Fast Li-ion Transport by Using Binary Solvent Systems for Glyme-based Electrolyte of Li-air Batteries

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In recent years, non-aqueous type Li-air batteries (LABs) have attracted much attention as large-scale energy storage devices for electric vehicles because of the high energy density over 5 times larger than that of the conventional Li-ion batteries (LIBs) [1]. However, there are some problems to be solved for the practical use such as smooth deposition/decomposition reaction of Li$_2$O$_2$ at air electrode and suppression of Li dendrite growth at Li metal negative electrode. Especially, for the electrolyte, high Li-ion conductivity and durability against O$_2$- radical generated at air electrode are quite important. To address the later issue, glyme solvent-based electrolytes are usually used for LABs because of the low electric constants $\varepsilon$ of glymes. However, the solvent property essentially lowers the dissociation degree of Li salt and increases the viscosity of electrolytes. In this study, for the purpose of improving the Li-ion conductivity, we prepared some binary solvent systems for glyme-based electrolytes, i.e. 1.0 M of LiTfO/tetraglyme (G4), LiNi(SO$_2$F)$_2$(LiFSI)/G4, etc., and investigated the viscosity $\eta$ of electrolyte, self-diffusion coefficients $D$ of ions and solvents by a PGSE-NMR [2] together with the apparent dissociation degree $\alpha_{app}$ of Li salts. To enhance both mobility $\mu$ and number $n$ of Li$^+$ carrier ion, DMSO and acetonitrile (AN) were used as the mixing solvents with lower $\eta$ and higher $\varepsilon$ (DMSO: 47, AN: 36) than G4 (7.9).

Figure 1 shows the $\eta$ and $\sigma$ for 1.0 M LiTfO/G4+X (X= DMSO, AN). The $\eta$ decreased with an increase in DMSO and AN contents, and as a result the $\sigma$ effectively improved. From the viewpoint of $\mu$ of Li$^+$ carrier ion, the $D_{Li^+}$ also increased by mixing the solvents (Fig. 2) especially for AN. On the other hand, the $\alpha_{app}$ estimated from the $D$ and $\sigma$ by using Nernst-Einstein equation [2] was also enhanced by increasing the solvents especially for DMSO (Fig. 3). Namely, the solvents with low viscosities and high electric constants effectively improved not only $\mu$ but also $n$ of Li$^+$ carrier ion in the electrolyte. The effect for the $n$ was more clearly confirmed for the electrolytes containing Li salts with low $\alpha$. The electrochemical stabilities and LAB cell performances will be reported in the meeting.

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