Modelling Solvation behaviour in highly concentrated Electrolytes

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Modelling of electrochemical systems supports designing improved chemistries for battery applications [1]. Electrolytes play an important role for the performance of batteries. As such, highly concentrated electrolytes constitute promising materials. However, due to their complexity, they are difficult to model. Here, we present a continuum transport theory for these materials, which incorporates solvation effects.

Solvation can influence transport in the electrolyte and intercalation behaviour, a notable example is cointercalation of the solvent with Sodium in graphite anodes. Previous solvation models [3], however, use a static ion-solvent coordination number, therefore the stripping of the solvation shell in the double layer cannot be described.

Our focus lies on the behaviour near electrified interfaces, i.e., the electrochemical double layer (EDL). To address this goal, we modify the transport theory for highly correlated electrolytes [3,4], which was recently proposed by our group. This description is based on modelling the free energy of the system. To incorporate solvation effects, we supplement it by an additional interaction energy which accounts for the correct mixing entropy due to modified statistics.

The theory is based on two novel parameters – the maximum number of solvent molecules binding to a single ion, and the binding energy. By using a local solvation parameter, we are able to model dissolution of the solvation shell in the EDL by an applied potential.

We supplement our analytic discussion by numerical double layer simulations of a ternary electrolyte. Our results capture the relationship of ion-solvent binding energy and the desolvation potential. The model is also able to give qualitative results down to a molecular scale, allowing us to predict coarse grained behaviour of MD-simulations. This shows that solvation effects have a significant influence on the EDL-structure.

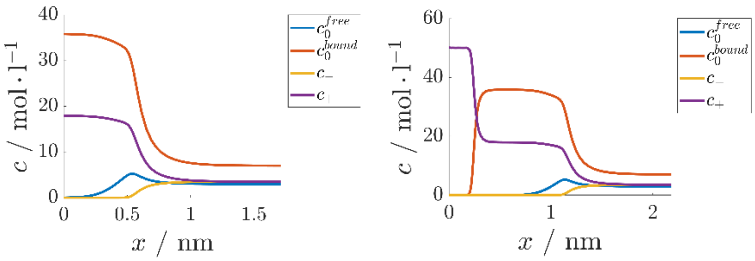

Figure: a ternary EDL at two different potentials, showing desolvation near the electrode surface at a higher potential (on the right)

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