The Liquid to Polymer Electrolyte Continuum in Lithium Ion (Li-Ion) Battery Electrolytes

The electrolytes influence the rates of discharge, low temperature performance, high temperature stability, and cycle and calendar life of lithium and lithium ion batteries. Consequently, knowledge of the ion transport mechanisms in electrolytes is important in designing new and improved electrolytes. Our recent results show that there are strong similarities between the ion transport processes in Li ion conducting liquid and polymer electrolytes so that there is a limit to the conductivity that can be achieved for conventional solid polymer electrolytes. Our data also have provided insights into the design of improved polymer electrolytes (1,2).

We measured the conductivities (K) of solutions of $LiPF_6$, $LiN(SO_2C_2F_5)_2$, $LiBF_4$ and $LiC(SO_2CF_3)_3$ in a variety of carbonate solvents as a function of temperature (T). The conductivity data from – 40 to +85 ^oC provided insights into the ion conduction mechanism in Li-ion conducting electrolytes. The K versus 1/T plots fit well to the Vogel-Tamman-Fulcher (VTF) relationship shown in equation 1 describing the dependence of ion conductivity to free volume in solution. In this equation, A and B are constants; A is a pre-exponential function, B is the energy needed to create free volume for ion movement in solution, and T_o is the temperature at which solvent structural relaxation becomes nonexistent.

$$K = AT^{-1/2} \exp\{-B/T-T_o\} \quad (1)$$

The closeness between the measured glass transition temperature Tg of the solutions and their T_o values calculated from conductivity data provides strong support for solvent coupled motion of ions in Li-ion conducting electrolytes. The solvent-assisted transport of ions in Li battery electrolytes is further supported by ^{13}C NMR data that show that the Li-ion are solvated by the solvent molecules and their mobility is coupled to the mobility of the solvent molecules.

The conductivity-temperature behavior of the liquid electrolytes we have observed is similar to the well-established behavior of Li-ion conducting solid polymer electrolytes. The polymer segmental mobility assisted mechanism of ion transport in polymer electrolytes is well recognized. This suggests that ions conduct via similar solvent–assisted mechanisms in both liquid and solid polymer electrolytes.

A good understanding of the ion transport mechanism in liquid and polymer electrolytes has allowed us to design improved electrolytes with superior low temperature performance, high temperature stability, and long life in Li-ion and Li-ion polymer batteries

References:

1. G.Y. Gu, R. Laura and **K. M. Abraham**, Electrochem. and Solid-State Lett., 2, 486 (1999).
2. B. Ravdel, K.M. Abraham, R.L. Gitzendanner and C. Marsh, in Batteries and Supercapacitors, The Electrochemical Society Proceeding Volume, PV2001-21 (2003)