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Segregation of nanoparticles by electrophoretic deposition technique: A mathematical model and its validation

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ABSTRACT

Electrophoretic deposition is the only technique available to fabricate nanoparticle thin films offering control on size distributions of nanoparticles on them. We describe the extensive efforts to understand this complex electrophoretic deposition process. One of the gaps in this research involves the size distributions achieved in the process. We address this particular issue by performing a lab scale experiment and providing a phenomenological model for size distributions.

Nanocrystalline iron oxide particles were electrophoretically deposited from a stirred sedimenting suspension using different applied voltages onto silicon substrates. The as-deposited particles were further characterized by X-Ray diffraction and Transmission Electron Microscopy. For understanding the size distributions of these deposited particles, a phenomenological (lumped) model has been proposed. Two parameters have been considered in this model viz. applied electric field during deposition and effective viscosity of the medium in which particles were dispersed. There is good agreement between experiments and theory proposed through the model for a range of voltages.

1. Introduction

Formation of thin films by particle assisted growth has been a field of extensive research. There have been different techniques like particle assisted MOCVD [1], spray pyrolysis [2], spin coating [3,4], pulsed laser deposition [5], particle atomic layer deposition [6] and electrophoretic deposition (EPD) [7] to obtain films from particle precursors. Some of these techniques need elevated temperatures to yield uniform films during deposition, whereas few others require post annealing treatment. EPD has been used for deposition of various types of materials [8–35]. EPD has been found to be more convenient for synthesis of thin films and coatings of ceramic and semiconducting materials for various reasons of advantage [27,36,37]. It has been used to obtain industrial coatings [14,16,38] and in controlling their properties [39,40]. There have been attempts to understand the detailed mechanisms of EPD [21,27,41].

EPD is in particular, capable of selecting the desired sizes of particles deposited on the films. The deposited particle size distribution (PSD) can be changed by controlling the electric field and therefore it can serve as an efficient method for application involving deposition of nanoparticles for immobilization on templates. In particular, there are medical applications wherein metal nanoparticles encapsulated with biofunctionalized dendrimers are immobilized on surfaces. Biological ceramic composites [7] and anodically oxidized alumina templates are useful for drug delivery systems [42]. Electrophoretic method is useful in such applications where desired particles of known dimensions are to be immobilized into pores of the templates. On account of such utility, it is desirable to understand the process of EPD and the resulting PSD of the deposited film. In EPD, the material used for the formation of the film is often deposited from a suspension maintained by stirring action which is a well-established method, for example for creating coatings [43,44]. We confine our work to depositions from stirred suspensions.

The size distribution of deposited particles has not been paid attention to, as most of the synthesis processes involve coagulation after deposition [16]. However, applications like the deposition of nanoparticles of iron oxide (Fe_2O_3) for magnetic memory applications do not involve any further agglomeration. Considering this as an example, we propose a lumped model which provides the PSD deposited on the electrode. The lumped model could be viewed as a way to extract essential parameters like effective viscosity in our case, for a phenomenon taking place in an experimental frame. Phenomena like electrophoretic deposition in stirred sedimenting suspensions have high levels of complexity and a detailed simulation based on scientific principles is prohibitively expensive. The issue of identification of effective parameters in such situations has been addressed in literature [45]. In such complex systems, when

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faced with ambiguities and controversies, certain normative assumptions regarding the simulations assume crucial significance bringing into focus the manner in which a lumped model is constructed [45]. We have attempted to relate our work to this framework using ideas similar to model isomorphism and model reduction [46].

The phenomenological lumped model though for a non-steady state process, incorporates an effective viscous drag which follows Stokes' law. This is viewed as an abstraction theme [46]. The process of stirring introduces vortices in the flow while maintaining the particles in suspension. The motion of the particles is similarly imagined under an abstraction theme [46] as migration from vortex to vortex along a linear path under the action of electric field. The proposed model is found to predict the PSD in good agreement with experiments for a range of electric fields. This model could be used as a prototype for further experiments as well as theoretical investigations into the process of EPD from sedimenting suspensions.

2. Materials and methods

The nanoparticles of iron oxide were synthesized by DC arc plasma (KEJE ARC, manufactured by KEJE Electronics) method [6]. Commercially available iron disc (2″ in diameter and 1″ in thickness) was used as anode. The arc was struck, in oxygen atmosphere, between graphite cathode and the water cooled iron anode by applying a voltage of 22 V. The arc current was maintained at 40 A and the powder formed during the process was allowed to settle on the walls of the chamber, and subsequently it was collected.

Further, these particles were deposited on the silicon substrate by using the technique of Electrophoretic Deposition (EPD). For this, the as synthesized powder was dispersed in a non-conducting (isopropanol) medium. Silicon and copper electrodes in parallel geometry were dipped in the medium as shown in Fig. 1. Regulated dc voltages were applied between silicon substrate as cathode and a copper electrode as anode leading to electric fields ranging from 10 to 200 V/cm. A magnetic stirrer was used to keep the particles dispersed in the solution during deposition. Under the action of the magnetic stirrer, vortices shown in Fig. 1 are formed in the container which carry the spherical suspended particles. Films were deposited for the time period of 20 min at room temperature by applying various voltages. The as deposited films were scraped out for further characterization. The scraped powder was dispersed on a copper mesh for Transmission Electron Microscopy (Technai G^2 F-30 model). X-Ray Diffraction (Bruker D8 Advance X-Ray Diffractometer) analysis was further carried out for the powder scraped out.

Fig. 2 shows the TEM micrographs of particles deposited at different applied electric fields and the cumulative distribution was obtained from the micrographs. It is observed that the cut off edge of largest particle size is increased with increasing applied electric field strength.

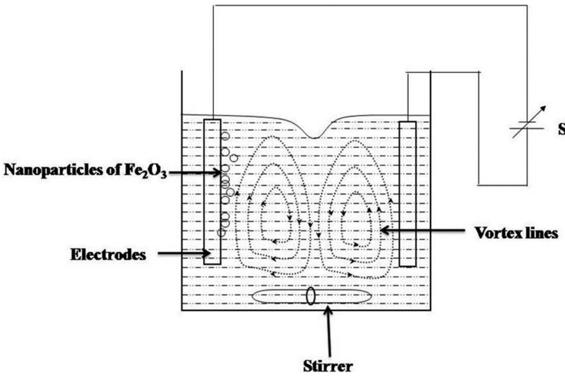

Fig. 1. Schematic for the experimental set up showing the cross section of the vortices formed due to the rotation of magnetic stirrer. The solid line indicates the surface profile during stirring.

The average particle size was measured for each experimental set from XRD data. These particle sizes are plotted as shown in Fig. 3. This plot shows the increasing trend with increasing electric field strength. The number of particles may vary on account of different regions of the sample viewed in TEM micrograph. The micrograph gives the information pertaining to very small area over grid.

3. Theory and calculations

3.1. Physics of suspensions: background

The general theory on models and mechanisms of electrophoresis and deposition of ceramic particles in the presence of an electric field is still open [47–52]. In case of specialized applications, there are experimental indications that the kinetics of EPD requires to be further deeply understood [50,53].

On one hand, suspensions can be studied from the point of view of rheology based on microscopic dynamics of the suspended particles. The rheology of such colloidal dispersions addressed viscous effects emerging from hydrodynamic interactions. Issues like viscous drag and stability are expected to be related to the distortion of electrical double layers [44,47,48,50] and surface charges of the dispersed particles [49,53]. In cases, where the medium for suspension is alcohol it is modeled as an amphiprotic solvent, like water. So we can expect viscous drag due to similar reasons in alcohol also. This drag would affect the PSD of the particles deposited on the substrate. Electrical double layers are one reason for the drag. There has been an attempt to explain viscous drag in suspension from the mesoscopic level upwards. Using evidence regarding formation of particle clusters by shear induced aggregation, it is suggested that the viscosity of the suspension relates to hydrodynamic rupture of such clusters [54]. Even then, the explanation remains partly phenomenological.

On the other hand, relating the PSDs to hydrodynamic interactions is further complicated by the stirring action needed to prevent sedimentation keeps the suspension very far from equilibrium. Problems like these arising in suspension dynamics are of considerable theoretical interest [55,56]. In particular, the theoretical context of our experiment remains to be explored. For example, sedimenting suspensions of spheres with even moderate Peclet numbers have been recently shown to display effects of hydrodynamic fluctuations [57] but the analysis is carried out for steady state sedimentation.

Suspensions (including sedimenting ones) have been modeled in literature at a mesoscopic scale using local PSDs and employing balance equations [58–61]. Discrete size distributions for finite number of sizes are assumed in the models in most of the works. There has been an attempt to extend the other assumptions of these models like the Masliyah Lockett Bassoon flux to continuous size distributions [61]. In such assumptions for the flux, the motion of particles of all sizes takes place with the same instantaneous local velocity. This limits the models to largely advective flows of particles in the suspension.

It is therefore not surprising that despite the widespread applicability, the process remains poorly understood and much of trial and error is required as far as optimizing the process control parameters are concerned [20,27]. Still, there have been attempts in literature to model EPD based on whatever systematics that has been successfully established [51,52]. None of the models have been sufficiently capable so as to address the size distribution of deposited nanoparticles as a function of the process parameters (applied electric field and deposition time). In this paper, we attempt to set up a phenomenological model for the same.

3.2. Modeling the EPD process

Following the understanding we have above, we attempt to create a phenomenological model for a non-steady state particle in fluid motion by incorporating an effective viscous drag which follows Stokes' law.