**No Flash Point Organic Electrolyte Containing Fluorinated Solvent and Lithium Tetrakis(trifluoroacyloxy) borate for Lithium Secondary Batteries.**

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**Introduction:** Flammability of organic electrolyte is a critical issue in lithium secondary batteries. We developed a no flash point organic electrolytes (NFE) by using non-flammable fluorinated solvents and lithium sulfonylimides as supporting electrolytes.[1,2] The challenge in the NFE is to improve their conductivities. Lithium tetrakis[haloacyloxy] borates were prepared by Kanto Chemical. These lithium borates showed better solubility and conductivity than lithium sulfonylimides in carbonate based solution. [3]

This work aims to improve the conductivity of NFE by using lithium tetrakis[trifluoroacyloxy] borate (LiTAB). The diffusion coefficients of $Li^+$, anion, solvents were also investigated by a pulse field gradient (PFG) nuclear magnetic resonance (NMR) technique.[4]

**Experimental:** Electrolytes were prepared by dissolving a lithium salt in mixed solution composed of methyl nonafluorobutyl ether (MFE, 3M Company) and ethyl methyl carbonate (EMC, Mitsubishi Chemical). Conductivity was measured with Toa CM-30V conductivity meter at 3 kHz and 25 ºC. Diffusion coefficients of $^{1}H$ (for solvents), $^{7}Li$ and $^{19}F$ (for anions) were estimated by a PFG-NMR technique with Varian Unity Plus 500 NMR spectrometer at 25 ºC.[1,4]

**Results and Discussion:** Figure 1 shows the conductivity of 1M (mol $dm^{-3}$) LiTAB and LiBETI-MFE/EMC as a function of MFE volume. The conductivity decreased with MFE mixing volume both in LiTAB and LiBETI. LiTAB showed considerably higher conductivities than LiBETI in all MFE mixing ratios. The conductivity of LiTAB had two times higher than LiBETI even at 80 vol% of MFE mixing solution that has no flash point.

The diffusion coefficients estimated from PFG-NMR for $Li^+$ ($^{7}Li$ data) and anions ($TAB^-$ and $BETI^-$, $^{19}F$ data) are plotted against MFE volume fraction in Fig.2.[1,4] The diffusion coefficients both for Li+ and anion in LiBETI were higher than those in LiTAB. The conductivity $\sigma$ is given by equation 1.[5]

$$\sigma = (1-\alpha)\left(\frac{Ne^{+}e^{-}}{K_b T}\right)\left(D_{Li} + D_{anion}\right) \qquad [1]$$

(α represents degree of association, N is total number of negative

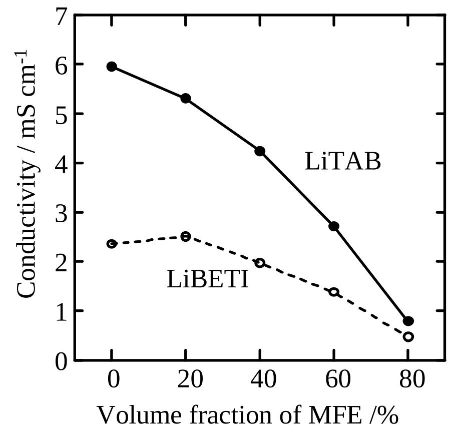


Fig.1 Conductivity of 1M LiTAB and LiBETI MFE/EMC electrolytes as a function of MFE volume.

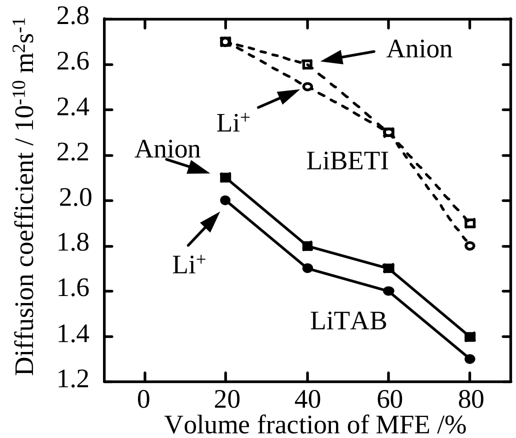


Fig.2 Diffusion coefficients of ions in 1M-LiTAB and LiBETI MFE/EMC as a function of MFE volume.

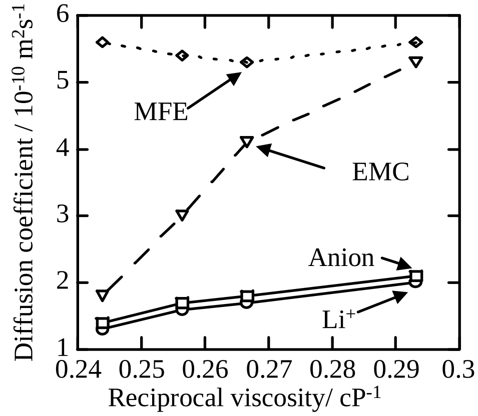


Fig.3 Diffusion coefficients in 1M-LiTAB and LiBETI MFE/EMC as a function of reciprocal viscosity