

Theory of Electrochemical Interfaces at High Voltage

Martin Z. Bazant

Departments of Chemical Engineering and Mathematics
Massachusetts Institute of Technology
bazant@mit.edu

Alexander Kuznetsov Prize Lecture in Theoretical Electrochemistry
Annual Meeting of the International Society of Electrochemistry, Den Haag, Netherlands, Aug. 22, 2016

In electrochemistry, the structure and dynamics of the electrode/electrolyte interface are typically neglected or represented by linear circuit elements. This talk will describe my personal journey in developing theories of the nonlinear dynamics of electrochemical interfaces under large voltages, motivated by applications in microfluidics and energy storage. The story begins with induced charge electro-osmotic flows around polarizable colloids and electrodes, driven by extreme capacitive charging of the double layer. The paradox of high voltage, high frequency flow reversals ($>1V$, $>kHz$) began to be resolved by new (and old) models of steric effects and Coulomb correlations¹, which in turn led to a simple theory of “overscreening and crowding” in the exotic double layers of room temperature ionic liquids² (Fig. 1). These models were formulated in terms of diffusional chemical potentials, defined as variational derivatives of the total free energy functional. Unifying this approach with electrochemistry resulted in a general theory of chemical kinetics based on nonequilibrium thermodynamics³, which explained driven phase transformations in Li-ion and Li-air batteries. Surprising theoretical predictions, such as suppression of phase separation at high insertion rates, have since been confirmed experimentally by *in operando* imaging of lithium intercalation in single nanoparticles and porous electrodes (Fig. 2).

1. M. Z. Bazant, M S Kilic, B Storey, and A Ajdari, Towards an understanding of induced-charge electrokinetics at large applied voltages, *Advances in Colloid and Interface Science*, 152, 48-88 (2009).
2. M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, Double layer in ionic liquids: Overscreening versus crowding, *Physical Review Letters* 106, 046102 (2011).
3. M. Z. Bazant, Theory of chemical kinetics and charge transfer based on nonequilibrium thermodynamics, *Accounts of Chemical Research* 46 (5), 1144-1160 (2013).

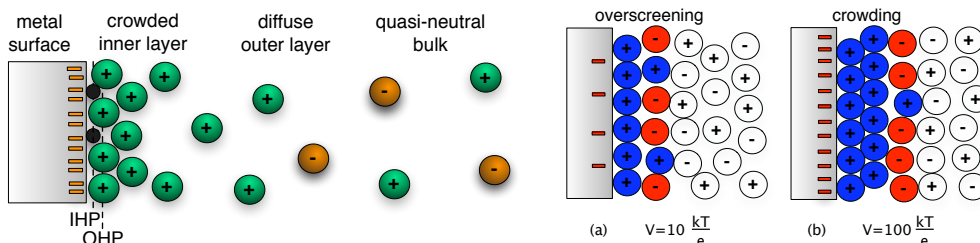


Fig. 1. Theoretical pictures of the induced double layer at high voltage in electrolytes¹ and ionic liquids².

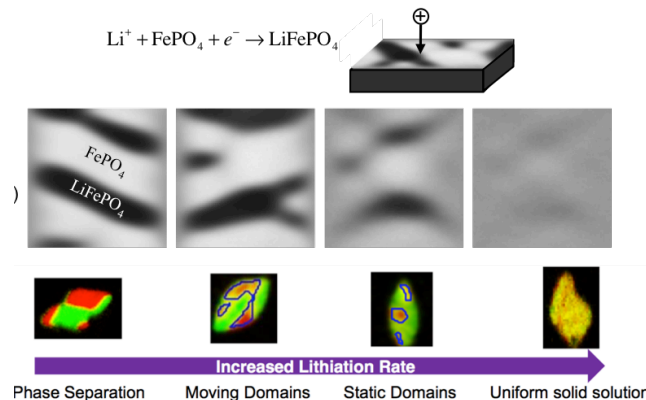


Fig. 2. Theoretical prediction³ and experimental confirmation [W. Chueh, Stanford, to be published] of anisotropic phase separation and its suppression at high rates in lithium iron phosphate nanoparticles.