

## CHAPTER III

### MECHANISMS FOR ELECTROPHORETIC DEPOSITION

#### Chapter Overview

Having reviewed how the particle-particle interactions in a suspension can be tuned to maintain a stable suspension, we turn to consider how particles can be driven out of the suspension to form a solid aggregation on the surface of a deposition electrode. The charges on the particles enable the electric field to move them toward the electrode. Once they arrive there, they need to be compelled to form a compact deposit. In short, the mechanisms that keep a suspension stable in the bulk region must be altered to allow the particles to become bound to each other at the electrode surface. In this chapter we discuss several mechanisms by which suspensions can be destabilized to facilitate electrophoretic deposition (EPD).

#### 3.1 Electrostatic Force

The applied electric field drives the suspended particles toward the electrode. In certain cases, the electrostatic force caused by the field is sufficient to overcome the repulsive force between particles. If we examine the diagram of interaction energy between two iron oxide particles in hexane (Figure 2-5), we can estimate the repulsive force ( $F$ ) from the derivative of the energy ( $U$ ) with respect to the surface-to-surface separation ( $r$ ) as shown in Equation (3.1). A positive value of  $F$  indicates that the force is repulsive, while a negative value of  $F$  indicates that the force is attractive.

$$F = -\frac{dU}{dr} \quad (3.1)$$

For the two nanoparticles described by Figure 2-6, the maximum repulsive force is approximately 0.5 meV/nm, which, after converting units, is  $\sim 8 \times 10^{-14}$  N. Assuming that the charge on each

particle is  $1.6 \times 10^{-19}$  C ( $Z = 1$  e), the electric field that exerts a force on the particle equal to the repulsive force is  $\sim 5.0$  kV/cm. In our laboratory, we have successfully deposited iron oxide nanoparticles from hexane suspension by applying electric fields of that order (between 1 and 10 kV/cm). Local fields can be even greater in magnitude as a result of nanoscale vertices and edges on the electrode surface. These high fields can be applied because the nanoparticles are suspended in hexane, which is a nonpolar solvent with an extremely low conductivity. Such a strong electric field could not be applied continuously to particles in polar suspensions because of unfavorable effects such as Joule heating, excessive fluid flow, and bubbling from electrolysis if water is present. Heating can cause flocculation in the suspension as well as damage to the film that is being deposited, while excessive fluid flow can disrupt the growing deposit.

### 3.2 Electro-osmotic Flow

Overall charge neutrality in the suspension dictates that the liquid around a charged particle will contain net charge opposite to that of the particle. Consider a negatively charged particle at the surface of a positively biased electrode. Immediately next to the particle, the liquid possesses a net positive charge, and therefore flows away from the electrode surface. The electro-osmotic flow is sustained as the liquid that flowed away from the electrode is replaced by liquid from adjacent locations along the electrode surface, as shown in Figure 3-1. Solomentsev, et al., demonstrated in an EPD experiment that two separate  $10 \mu\text{m}$  spherical polystyrene particles in water, localized at the electrode surface, could be made to aggregate via electro-osmotic flow [37].

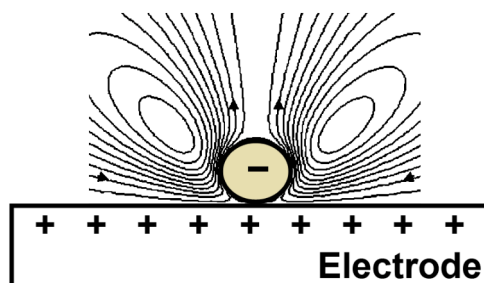


Figure 3-1. Pattern of electro-osmotic flow around a stationary particle near an electrode surface. Adapted from [37].

### 3.3 Electrochemical Effects

While EPD is not an electrochemical deposition process, like electroplating for example, electrochemical changes at the deposition surface can facilitate the formation of a deposit by reducing the particle-particle repulsive energy barrier. In other words, the electrochemical changes reduce the magnitude of the electrostatic repulsion. The specific mechanisms by which the repulsion can be decreased are discussed in the following sub-sections.

#### *3.3.1 Charge Neutralization*

In the simplest concept, the charged particles themselves lose protons or electrons, decreasing the particles' surface charge and hence the strength of the electrostatic repulsion between them. The ionic strength of the liquid around the particles is not altered significantly. This mechanism typically is not observed in depositions exceeding a single layer of particles since the particles need to come in contact with the electrode or a path of charge conduction to the electrode before they are neutralized [38].

#### *3.3.2 Ion Generation*

An increase in ionic strength near the electrode surface (due to electrolysis, for example) can trigger aggregation of particles in the vicinity of the electrode. Consider negatively charged particles in water. Their charge causes them to move toward the positively biased electrode. At the positively biased electrode, water is electrolyzed to yield O<sub>2</sub> gas and dissolved protons. The protons, being of opposite charge to the particles, screen their electrostatic repulsion. If sufficient quantities of protons are generated, the Debye length decreases, resulting in a decrease in the repulsive interaction at a given particle separation. As we show in Chapter 7, the mechanism of ion generation (due to electrolysis) facilitated the deposition of graphene oxide colloids suspended in water.

### 3.3.3 Ion Depletion

Even if ions are consumed in the vicinity of the electrode, deposition of particles may still be possible. Consider an EPD system in which protons are adsorbed to the particles. These positively charged particles are drawn toward the negatively biased electrode. Simultaneously, negative ions in the suspension are driven away from that electrode. If the protons are consumed at that electrode (for example, by combining with electrons to produce H<sub>2</sub> gas) then the ionic concentration in the vicinity of the electrode will decrease, especially since negative ions will migrate away to maintain charge neutrality. Thus, an ion-depleted layer grows outward from the electrode surface. The ionic concentration gradient between this layer and the bulk suspension triggers a voltage rise, which in turn engenders a strong electrostatic force to compact the deposited particles toward the electrode. Van Tassel, et al., have written extensively about ion depletion in constant-current depositions [39, 40]. They have observed upwards of a twenty-fold increase in voltage across the growing deposit. Because our laboratory uses constant-voltage EPD rather than constant-current EPD, if ion depletion occurs in our experiments, we should observe a significant decrease in the current resulting from the decreased conductivity of the ion-depleted layer.

With knowledge of these EPD mechanisms, we were able to analyze and optimize the deposition of nanomaterials in our experiments. Electrochemical effects were central to the EPD of graphene oxide suspended in water described in Chapter 7. In the next chapter, we describe EPD of hexane-suspended nanoparticles, which is driven by the electrostatic force.