Electrolyte concentration dependence on electrode SEI formation revealed by *operando* SANS

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In recent years it has been shown that concentrated electrolytes can form a much more stable, conducting solid electrolyte interphase (SEI) as compared to traditional, more dilute electrolyte concentrations. The solid-electrolyte interface in electrochemical energy storage systems is critical for controlling both performance and safety. With this in mind, research related to the development of new electrolytes remains a key area of focus for battery researchers. It is a challenge to understand not only the differences in chemistry of the SEI with electrolyte formulation, but also the mechanism of SEI formation during cycling, and how this connects with the processes of cation intercalation and corresponding electrode microstructural changes. To address this challenge, the dynamic evolution of microstructure and surface chemistry for an ordered mesoporous carbon (OMC) electrode was probed during cycling using *operando* measurements on the NGB 30 small-angle neutron scattering (SANS) beamline [1]. Many different electrolytes have been developed, all with tradeoffs in viscosity, electrochemical stability and conductivity. The choice of salt and solvent for the electrolyte is similarly important, and the standard $LiPF_6$ salt and ethylene carbonate (EC) based solvent used in most commercial batteries is a compromise amongst other commercially available Li salts each with too many potential disadvantages, such as toxicity, an unstable or uneven passivation layer (SEI), or high corrosion of the current collector. Replacing $LiPF_6$ with $LiN(SO_2CF_3)_2$ (LiTFSI) can improve thermal and chemical stability of the electrolyte, but unfortunately result in corrosion of the cathode current collector (made of Al) at high voltages. In addition, replacing the standard EC-based solvent with propylene carbonate (PC) results in an electrolyte with better ionic conduction at room temperature, but the PC suffers from an inability to form a stable SEI and thus produces exfoliation of graphite in battery anodes. However, it has been shown that by increasing the salt concentration in electrolytes, Al corrosion and exfoliation of graphite is suppressed. It is reported that the salt in concentrated electrolytes are sacrificially reduced to form more stable passivation layers high in LiF content. These LiF based SEIs are superior in adhesion to the electrode surface, and thinner and denser with superior mechanical properties. Given the importance of the inorganic salt layer, a key question is therefore to understand how the concentration of LiTFSI, along with the increase in electrolyte viscosity, influences the formation of inorganic salt products (i.e., LiF, LiOH) versus carbonaceous products in the SEI during the critical initial discharge cycle.

Given the sensitivity of neutron scattering to light elements (e.g., H, Li, C, F), SANS is a powerful technique to probe the formation of the SEI layer during battery discharging. In order to study the SEI evolution *operando*, a suitable neutron scattering battery cell has been designed, as shown in Figure 1, that provides minimal contribution to the scattering data, along with minimal absorption. Separate cells for dilute and concentrated LiTFSI/PC electrolytes on mesoporous hard carbon were simultaneously cycled on the beamline. The resulting data (Figure 2), demonstrate that *operando* SANS, in combination with ex-situ X-ray photoelectron spectroscopy (XPS), provides unprecedented detail on the concentration dependent filling of mesopores and micropores with Li-rich and carbonaceous products, co-intercalation of solvated Li^+, and corresponding electrode microstructure expansion.

There are several key findings from this work derived from the SANS and supporting XPS data. SANS intensity changes indicate a displacement in the pore surface electrochemical processes to lower voltages, which is a physical effect related to pore filling – the filling of pores is shifted to lower voltages with the higher viscosity concentrated electrolyte, which can be influenced by the viscosity of the electrolyte and wetting of the surface. Moreover, the pore filling influences the expansion of the carbon framework,

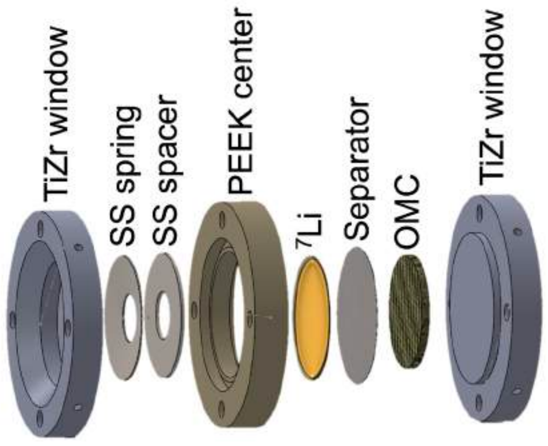

FIGURE 1: Schematic view of the *operando* SANS cell.

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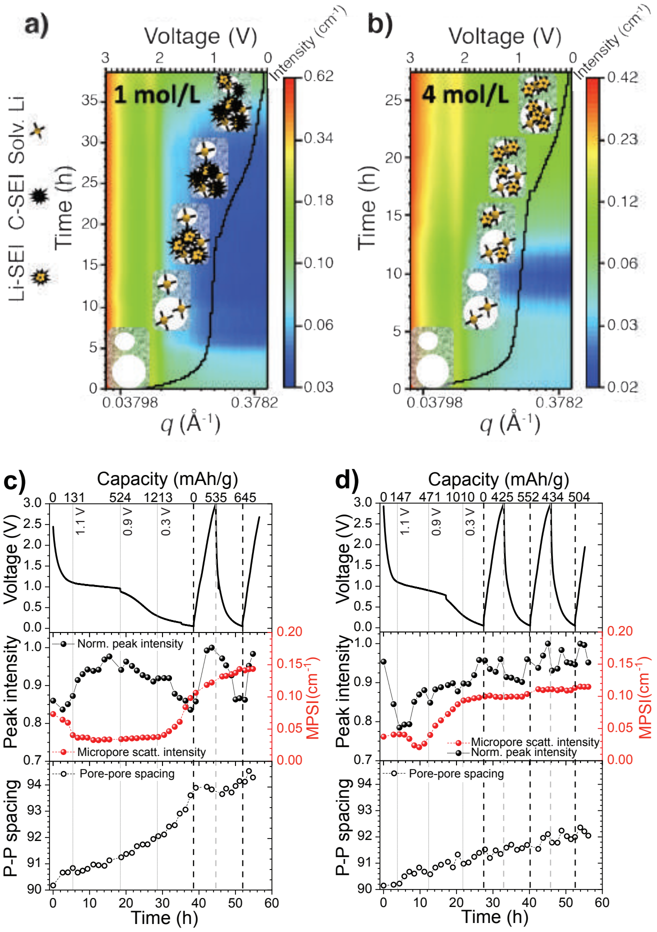

FIGURE 2: Scattering intensity is shown as a function of the scattering vector *q*, first discharge time and voltage for (a) the 1 mol/L and (b) 4 mol/L LiTFSI/PC (propylene carbonate) electrolyte systems. The development of carbonaceous and fluoride-rich reduction products in the SEI differs based on concentration as can be clearly seen from the extracted data for (c) the 1 mol/L and (d) 4 mol/L electrolyte systems.

with electrolyte concentration dependent results. The expansion occurs just below the open circuit voltage in the 1 mol/L cell and below 1.1 V in the 4 mol/L cell. The size of the solvation shell around Li^+ is found to influence the framework expansion during the first discharge, with the larger PC coordinated Li^+ in 1 mol/L electrolyte producing an overall 3.5 Å (≈ 4 %) increase in the pore–pore separation as compared to the 1.4 Å (≈ 1.5 %) increase for the Li(PC)-TFSI aggregates. The overall change in framework volume during the discharge can be explained by the combination of pore filling and co-intercalation into graphitic layers, which are reflected in SANS intensity changes during *operando* cycling. Furthermore, the intensity changes can be correlated with the electrochemical discharge profile to provide more information on the mechanism of SEI formation (Figure 2(c, d)). Both the low and high concentration electrolytes show electrochemical double layer (EDL) formation by adsorption of solvated PC to the electrode surface. In the 1 mol/L electrolyte system it is known that the inner Helmholtz layer is dominated by free PC molecules and that of the 4 mol/L by salt anions. Despite the prevalence of PC in the inner Helmholtz layer of the 1 mol/L electrolyte system, the $TFSI^-$ anions present at the anode surface begin to reduce at a higher potential and at a faster rate as compared to the PC, due to the higher reduction potential of the $TFSI^-$ anions. We find that Li-rich salts (e.g., LiF, LiOH) form at higher voltages for the 1 mol/L electrolyte, but that in the sloping discharge region of 1.1 V to 0.9 V the salts begin to dominate the mesopore scattering for the 4 mol/L electrolyte, while carbonaceous products such as C–O and C–F containing compounds begin to dominate for the 1 mol/L electrolyte.
By the end of the first discharge the 4 mol/L electrolyte has a passivation layer richer in low SLD Li-rich reduction products than the 1 mol/L electrolyte. Finally, with the subsequent charges and discharges PC or solvated PC is desorbed (charge) and adsorbed (discharge), which is shown to have significant reversibility in the mesopores but not in the micropores. As we have shown, *operando* SANS studies can provide knowledge about the dynamic cell chemistry that is microstructure specific in new candidate electrolyte systems for high-energy density batteries, which cannot be seen from other probes such as electrochemical cycling or XPS studies. This approach has the capability to impact a wide range of electrochemical systems, taking advantage of the unique contrast provided by neutron scattering.

References

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