is assumed to contain m grams of powder ($\Delta V = m/C_p$).

$$\frac{m}{C_p} = \frac{2V_0\varepsilon_0\varepsilon_r\xi}{3d_e\eta f} \cdot A \tag{10}$$

Assuming the particles' mobility ($\mu = 2\varepsilon_0\varepsilon_r\xi/3\eta$) and the definition of the electric field ($\vec{E}$ V_0/d_e), the deposited mass of particles under the application of an AC electric field (with the applied frequency of f) would be obtained as

$$m = \frac{\mu \vec{E} A C_p}{2f} \quad (11)$$

This is the amount of mass deposited in one-half cycles. After n cycles, the mass of deposition equals

$$m = \frac{\mu \vec{E} A C_p}{2f} \cdot n \quad (12)$$

where n (the number of cycles) is related to the total deposition time through $\Delta t = n/f$ (see Table 1 for the process parameters to obtain the mass of deposition).

Table 1. Process Parameters to Obtain Mass of Deposition

process parameters	symbol and dimension	values
mobility of particle	μ (m^2/s·V)	2.035×10^{-8}
deposition surface area	A (m^2)	17.860×10^{-4}
concentration of particle in suspension	C_p (g/m^3)	2000
electric field strength	E (V/m)	from 50×10^4 to 600×10^4
number of cycles in deposition time	n	60
applied frequency	f (1/s)	1

Equation 12 indicates that in addition to the effective parameters expressed by the Hamaker equation, the deposited mass is an inverse function of the applied frequency in an AC electric field. In other words, as the electric field frequency is increased, particles will have less of a chance to reach the electrode surface and deposit. This phenomenon is a result of diminished EFAZ at higher frequencies due to faster oscillations of particles and shorter distances traveled in one cycle.

To validate eq 12, TiO$_2$ particles were deposited at 1 Hz and a potential range of 50−600 V, where the deposited mass was measured after each test. In Figure 5, the eq 12 and
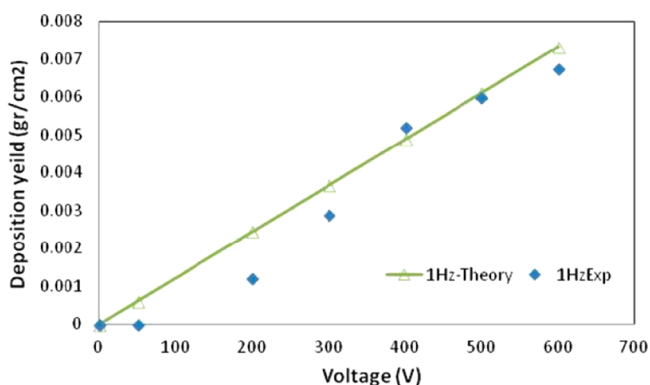

Figure 5. Experimental results and theoretical prediction of the deposition weight as a function of the applied voltage at 1 Hz.

experimental results are compared. It can be seen that while at lower voltages experimental results are less than the predicted values at higher voltages, the amount of deposition can be effectively approximated using eq 12.

On the basis of the EFAZ definition, there must be a threshold dimension for the EFAZ below which deposition will not occur. As shown in Figure 1b, for 50 V and 1 Hz, no deposit was formed even at longer deposition durations (10

min). Also, as revealed by Figure 5, the weight of deposition at 200 and 300 V is less than that anticipated through theoretical equations. However, by increasing the applied voltage, this deviation from the theory was diminished, which is attributed to the extension of the EFAZ at sufficiently high potentials.

CONCLUSION

Electrophoretic deposition of TiO$_2$ nanoparticles under symmetric uniform AC electric fields at 1 Hz in acetone showed that at sufficiently strong electric fields, the ceramic particles will become able to deposit on both electrodes. Under such fields, particles within the area affected by the electric field in front of the electrode surface (EFAZ) are considered to have the chance to reach the electrode and deposit. The width of the EFAZ was found to be proportional to the electric field strength as well as the electrophoretic mobility of particles, meanwhile in inverse relation with the electric field frequency and the fluid viscosity. A kinetic model was derived based on the Hamaker approach to predict the mass of deposition in an AC electric field. Although this model is in agreement with experimental results at high voltages, it deviates at lower potentials. This indicates that there is a threshold limit below which EFAZ is not wide enough to let particles deposit under an AC electric field.

AUTHOR INFORMATION

Corresponding Author
*Tel: +98 912 5398676. E-mail: babakraissi@yahoo.com.
Notes
The authors declare no competing financial interest.

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NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on November 27, 2012. The first author's name was misspelled. The corrected version was reposted on December 19, 2012.

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