

The Nanoscale Structure of the Electrolyte-metal Oxide Interface

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Amongst the most important renewable energy storage technologies are lithium-ion batteries (LIBs). Whereas industrial products are widely available today, there are still open scientific questions as to the basic structural motifs of the electrolyte/electrode interface, especially the structure of the electrolyte, which is essential to the operation of LIBs. In particular, the arrangement of the electrolyte molecules directly at the electrode interface is expected to govern the ion transport during charge/discharge, as well as affect the origin and properties of the solid electrolyte interphase layer (SEI). While there have been simulation efforts to shed light on these issues, molecular resolution experimental studies of the electrolyte/electrode interface with particular focus in the ordering of the electrolyte are still missing. Such experimental evidence is extremely important to test the simulations and to gain insight into systems under realistic conditions.

In the present study, we have explored, via surface sensitive sub-Ångström resolution X-ray reflectivity (XRR), the structure of Lithium hexafluorophosphate (LiPF₆) in a non-aqueous solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a weight ratio of 1:1 at the solid-liquid sapphire (001) interface. We complemented our experimental results with molecular dynamics (MD) simulations of pure (EC:DMC) solvent mixture and 1 M LiPF₆ in EC:DMC (weight-ratio 1:1). Our results for various salt-concentrations show distinct layering of the electrolyte molecules at the surface, which decays into the bulk with a characteristic decay length of about one molecular layers after which bulk properties are reached. The XRR fit-derived surface normal electron density profile is in good agreement with the one obtained from our MD simulations. The layering periodicity increases with increasing salt-concentration, likely due to a reorientation of solvent molecules in the presence of ions. A comparison of the surface structure factor with the bulk structure factor, which remains fairly unchanged as a function of concentration, indicates that the solid interface not only induces liquid layering but also influences the ions' arrangement within the organic electrolyte.

We discuss implications of our results to Li-ion batteries, with focus on the relation between interfacial structure and ion transport in and out-of the electrode.