

Physical Models and Statistical Methods for Understanding Electrochemical Kinetics

by

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Decarbonization of the global economy in order to limit rapid global surface temperature growth is a critical industrial and societal challenge for the next several decades. Yet, several sectors of the economy remain stubbornly difficult to decarbonize, such as commodity chemicals production, cement and steel manufacturing, and synthetic fertilizer synthesis, to name only a few. Emerging efforts to decarbonize these processes rely on electrochemical techniques, which use emissions-free sources of electricity to drive relevant chemical reactions. Much remains to be understood about the fundamentals of electrochemical kinetics, hampering efforts to rationally engineer decarbonized electrochemical processes. This thesis develops new physical models and applies rigorous statistical methods towards developing a more complete understanding of electrochemical kinetics.

Studying electrochemical kinetics is challenging because the relevant reactions occur at a metal-electrolyte interface characterized by stark spatial anisotropy, strong electric fields, and the persistent presence of an electronic reservoir. In response to these constraints, molecules are forced to adopt typical configurations that are highly atypical in the bulk; fluctuations around these configurations are also highly constrained. Although experimental approaches can provide a wealth of information about the nature of chemical dynamics at an interface, they often convolve the numerous physical effects at play in this setting. Physical models are essential because they allow us to assess the relevance of microscopic physical phenomena to macroscopically observable behavior. In this thesis, I develop two new extensions to the classical Marcus theory of electron transfer kinetics, both of which account for the effects of diffusive transport phenomena in the electrochemical double-layer (EDL). Additionally, I examine the structure of electrostatic potential variations in the EDL using molecular simulations, and point out where existing continuum theories may fall short.

Modern techniques in statistics and data science can help accurately quantify the uncertainty associated with a reported experimental result. Despite finding more use across science and engineering in recent years, rigorous statistical techniques are still woefully underemployed in the analysis of electrochemical data. Experimental electrochemical techniques of various stripes are often hampered by outmoded approaches to data handling: for example, linear fitting techniques for analysis of results reign supreme, and uncertainties in analysis results are often incompletely quantified and reported, if at all.

This thesis advances two major thrusts along these lines, proposing the use of rigorous statistical techniques when collecting and analyzing current-voltage measurements on electrochemical systems. First, I develop a Bayesian data analysis approach to estimate the Tafel slope (a key parameter often quoted to characterize the efficacy of an electrochemical catalyst) from experimentally-measured current-voltage data, and use it to dispel the commonly held notion that Tafel slopes cluster around certain “cardinal values” reported in the

literature. Finally, I develop a new electrochemical characterization technique that hinges on analyzing the nonlinear current response of an electrochemical system to a small amplitude oscillating voltage signal. This technique is a complementary tool to traditional cyclic voltammetry approaches to characterization, and may be better suited for high-throughput experimentation applications.

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