A model for Solvation in Battery Electrolytes and analysis of Electrochemical Double Layer differential capacitance

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Accurately modelling complete batteries provides a path to improved chemistries for sustainable energy development [1]. Recently, highly concentrated electrolytes promised to enable battery cells with higher energy density [2]. The complexity of these systems due to intermolecular interactions can however surpass the commonly used continuum models like Doyle-Fuller-Newman. Improved models are required to accurately predict the EDL structure due to strong forces acting on the particles.

Here, we present a continuum transport theory for highly concentrated electrolytes incorporating the solvation of ions by solvent molecules. Our model is made to conform with the second law of thermodynamics by enforcing positive entropy production, and relies on the continuum framework derived by some of the authors in the previous years [3,4]. The focal quantity in our modelling is the Helmholtz free energy of the system, which we modify by solvation effects. Our continuum model describes the electrolyte dynamics both in the bulk and in the EDL. Here, we focus on solvation effects occurring in the EDL, and consider the stationary description.

Solvation plays a fundamental role for reactions at the electrode / electrolyte interface. For example, while most analyses assume the same concentration at the electrode surface as in the bulk, we can show this depends on the electrolyte concentration, binding energies and other factors. To incorporate the interplay between the ion-solvent binding and the electrostatic forces in the EDL, a local solvation model is required.

We model solvation by adding to the free energy of the system an entropic contribution, and a contribution from the ion-solvent interaction energy. Thus, two novel parameters are used to define the interaction – the maximum number of solvent molecules binding to a single ion, and the binding energy.

We supplement our analytic discussion by numerical simulations of the EDL of an electrolyte mixture composed of an IL mixed with a solvent. Analysing the differential EDL capacitance, we can both reproduce known effects, as the shift from a “camel”-shape curve to a “bell”-shape for larger salt concentrations [5], and previously not described effects, like the effect of ion size asymmetry on the capacitance minimum.

Furthermore, we introduce an extended model, which can investigate the change in solvation when adding a cosolvent, and the competing solvation of anions and neutral solvents. We can examine the balance of energetic contributions, arising from the specific binding energy of each species to the cation, and the entropic contributions, which aim to equalise the distribution of species in the solvation shells. Using this model, we find a temperature dependence of the solvation structure, due to the entropic free energy scaling with temperature.

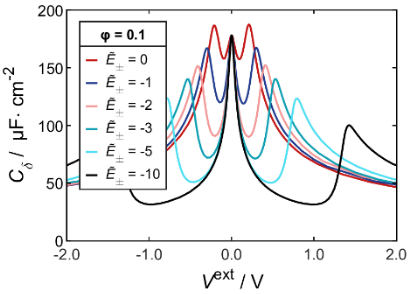

Figure 1: Differential capacitance for a diluted electrolyte as function of the ion-solvent binding energy. The off-centre peaks result from the stripping of the solvation shell. It can be seen, that a stronger binding energy increases the potential required to desolvate the ions.

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