# Ion Aggregation, Correlated Ion Transport and the Double Layer in Super-Concentrated Electrolytes

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In the dilute regime, properties of electrolytes are well known and their mathematical descriptions are well established. The physical picture of dilute electrolytes, in which ions are pristinely solvated, fully dissociated, and immersed in an excess of structureless solvent medium, lends itself naturally to elegant and tidy mathematical descriptions. Owing in large part to their simplicity and physical transparency, these descriptions have guided our intuition of electrolytes for the better part of the last century.

However, with the recent explosion of interest in super-concentrated electrolytes, particularly for electrochemical energy storage applications, theoretical descriptions of electrolytes within this regime are greatly needed. The physical description of super-concentrated electrolytes gets completely flipped from that of their dilute counterparts: ions have complex solvation structures, they are only partially dissociated, and they outweigh or even outnumber the solvent. This complex environment imparts unexpected properties to super-concentrated electrolytes, such as their observed extended electrochemical stability, asymmetric ion transport, and heterogeneous nano-structure. Understanding the origin of these unexpected properties could unlock the key design principles for the next generation of super-concentrated electrolytes.

In this thesis, we develop simple, chemical-specific, theoretical models of super-concentrated electrolytes. First, we develop a continuum model of the electrical double layer in water-in-salt electrolytes that unravels the physics behind a potential mechanism for oxidative stability in WiSEs. We find that asymmetric ion solvation leads to very asymmetric water distributions within the double-layer, depending on the charge and bias of the electrode. Next, we develop a thermodynamic model of ion aggregation and solvation in super-concentrated electrolytes. The model is deeply rooted in polymer-physics and treats the electrolyte as a poly-disperse mixture of branched ion clusters. In addition to cluster distributions and thermodynamics, our model predicts the onset of a percolating ion network, termed an ionic gel, at a critical salt concentration, which has been observed extensively in molecular simulations. We apply our model to two important classes of super-concentrated electrolytes: room temperature ionic liquids (RTILs) and water-in-salt electrolytes (WiSEs). For these classes, our model was able to be greatly simplified, permitting a plethora of analytical results, such as the critical conditions for gelation, as well as the mean cluster size. For both RTILs and WiSEs, our model was parameterized and validated by extensive molecular dynamics simulations. Furthermore, we consider the effects of extensive ion clustering and gelation on ion transport, electrochemical stability window (including the driving force to form a passivating solid-electrolyte interphase), and the emergence of nano-heterogeneity observed in super-concentrated electrolytes.

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