

Theoretical Aspects of Electrodeposition in Charged Porous Media

by

Edwin Sze Lun Khoo

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Abstract

Electrodeposition is a fascinating electrochemical phenomenon that contains deep physical insights and has broad practical applications. At the heart of the physics governing electrodeposition is a competition between a destabilizing force caused by surface crests growing more rapidly than surface troughs in a positive feedback loop and a stabilizing force arising from surface energy effects that prevent the surface from roughening excessively. The physical manifestation of this surface instability is the formation and propagation of dendrites. Some applications of electrodeposition include electroplating of metals such as copper and charging of next-generation high-energy-density metal batteries such as lithium metal batteries.

From both theoretical and practical standpoints, it is important to understand how to control and exploit electrodeposition. In this thesis, we explore electrodeposition in a homogenized charged porous medium that contains a fixed background charge density, which affords us a new knob for controlling electrodeposition. In practice, such a background charge density can be generated through experimental techniques such as layer-by-layer deposition of polyelectrolytes on the pore surfaces.

We investigate the theoretical aspects of electrodeposition in charged porous media in three different ways. First, we introduce a simple transport model that accounts for the background charge density and couple it with electrochemical reaction kinetics for electrodeposition. We then validate the coupled model by comparing predicted steady state current-voltage relations and linear sweep voltammetry with experimental data for copper electrodeposition in a variety of nanoporous media. Second, we perform linear stability analysis on the model to understand how key system parameters such as the background charge density affect the linear stability of the metal surface. We then show good agreement between theoretical predictions and experimental observations of the critical and instability wavelengths for copper electrodeposition in cellulose nitrate membranes. Third, we carry out impedance analysis on the model and explain some intriguing features in the experimental impedance spectra for copper electrodeposition in anodic aluminum oxide membranes. Through these three different types of analysis, we demonstrate the predictability and robustness of

the theory despite its simplicity.

Thesis Supervisor: Martin Z. Bazant

Title: E. G. Roos (1944) Professor of Chemical Engineering

Executive Officer, Chemical Engineering

Professor of Mathematics