

Insights into the Molecular Scale Structure of Electrolyte-Metal Oxide Interface

Li-ion batteries (LIBs) are key components of portable electronic devices, as well as in electric vehicles, military and medical equipment, backup power supplies, and even grid storage. However, the energy storage capacity and rate capability of current LIBs is still too low to meet the increasing demand of key markets. For the latter, the properties of the electrolyte-electrode interface play a decisive role.

From a more general point of view, interfaces, or surfaces, are the outer boundary of any condensed matter. Due to the resulting symmetry breaking, the arrangement of atoms or molecules at the interface often varies significantly from that in the bulk. Studies of the molecular scale structural properties of liquids at interfaces are intriguing, as these give insights into the fundamental molecule–molecule and molecule–substrate interactions. Investigations have included layering of ionic liquids [1], layering of metallic [2] and non-metallic liquids [3], and the (potential-dependent) structure of water adsorbed on solid surfaces [4]. However, basic insights into how a non-aqueous electrolyte–salt solution organizes at a solid interface, in particular from experiments, is still missing [5]. In many technological applications, the atomic scale properties of interfaces govern the functionality of the system. A prominent example is the importance of the structure and molecular arrangement of the liquid at the functional solid–liquid interface in batteries. More specifically, in LIBs, the arrangement of the electrolyte molecules directly at the electrode interface, and the electric double layer (EDL) formation are expected to govern the interfacial ion transport during charge/discharge, as well as affect the origin and properties of the solid electrolyte interphase (SEI).

A major and intrinsic challenge regarding the *in situ* investigation of “buried” solid–liquid interfaces is the availability of experimental methods. Accordingly, reports on solid–liquid interfaces, in particular for non-aqueous lithium ion battery electrolytes, are sparse. In this context, x-ray surface diffraction is a good tool to provide detailed, non-element-specific structural insights into the electrolyte–electrode interface. While quite challenging, this technique allows probing non-destructively the buried interface with atomic resolution.

Researchers at SSRL have utilized high-brilliance x-ray reflectivity (XRR) at Beam Line 7-2 in combination with molecular dynamics (MD) simulations to determine the structural properties of solid–liquid interfaces relevant to LIBs, specifically an organic electrolyte of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing various concentrations

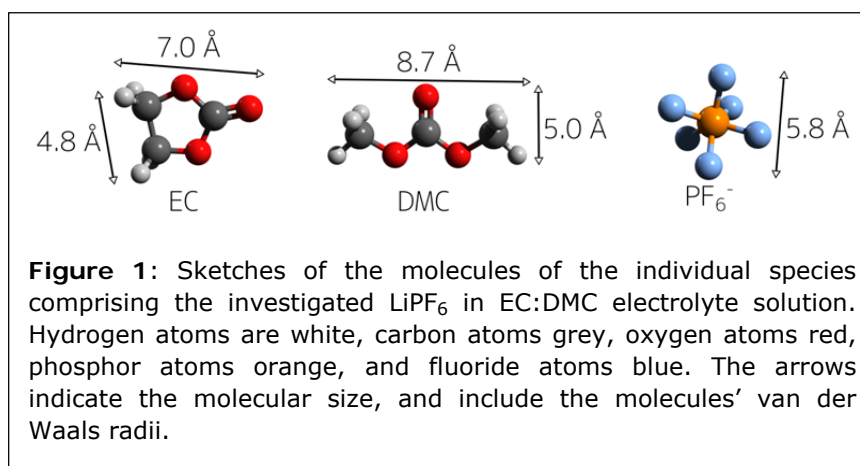
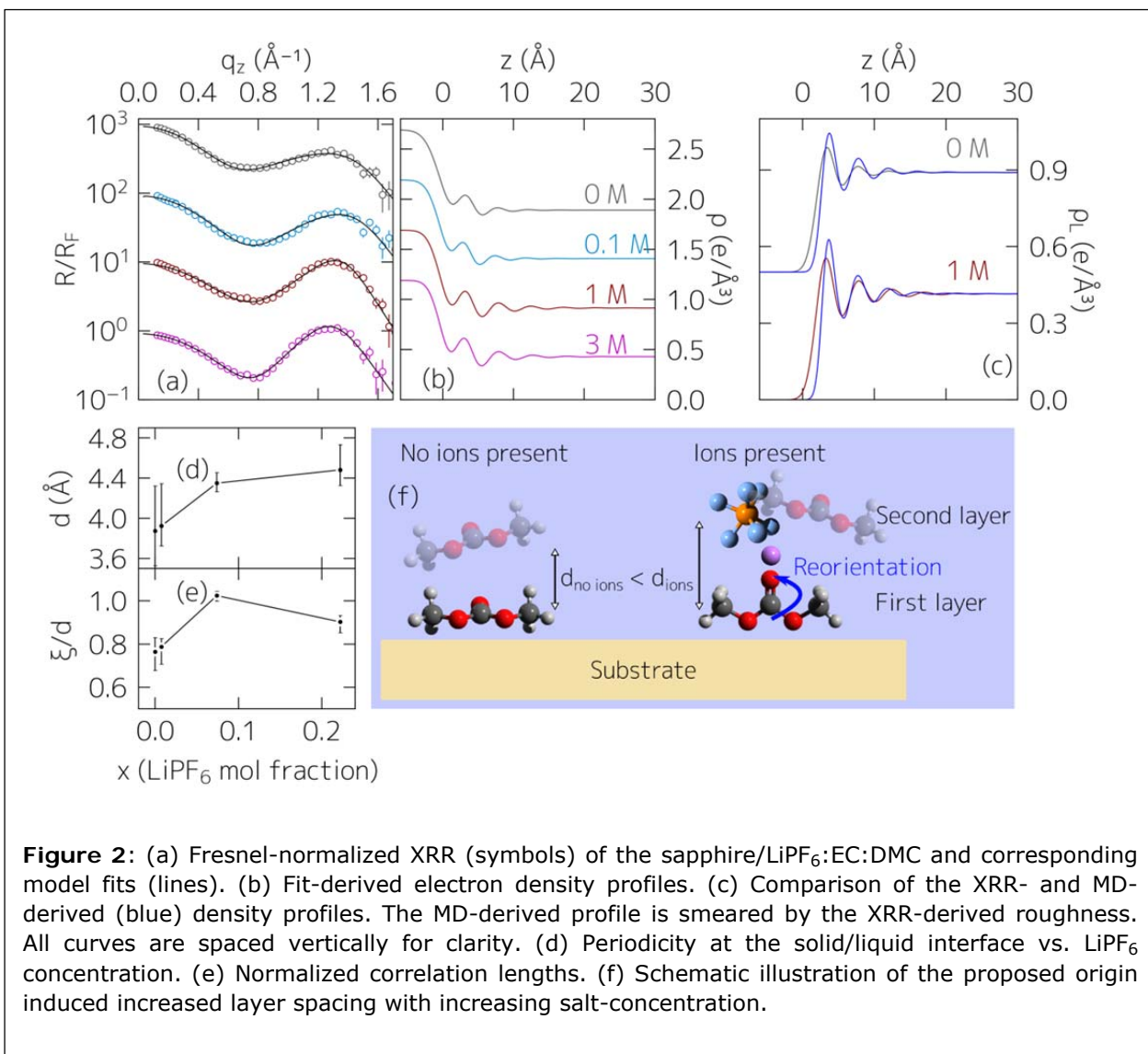


Figure 1: Sketches of the molecules of the individual species comprising the investigated LiPF₆ in EC:DMC electrolyte solution. Hydrogen atoms are white, carbon atoms grey, oxygen atoms red, phosphorus atoms orange, and fluoride atoms blue. The arrows indicate the molecular size, and include the molecules' van der Waals radii.

of lithium hexafluorophosphate (LiPF₆) salt at a metal oxide interface. Molecular sketches of the individual components of this baseline LIB electrolyte are shown in Fig. 1. The metal oxide used was sapphire, motivated by its atomic scale smoothness (roughness $\sigma < 2$ Å),

allowing for XRR measurements over a large scattering vector-range, which yields molecular resolution. While sapphire is an insulator, prohibiting potential-dependent experiments, its surface is a realistic model mimicking electrode surfaces.

By modeling the XRR data, shown in Fig. 2a, together with the model fits, the scientists obtained molecular-resolution information of the arrangement of electrolyte molecules and corresponding EDL layer within the first few nanometers of the surface. The fit-derived electron density profiles (EDPs) are shown in Fig. 2b, showing distinct molecular layering for all concentrations, which gradually decays into the bulk; the distance between layers of ≈ 4 Å indicates that surface near solvent molecules are aligned surface-parallel. A quantitative analysis (Fig. 2d/e) of the derived parameters shows that the distance between molecular layers, d , and the interfacial correlation length, ξ/d , which encodes the degree of order, increase as a function of salt concentration. The team's MD simulations, performed at the



US Army Research Laboratory, of EC:DMC mixture and 1 M LiPF₆ in EC:DMC at the graphite interface complemented the experimental results and were found to predict EDPs in good agreement with experiments on sapphire (see Fig. 2c). Furthermore, they show that EC,

DMC, and PF_6 molecules reside within the layers, whereas Li ions tend to reside between layers.

Combining the experimental and simulation observations, it was unraveled that the presence of a Li^+ ion, which is coordinated with a carbonyl group, will orient the corresponding EC or DMC molecule with its carbonyl group slightly towards the next layer, i.e. towards PF_6 , as this minimizes the distance between the two salt molecules. This is consistent with the observation of Li^+ and PF_6^- ion pair formation, and a slight preference for Li^+ ions to be found in between the layers. This in turn results in a reorientation of the corresponding EC and DMC molecules away from parallel to the surface and with their largest axes along the surface. A schematic of this phenomenon is shown in Fig. 2f, which illustrates how the discussed reorientation of DMC will yield, on average, a larger layering periodicity with the addition of salt. Increasing the molar ratio of ions will thus result in a larger spacing as a larger number of EC and DMC molecules change their orientation. These observations suggest that the presence of ions, at least in the regime of concentrations investigated, may act as a driving force for the surface-induced structuring of solvent molecules. This explains the increase of the correlations length for larger concentrations.

The researchers' new understanding of LIB relevant solid-liquid interfaces has several implications for understanding battery performance. One important finding is that the experiment- and MD-derived interfacial structures of LiPF_6 in EC:DMC are in good agreement, despite the two different types of substrates. This suggests that the non-aqueous liquid's arrangement at the electrolyte-electrode interface at open circuit potential (OCV), and the corresponding EDL, is primarily determined by the specific interactions between the solvent molecules and ions, rather than being governed by specific substrate-molecule interactions. These observations also suggest that their results may be translated to solid-electrolyte interfaces in lithium ion batteries, e.g. anodes, cathodes, and SEI layers. Furthermore, the orientation and spatial distribution of the solvent molecules at the electrode-electrolyte interface affects the interaction with the electrode surface, and therefore influences the interfacial chemistry [6]. Consequently, the electrolytes' electrochemical stability, chemical and electrochemical reaction mechanism on the electrode surface as well as the nature of the decomposition products in the SEI are expected to strongly depend on the electrolyte molecule adsorption on the surface. In particular for mixed solvent electrolytes like the one studied here, an important factor determining the SEI properties is the specific adsorption of the individual species onto the surface [7].

The study demonstrates that, near OCV, the ratio between EC and DMC at the surface is close to that in the bulk, and thus there is no preferential adsorption of EC or DMC onto the sapphire substrate. Perhaps most importantly, it has been reported that the interfacial resistance may depend on the degree of surface structuring of the electrolyte, and the ion-transfer into the electrode is mainly limited by the breakup of the Li^+ solvation sheath [8]. Accordingly, a strongly surface-structured electrolyte would increase the interfacial impedance. It can thus be assumed that a less structured solid-liquid interface eases the loss of the Li^+ sheath, which in turn eases the ion transfer into the electrode. Consequently, the team's results, showing different degrees of structuring and a change in molecular orientation as a function of ion concentration in a non-aqueous electrolyte, provide a strategy to reduce interfacial transport limitations in LIBs by reducing the salt concentration, although including a penalty for bulk ion transport. The novel understanding of interfacial properties of electrolyte-electrode structures can be transferred from LIBs to other types of ions batteries, such as Mg^{2+} or Na^+ batteries.

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