DREXEL UNIVERSITY
Materials Science and Engineering
College of Engineering

Department of Materials Science and Engineering,

PhD Defense
July 30th
COE Hill Conference Room 10 am

AC and DC Methods to Investigate Colloidal Microstructure

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Abstract

The performance of a colloidal film is largely dependent on its microstructure. When dispersed in a solvent, colloidal particles form non-Newtonian fluids, meaning their microstructure evolves in response to the specific processing conditions. Since each film differs in particle size, density, surface charge, and intended application, there is no one-size-fits-all approach to processing.
As a result, monitoring microstructural evolution is essential for understanding how each processing step influences the final film properties. Currently, in-situ techniques for probing the microstructural evolution of drying thin films are often limited by cost or accessibility. Electrical measurements present a much simpler, cheaper and more convenient alternative. This work presents the development of electrical characterization methods designed for both academic research and industrial applications, with a particular focus on energy storage technologies.

Chapter 1 introduces the background and motivation for this work and presents a review of methods previously used in literature. In Chapter 2, we explore the potential of alternating current (AC) methods for probing colloidal microstructure, focusing on the use of dielectric spectroscopy to assess carbon black aggregate size in a carbon black–N-methyl pyrrolidone (NMP) slurry. Dielectric spectroscopy is appealing for its ability to distinguish charge storage processes based on their characteristic frequencies or timescales. We hypothesize that the frequency of the peak observed in dielectric loss (ε'') corresponds to the polarization timescale of the electrical double layer surrounding carbon aggregates, serving as a qualitative indicator of aggregate size.
To validate this, we attempted to replicate a published study on the same polarization mechanism using silica particles in water but were unsuccessful. Following several additional unsuccessful attempts to verify the signal, this line of research was ultimately discontinued.
This outcome highlights a common challenge with AC measurements: the difficulty in unambiguously identifying the specific processes contributing to the observed signal.

DC-based techniques offer more straightforward interpretation of resistivity and microstructural changes. Chapter 3 of this thesis details the development of a method that utilizes four-electrode resistivity measurements at variable probe spacings to detect changes in the vertical particle concentration profile. We first demonstrate the feasibility of this idea by developing a drying model to simulate the measurement. The model describes the particle distribution during drying in terms of the relative effects of Brownian diffusion, sedimentation and evaporation.
For sedimentation and evaporation dominated drying, the film is modelled as two stratified layers of different concentration. Solving this model simultaneously alongside Laplace's equation for electrostatic resistance identifies the parameters necessary to distinguish between diffusion, sedimentation and evaporation dominated drying. For resistive particles in a conductive solvent, simulations predict that the normalized thickness of the top layer, δ_t/H_0, must exceed 0.15 or 0.1 to distinguish evaporation and sedimentation dominated drying, respectively, from diffusion dominated drying. The heuristic model results are then validated theoretically by comparison to a physics-based drying model. Finally, model predictions are experimentally validated by fabricating a custom microlithography four-line probe device and measuring the transient resistance of systems for which the drying mechanism is known.

While Chapter 3 establishes the functionality of the four-line probe, it is only tested on simple systems such as monodisperse colloidal films and particle-free ionic solutions. In contrast, lithium-ion battery (LIB) electrode slurries are more complex, containing particles of two vastly different sizes and densities, along with a dissolved polymer binder in NMP. Chapter 4 applies the four-line probe to these slurries, coated onto the device—mimicking a current collector—at different shear rates to investigate how coating shear influences electrode microstructure and drying behavior. Previous studies have reported improved performance in LIB electrodes coated at high shear rates, attributing this to enhanced carbon connectivity, partially supported by EDS-based atomic distribution analysis. Our resistivity measurements at varying depths reveal distinct microstructural dynamics between high and low shear rate coatings, suggesting different drying mechanisms. Heuristic models help interpret these results, showing, for example, that low shear rates promote early aggregation and sedimentation of carbon particles.
Both shear rates result in the formation of a carbon-rich top layer during drying.
These findings are further validated by electrochemical fluorescence microscopy (EFM) and EDS imaging of the dried electrodes. Ultimately, we conclude that the relative spatial distribution of carbon and NMC particles—not just the vertical profile of carbon—is more critical to overall electrode performance. Finally, Chapter 5 provides a summary and potential avenues of future research.