Theory of Electrochemical Interfaces at High Voltage

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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, prompted 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 lead 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).


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.