

Characterization of Li⁺ solvation and SEI formation on graphite for LiPF₆/PC electrolytes

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Lithium ion batteries have been successfully used in portable electronic devices and electric vehicles (EV). However, among the most important aspects of lithium ion batteries are the interfacial reactions of the electrodes with the non-aqueous electrolytes.¹⁻² In our present work, novel binder free graphite electrodes with integrated TEM grids have been investigated with various concentrations of LiPF₆/PC electrolytes in order to understand the role of solvation in solid electrolyte interface (SEI) formation and cycling performance.

The solvation properties of the electrolyte have been investigated with NMR and IR spectroscopy. In addition, the diffusion rates of the Li⁺ and PF₆⁻ have been investigated with NMR spectroscopy. After cycling binder free (BF) graphite/Li cells, ex-situ analysis of the BF-electrodes were conducted via a TEM, XPS and solution NMR spectroscopy.

The BF-graphite electrode/Li coin cells revealed different cycling performance with different LiPF₆ concentrations in LiPF₆/PC electrolytes. Once the LiPF₆ concentration is increased to 2.8M, the cells cycle reversibly and have good capacities. (Figure 1)

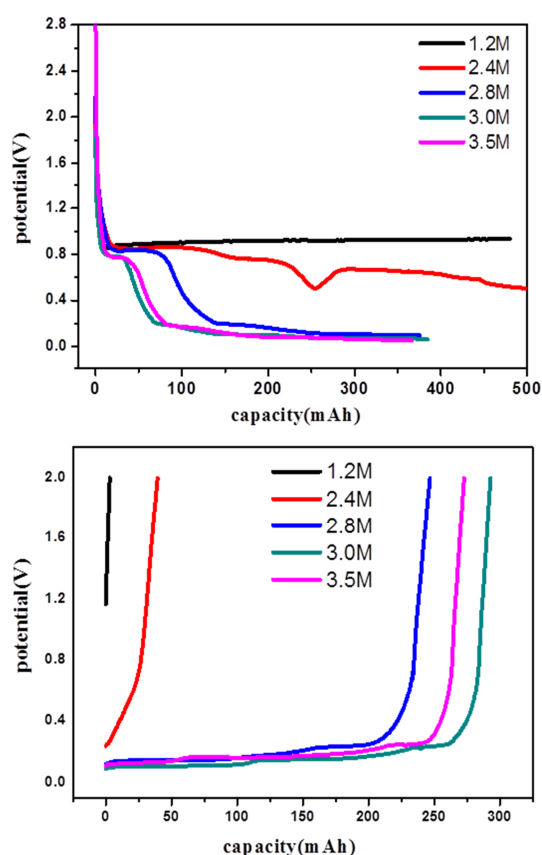


Figure 1. Lithiation and delithiation plots for BF Li/BF graphite cells cycled with various concentrations of LiPF₆/PC.

FTIR and DOSY NMR were carried out with various concentrations of LiPF₆/PC electrolytes in order to understand how Li⁺ solvation and diffusion change with LiPF₆ concentration. In FTIR, the characteristic $\nu(\text{C}=\text{O})$ band of pure (non-solvated) PC (1779 cm⁻¹) decreases in intensity with increasing LiPF₆ content and is barely visible for concentrations >2.4M. In addition, the diffusion coefficients of Li⁺ and PF₆⁻ from DOSY NMR support a change in solvation structure 1.2 M to 3.5 M LiPF₆/PC.

To investigate composition of the SEI formed on BF-graphite electrodes. NMR analyses of electrode extracts after one cycle were conducted. The LiPF₆/PC electrolyte generates peaks consistent with the formation of lithium propylene dicarbonate (LPDC) and LiF. However, the content of LPDC on electrodes cycled with different concentrations of LiPF₆ in PC are quite different. Comparing the ¹H spectrum of 1.2M LiPF₆/PC and 3.5 M LiPF₆/PC, a significantly lower concentration of LPDC is present with the high concentration electrolyte. The opposite trend is observed in the ¹⁹F spectra. The concentration of LiF is very high with high concentrations of salt (3.5 M LiPF₆/PC) and low with low concentrations of salt. The changes to the BF graphite anode surface are further supported via ex-situ analysis of the electrode surface by TEM and XPS.

Changes to the solution structure of LiPF₆/PC electrolytes as a function of the concentration of LiPF₆ correlate with changes in cycling performance and composition of the anode SEI. The results support a change in the mechanism of SEI formation as a function of LiPF₆ concentration. The results provide new insight in SEI formation reactions and the role of salt and solvent.

Acknowledgement

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References

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