

# A PHASE FIELD MODEL OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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## Abstract

One of the fundamental tenets of Material Science is the link between microstructure and material properties. As such, there is a need for a microstructure-sensitive model of electrochemistry. Phase field models have been designed to simulate systems with complex and evolving microstructures such as eutectic solidification and dendrite growth. The goal of this work is to extend phase field models into electrochemistry: with a chemical reaction model and a method of simulating electrochemical impedance spectroscopy (EIS). The model given in the present work also forms the foundation for a microstructure-sensitive model of electrochemistry.

EIS is a widely-used and powerful diagnostic technique in which the frequency-dependant impedance is measured. Though popular, data from EIS can be notoriously difficult to interpret.

The present work also presents simulated EIS data, as well as explanations into the origins of common Nyquist plot features. At high-frequency, an analytic expression for the resistances is derived by analogy to Ohm's law. At low-frequency, the value for the resistance can be predicted by a simulated DC experiment. High-frequency capacitance originates in a difference in the current between the electrode and electrolyte. Low-frequency capacitance is defined by an "effective" surface charge, calculated by integrating the current over time rather than the charge density over distance.

Depressed semicircle constant-phase element (CPE) behavior is also observed in the simulated data. Simulations with fast reaction kinetics exhibit power-law CPE impedance behavior, while simulations with a slow or no reaction are best explained by a combination of finite-length diffusion and electromigration.

The model developed in this work is a tool to simulate, study, and interpret EIS data. Ultimately, it will serve as the foundation for a microstructure-sensitive model of electrochemistry.