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An analysis of current transients during electrophoretic deposition (EPD) from colloidal TiO_2 suspensions

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ABSTRACT

This is a simple quantitative analysis of the electrical current transients recorded during the electrophoretic deposition (EPD) of TiO_2 particles from ethanol-based suspensions in which the linear correlation between the mass deposited and the charge passed was verified experimentally. Using this experimental knowledge as our starting point, we were able to test a simple electrical model of a deposition cell for its consistency with electrical current density data measured during EPD. Assuming that the background electrochemistry was controlled resistively rather than diffusively, we then tentatively exploited the electrochemical data to gain information on the structure of the deposit during its growth.

1. Introduction

The electrophoretic deposition (EPD) of particles from colloidal suspensions was discovered in the 18th century [1], and has since been employed in a large number of industrial processes. In the EPD process, an electric field is established between two electrodes immersed in a colloidal suspension, which causes the electrically charged colloidal particles to travel to and accumulate on the electrode with opposite polarity to that of the surface charge they carry. EPD of mineral particles has been used in a wide array of applications, from the deposition of ThO_2 particles on tungsten filaments for enhanced thermionic emission [2] to the production of thick ceramic coatings [3]. Such flexibility has motivated the popularity of the technique in the deposition of thin and thick ceramic films, which has enjoyed growing attention during the last century.

Ceramic particles can be easily deposited by EPD on virtually any conductive substrate. EPD successfully competes with other techniques, in that it allows the controlled deposition of ceramic particles on nonplanar substrates. Furthermore, much thinner films can be produced than those obtained by other techniques, such as tape casting. It has been demonstrated that self-ordering occurs during EPD in monolayers of certain colloidal particles [4], which paves the way for the production of highly ordered 2-D structures displaying interesting properties. Virtually any type of ceramic material can be deposited by EPD, so long as a sufficient density of surface electrical charge has been achieved. For example, oxide powders [5–7] and electroceramics [8–10] have all been successfully deposited by this technique.

EPD is easily implemented, in that it requires only a well-stabilized colloidal suspension, a pair of conductive electrodes, and some basic electrical gear, the latter usually consisting of a DC potential source. The flux of particles to the substrate can be controlled by increasing or decreasing the electric field, by varying the solid loading, and/or the ζ-potential of the particles. The latter can be tuned either by setting the pH of the suspensions to a previously determined optimal value or by adding proper amounts of dispersants. In EPD the particles must be charged to reach typical values of ζ-potential of a few tens of mV, and values of the electric field from a few V cm^{-1} to several hundreds of V cm^{-1} can be employed in the process. Such a large number of parameters makes a rich set of deposition conditions available, and allows the production of different film morphologies.

The structure of an EPD film is known to depend on the value of the electrical parameters, which include the externally applied potential and the faradic current flowing in the cell. As to the former, there is consensus on the fact that high values of the electric field increase the yield (amount of material deposited per unit time) and the compactness of the film. At high electric field, the compacting action may be caused by a strong electrical force that pushes the charged particles together [11] or by the pressure exerted by the incoming particles on those already deposited on the substrate [11,12]. As to the latter, faradic currents are customarily observed during EPD, and seem to some extent to be inherent to the process. Experimental clues as to their role may be given by a number of

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circumstances, among which are the linear correlation between the amount of material deposited and the total charge passed through the cell [13], and the presence of an electrohydrodynamic flux, which has been observed to induce coalescence of colloidal particles at the electrode [4].

The magnitude of faradic currents typically declines as the deposition proceeds, and the related current–time curves are occasionally reported in the literature. Monotonically decreasing, nonlinear current transients observed during EPD at constant applied potential have sometimes been interpreted as being due to the establishment of an ionic concentration profile under a diffusion-limited regime [14]. In such a case, plots of currents vs. the inverse square root of the time elapsed should result in straight lines, which are in fact seldom observed. Even making allowance for mild nonlinearity in these plots due to experimental artifacts (compliance of the DC voltage source, convection effects [15a], formation of ultrathin films on the electrode, etc.), it remains to be seen in which region of the cell such a concentration profile would be established. Indeed, as EPD processes are carried out in colloidal suspensions rather than solutions, standard electrochemical transients can hardly be expected to obey the simple laws that rule diffusion-limited processes in ionic solutions. In the latter case, the kinetics of the electrochemical processes must be assumed to be fast enough to keep the concentration of reactant at the electrode close to zero, which is by no means assured in many processes taking place under kinetic control. Since in EPD a deposit is formed which is usually made of nonconducting substances and which has a different density from that of the suspension, it may be surmised that other factors might hinder the access of the reactants to the electrode. Therefore, other possibilities which take into account the complex structure of the EPD interface should be investigated.

In this paper, we investigate the possible connections between the structure of the EPD deposit (thickness, density, resistivity, etc.) and the trend of electrical current flow during the potentiostatic EPD of submicrometric TiO_2 particles in an ethanol-based colloidal suspension. We believe that establishing such a correlation between the evolution of the electrical parameters and the changing structure of the deposit may be helpful in clarifying some of the fundamental aspects of the EPD process.

2. Experimental

Titania particles (Degussa P-25) were mixed with absolute ethanol (Fluka, >99.8% assay) at a concentration of 10 g/100 ml, and then ball-milled for 2 h. A dispersant (alkyl phosphate ester, Phospholan PE65, Akzo Nobel) and a binder (polyvinylbutyral (PVB), Butvar, Solutia) were added at various concentrations to examine their effects on the faradic current. The suspensions were sonicated for 20 min after ball-milling to improve dispersion, and immediately used for EPD experiments. EPD was performed either in a coaxial cylinder or in a plane-parallel geometry cell.

Coaxial-cylinder geometry was employed to investigate the dependence of the faradic current on the concentration of dispersant and binder, and to determine the correlation between deposited mass and passed charge. Stainless steel (SS) wire cuttings (diameter 0.90 mm, projected surface area 0.53 ± 0.01 cm^2) were used as working electrodes (WE), and were always positioned along the axis of the cell. Whenever it was necessary to perform a high-resolution comparison of current values, the same SS electrode was used in order to keep the value of the projected area rigorously constant. In this case, the electrode's surface was rejuvenated by polishing with 1-μm alumina slurry in DI water, followed by rinsing in water and ethanol. To determine the correlation between deposited mass and passed charge, slightly larger aluminum foil electrodes were used, which clipped elastically to a glass pipe and which allowed easy postdeposition harvesting of the deposited material. The latter was weighed on a Toledo-Mettler Electronic Balance (resolution ±5 μg).

A much larger cylindrical SS counterelectrode (CE) (47 mm diameter, 50 mm height, $\approx$75 cm^2 active area) was placed coaxially around the working electrode, its large surface ensuring that the WE was the current-limiting electrode in the system. The potential between the electrodes (±5 V max) was established by means of a computer-assisted, three-electrode electrochemical workstation (FRA2 μAUTOLAB, Type III from Eco Chemie, Holland). The reference electrode (RE) terminal was electrically connected to the CE, which made it possible to establish the desired potential drop between WE and CE; accordingly, in this work all potentials will be given vs. CE, employing the notation V(CE). All experiments were planned and performed within the GPES software environment, and both current and charge data were automatically displayed and recorded.

3. Diffusive vs. resistive modeling of EPD cells

Purely diffusive control in deposition electrochemical cells, in which the potential is abruptly stepped to the desired value, produces a current density transient described by Cottrell's equation [15b]

$$j(t) = \frac{nFD^{1/2}C^*}{\pi^{1/2}t^{1/2}}, \tag{1}$$

where j is the current density, n is the number of electrons involved in the electrochemical reaction, F is Faraday's constant (96,845 C mol^{-1}), D is the diffusivity of the reacting chemical species, C^* its bulk concentration, and t is the time. For (1) to rigorously apply, the concentration of electro-active chemical species at the electrode must approach zero at all times, due to the fast kinetics of the electrochemical reaction. Eq. (1) applies to classical plane-parallel geometry. A modified Cottrell equation to be used in the case of coaxial-cylinder geometry is [16]

$$j(t) = \frac{nFDC^*}{r}\left[\frac{2\exp(-0.05\pi^{1/2}\tau^{1/2})}{\pi^{1/2}\tau^{1/2}} + \frac{1}{\ln(5.2945 + 0.7493\tau^{1/2})}\right],$$
$$\tau = \frac{4Dt}{r^2}, \tag{2}$$

where the symbols have the same meanings as previously indicated and r is the radius of the cylindrical WE. Both transients yield straight-line plots when the current is plotted vs. the inverse square root of the elapsed time and r is sufficiently large, as in this work (r = 0.45 mm). However, (1) and (2) can only be observed at metallic electrodes that can be freely accessed by the electro-active chemical species. If a resistive film grows on the conductive WE during the process, free diffusion of electro-active species to and from the electrode is hindered, and a diffusively controlled regime cannot be established. This may be the case of the background electrochemistry in EPD, since a deposit is always grown on the WE. For this reason a resistive element must in some way be introduced in a model of the EPD cell when drawing information from current transients recorded during EPD.

Based on the standard modeling of electrochemical cells, a combined resistive–capacitive model of the EPD cell can be envisaged, which also accounts for the presence of a thick deposit of ceramic particles at the WE (Fig. 1).

In Fig. 1, resistors model the electrical resistance of the various components of the cell, while capacitors account for transient charge storage when the applied potential is stepped at the beginning of the deposition. Resistances can be classified either as faradic (at the WE/deposit and suspension/CE interfaces) or bulk