

## Transport Properties of LiPF<sub>6</sub> based Li-ion Battery Electrolytes

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### Introduction

In recent years there has been increasing interest in utilizing Li-ion technology for high power/current applications. One key bottleneck for running high currents through Li-ion cells is ion transport in the liquid electrolyte. This has stimulated interest in characterizing the conductivity of various Li-ion electrolytes. However it is impossible to predict performance at high currents, from the conductivity alone, one must also know the cation (or anion) transference number, salt diffusivity and salt activity. This is further complicated by the fact that high currents will change the cell temperature and create strong concentration gradients in the electrolyte. In order to understand and predict cell performance, knowledge of all four properties, over a wide range of temperatures and concentrations is required. With this in mind we have undertaken the complete characterization of a common Li-ion electrolyte recipe that employs LiPF<sub>6</sub> as the salt.

### Experimental

The LiPF<sub>6</sub> concentrations in the PC/EC/DMC mixture used ranged from  $7.7 \cdot 10^{-6}$  to 3.9M. Concentration potentials were measured in a Li-Li cell with two chambers separated by a Teflon tube filled with inert Polyethylene beads. The entire cell was submerged in a controlled temperature bath and the cell potential was measured using an E-One Moli Energy charger system. The transport number was obtained from a similar two-chamber Li-Li cell, with a stir-bar in each chamber to ensure homogeneous concentration. A small current was applied for a given time, and the cell was then allowed to rest. The rest potential was used to calculate the concentration difference created by the applied current. Diffusion coefficients were extracted using the galvanostatic polarization method [1]. Li metal electrodes were put on each end of the cell, and the cell ends were sealed off. The cells were placed vertically inside a controlled temperature chamber, and the semi-infinite diffusion regime was applied for a given time. Typically these measurements will only determine an algebraic combination of 2 or more transport properties. These combinations must then be disentangled in order to isolate the individual transport properties.

### Results and Discussion

The transference number, in combination with the diffusion coefficient, determines how fast concentration gradients will form under load. The activity coefficient determines the voltage drop associated with a given concentration gradient. The Li<sup>+</sup> transference number at room temperature was measured to be  $0.38 \pm 0.04$ , with no significant variation with concentration. This transference number was then used for determining diffusion and activity coefficients. Figure 1 shows the LiPF<sub>6</sub> diffusion coefficient in PC/EC/DMC as a function of temperature for different concentrations. It shows, as expected, very strong temperature dependence and it decreases with increasing concentration. The difference in the absolute value of the diffusion coefficient between the different concentrations tested was found to increase with increasing temperature whereas the relative difference stayed roughly the same.

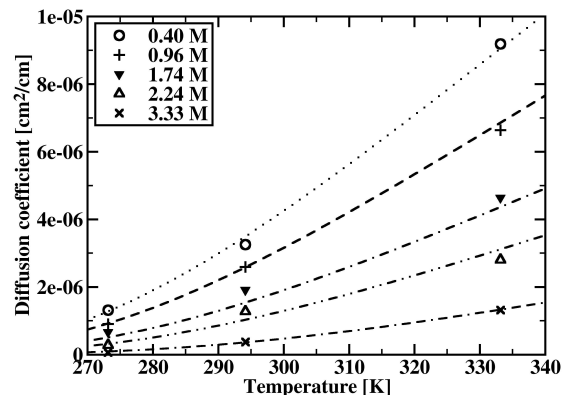


Figure 1: Diffusion coefficient as a function of temperature for different concentrations.

Figure 2 shows the activity coefficient as a function of the ion/solvent ratio for LiPF<sub>6</sub> in PC/EC/DMC.

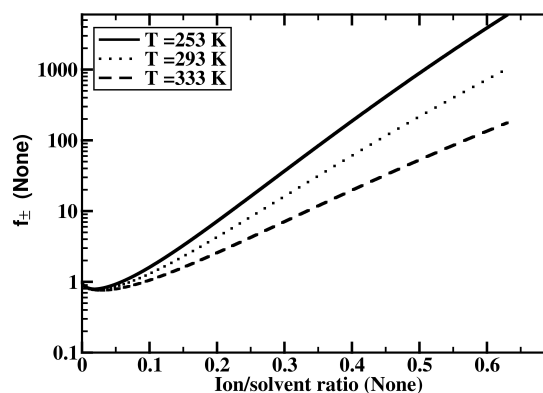


Figure 2: Activity coefficient as a function of LiPF<sub>6</sub> ion/solvent ratio for different temperatures.

From figure 2, one can observe that the activity falls slightly with increasing ion/solvent ratio as predicted by Debye theory [2] before it rises in a linear fashion. From the figure, one can also observe that the activity decreased with increasing temperature.

### Conclusion

The transport properties of LiPF<sub>6</sub> in PC/EC/DMC were measured as a function of concentration and temperature. The Li<sup>+</sup> transference number at room temperature was measured to be  $0.38 \pm 0.04$ , with no significant variation with concentration. The LiPF<sub>6</sub> diffusion coefficient showed a strong temperature and concentration dependence and increased with decreasing concentration and increasing temperature. The activity of LiPF<sub>6</sub> in PC/EC/DMC was found to decrease slightly with ion/solvent ratio for low concentrations and then increase close to linearly with the ion/solvent ratio as the concentration increased.

### References

- [1] H. Hafezi, and J. Newman. *J. Electrochem. Soc.*, 147, 8, 3036-3042, 2000
- [2] J. O'M. Bockris and A.K.N Reddy. *Modern Electrochemistry*, volume 1. Plenum Press, New York, 2<sup>nd</sup> edition, 1998