

Transport Property measurements for LiPF₆ in EC:DEC (1:1)

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To better understand and model limitations in the electrolyte phase of Li ion batteries, reasonable estimates of the concentration dependent transport properties of the electrolyte becomes imperative. One commonly used electrolyte is LiPF₆ in EC:DEC (1:1 by weight). Unfortunately, the complete set of concentration dependent transport properties for this electrolyte isn't available in literature. Stewart and Newman¹ measured the salt diffusion coefficient (using UV Vis absorption) and the conductivity as a function of concentration for this particular electrolyte. However, the diffusion coefficient was measured between 0.2 M and 1 M and one has to extrapolate the values beyond this range. Also in their study the experimental error bar for the diffusion coefficient for 1 M is approximately an order of magnitude. To establish a consistent and comprehensive set of transport properties, in this study, a custom Li-Li symmetric diffusion cell was designed to measure the transport properties using restricted diffusion and galvanostatic polarization.

According to Onsager reciprocal relations, there are $n(n-1)/2$ independent transport properties, where n is the number of species in the electrolyte. If the solvent mixture (EC and DEC) is treated as a single species, the number of transport properties become three: (a) conductivity; (b) salt diffusion coefficient; (c) transference number. In addition to these three properties, the salt activity coefficient (which is a thermodynamic property) also needs to be measured. The salt diffusion coefficient and the transference number determine the concentration gradients that forms under polarization whereas the salt activity coefficient determines the concentration overpotential resulting from the gradient.

To measure the Diffusion coefficient using restricted diffusion, constant current was passed for certain time, which resulted in a build up of a concentration gradient. Current was then stopped and cell potential measured during this open-circuit relaxation period. Chapman and Newman² have shown that at long relaxation times the slope of $\ln V$ vs. time curve is a straight line, which is proportional to the salt diffusion coefficient at that particular electrolyte concentration. The procedure was repeated for different electrolyte concentrations and at different polarization times to check for reproducibility. The experimental results of diffusion coefficient (D) values obtained using restricted diffusion are shown in Figure 1. These values are higher by one to two orders of magnitude when compared to data available in literature.

To crosscheck the D values obtained, reference electrode experiments were performed. Progression of concentration wave and time it takes for it to reach the reference electrodes depends on D values. Modeling the concentration profiles confirmed that results obtained by the reference electrode experiments were consistent with restricted diffusion experiments. Limiting current experiments were also performed to validate the numbers obtained by restricted diffusion. In a limiting current experiment, cell was run at constant current and in the process, Li⁺ concentration rises at one electrode and

drops at the other. If current density is high and there is mass transfer limitation (low D values), concentration of Li⁺ on one electrode drops to zero and overall cell potential rises to infinity. These experiments further validated the D values measured by restricted diffusion were consistent.

The transference number was measured using galvanostatic polarization where the cell was polarized for a short period of time so that a semi-infinite boundary condition was maintained. Open circuit voltage was measured with time and transference number was calculated using the methodology outlined by Hafezi and Newman³. The functionality of the salt activity coefficient as a function of concentration was obtained using a concentration cell. The cell consisted of two separate chambers that were separated by a glass frit to prevent rapid mixing of the electrolyte. The concentration in one of the chambers was kept constant at 2M whereas in the other chamber it was varied in between 0.2M to 2M. The open circuit voltage was measured for each concentration and lithium metal was used as the electrode in the experiments. Debye-Huckel theory for concentrated solutions was then used to get the concentration dependence of the salt activity coefficient.

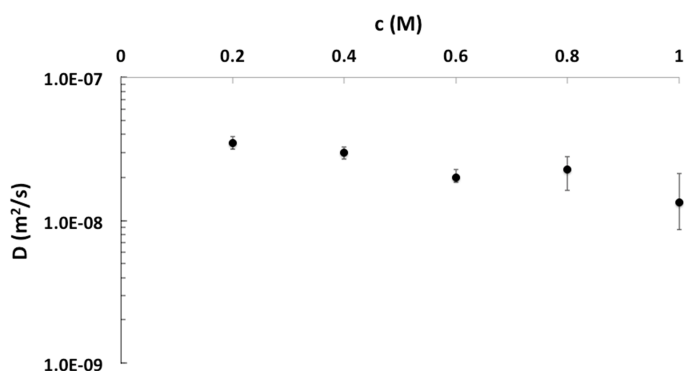


Figure 1 : Diffusion coefficient measurements using restricted diffusion for LiPF₆ in EC:DEC (1:1)

References

1. S. Stewart and J. Newman, J. Electrochem. Soc., 155, F13 (2008)
2. J. Newman and T. W. Chapman, AIChE J., 19, 343 (1973)
3. H. Hafezi and J. Newman, J. Electrochem. Soc., 147, 3036 (2000)