Temperature Dependence of the Conductivity of Lithium-Ion Battery Electrolytes

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The limited operational and storage temperature window of lithium-ion batteries is partly attributed to the limitations of the electrolyte. In order to understand this behavior we have carried out conductivity measurements of organic carbonate solvent-based electrolytes within temperature range of –40 to 80°C. For this investigation, the binary EC/EMC (mass ratio 1:3) and the ternary EC/DMC/DEC (mass ratio 1:1:1) solvent mixtures were chosen. The salts $LiPF_6$, $LiBF_4$, and $LiN(SO_2C_2F_5)_2$ (LiBETI) were used. We studied the conductivity of the solutions of individual salts and of their binary mixtures.

The dependence of specific conductivity (k) on temperature (T) of 1 M solutions of LiBETI, $LiPF_6$ and $LiBF_4$, is shown in Fig. 1. Conductivities of these salts follow the order $LiPF_6$>LiBETI>$LiBF_4$ within the temperature range of –40 to +80°C in both mixed solvent systems. It should be noted that the $LiPF_6$-containing solutions are not stable at 60°C and above; at 80°C, a significant decrease in conductivity is observed in two to three hours.

The effect of temperature (T) on conductivity is not governed by the classical theory, that is the dependence of conductivity on temperature does not follow the Arrhenius law [1]

$$k = k_o \exp(-E_a/RT),$$

where k_o is a constant, and E_a is the activation energy for the ion's motion in solution. None of the solvents we have studied has shown a linear behavior for the *log k – 1/T* plot within the temperature range of –40 to +80°C.

When ion transport is facilitated by the mobility of the solvent molecule, the conductivity may obey the Vogel-Tammann-Fulcher (VTF) relation [2,3]

$$k = AT^{-1/2}\exp[-B/(T-T_0)],$$

where A, B, and T_0 are constants; B is related to the critical free volume for ion transport, and T_0 is the temperature at which the transport function ceases to exist or the solvent structural relaxation becomes zero. T_0 may be considered as the glass transition temperature or a temperature near it.

Using the least squares method, we have determined the VTF-parameters for all the k - T curves. As it can be seen from Fig. 1, the agreement between experimental data (points) and the VTF approximation (lines) is very good (the relative residual standard deviation was typically less then 1.5%). The B parameter does not appear to depend on the nature either the salt or solvent, while T_0 in some cases does, and in the others does not depend on the concentration of the salt or the composition of the electrolyte (Fig. 2). The dependence of these parameters on salt concentration and electrolyte composition will be discussed.

The conductivity of electrolytes with $LiPF_6$ + LiBETI, $LiBF_4$ + LiBETI, and $LiPF_6$ + $LiBF_4$ mixtures were also measured at various temperatures. In these studies, the total salt concentration was kept at 1 mol/l while the mole ratios of these salts were varied. As an example, the conductivity vs. composition data for $LiBF_4$ + LiBETI mixture in binary and ternary solvent systems is shown in Fig. 3.

In general, the conductivity of the solutions in the ternary solvent mixture is higher than that in the binary solvent mixture.

We also studied the effect of lithium salt concentration on molar conductivity (λ). The observed non-linear behaviour of λ vs. $\sqrt{C}$ is consistent with the strong ion association usually observed in organic solvents for lithium salts with complex anions such as the ones used here.

1. J. O'M. Bockris and A. K. N. Reddy. Modern Electrochemistry, Vol. 1. McDonald, London, 1970.
2. G. Y. Gu, R. Laura, and K. M. Abraham. *Electrochem. and Solid-State Letters*, **2**, 486 (1999).
3. G.Y.Gu, S.Bouvier,C.Wu, R.Laura, M. Rzeznik and K.M.Abraham, *Electrochim.Acta.*, **45**, 3127 (2000).

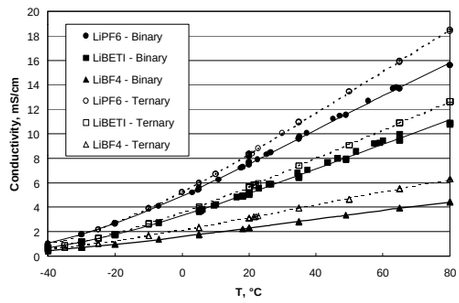

Figure 1. Conductivity of 1 M salt solutions in binary (EC/EMC) and ternary (EC/DMC/DEC) solvent systems.

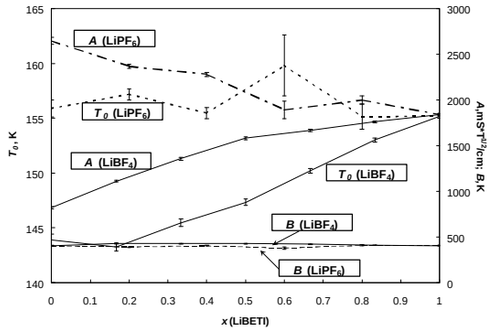

Figure 2. The VTF parameters for the mixtures of $LiBF_4$ or $LiPF_6$ with LiBETI in ternary (EC/DMC/DEC) solvent system.

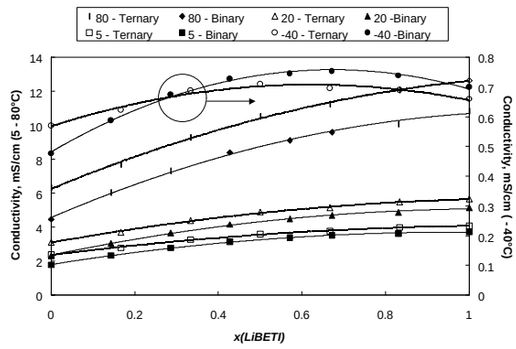

Figure 3. Conductivity of mixed LiBETI + $LiBF_4$ electrolyte in binary (EC/EMC) and ternary (EC/DMC/DEC) solvent systems at various temperatures (°C).