From bulk thermodynamics to Nano-structuring near electrified interfaces: a continuum transport theory for ionic liquids incorporating solvation effects

Theoretical studies and simulations are efficient means for the evaluation of materials and for improving the design of electrochemical devices. Here, we present a thermodynamically consistent transport theory of ionic liquids (ILs) and IL-based electrolytes. Our continuum approach offers a holistic framework for the description of highly correlated electrolytes both in the bulk phase and near electrified interfaces, thus spanning a wide range of length-scales from cell-level (micrometers) to microscopic interactions (nanometers).

Our transport theory is based on the framework of rational thermodynamics, which couples non-equilibrium thermodynamics with mechanics and elements from electromagnetic theory. Material specific properties are cast into our description via modeling the Helmholtz free energy. This approach yields a consistent description for effects occurring on different length scales. In addition, we use an Onsager Ansatz to obtain the thermodynamic fluxes, and to identify the set of independent transport parameters.

Our bulk description comprises the transport mechanisms of diffusion, migration and convection, and predicts the evolution of the electrolyte species. We validated this description by applying it to a secondary zinc ion battery described in the literature, where the simulation results for charging and discharging the cell are in good agreement with the experimental results. From the numerical results we obtain a detailed understanding of the internal dynamics of each electrolyte species during discharging the cell, as well as the influence of enhanced discharge dynamics on the electrolyte performance. In addition, in a joint theoretical and experimental collaboration, we applied our framework to electrophoretic NMR experiments of pure ILs and IL-salt mixtures. Thereby, we rationalized the influence of the reference frame on the sign and magnitude of transference numbers, and clarified the role of convection in incompressible electrolytes.

In order to describe highly charged regions in confined geometries, e.g. the EDL, we supplement the bulk description by non-local ion interactions. Thereby we identify three competing energy scales, related to short-ranged ion-correlations (accounting for excluded volume of hardcore ions), to the thermal energy, and to the electrostatic energy of Coulombic interactions, which determine the equilibrium structure of the EDL. We predict the emergence of three screening-phases, consisting either of a saturation-profile ("crowding") followed by an exponentially decay towards the bulk, a profile of damped oscillations ("overscreening"), and a crystalline phase of undamped oscillations. Our description yields an analytical prediction for the key parameters of the screening, i.e. the damping ratio and the frequency of the oscillations, and for the phase boundaries between the different screening phases. In a joint experimental/theoretical publication, we validated this theoretical approach with AFM experiments. Furthermore, our multiscale methodology relates directly to the methodology used by atomistic models like molecular dynamics simulations, and comprises the seminal BSK theory as limiting case. In addition, we study the influence of a charged and uncharged solvent species on the screening profile and incorporate solvation effects into our description.