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_2O_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 ε 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), $LiN(SO_2F)_2$(LiFSI)/G4, etc., and investigated the viscosity η of electrolyte, self-diffusion coefficients D of ions and solvents by a PGSE-NMR [2] together with the apparent dissociation degree α_{app} of Li salts. To enhance both mobility μ and number n of Li^+ carrier ion, DMSO and acetonitrile (AN) were used as the mixing solvents with lower η and higher ε (DMSO: 47, AN: 36) than G4 (7.9).

Figure 1 shows the η and σ for 1.0 M LiTfO/G4+X (X= DMSO, AN). The η decreased with an increase in DMSO and AN contents, and as a result the σ effectively improved. From the viewpoint of μ of Li^+ carrier ion, the D_{Li+} also increased by mixing the solvents (Fig. 2) especially for AN. On the other hand, the α_{app} estimated from the D and σ 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 μ 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 α. The electrochemical stabilities and LAB cell performances will be reported in the meeting.

[1] P. G. Bruce et al., Nature materials, 11 (2012) 19-29.
[2] M. Saito et al., RSC Adv., 7 (2017) 49031-49040.

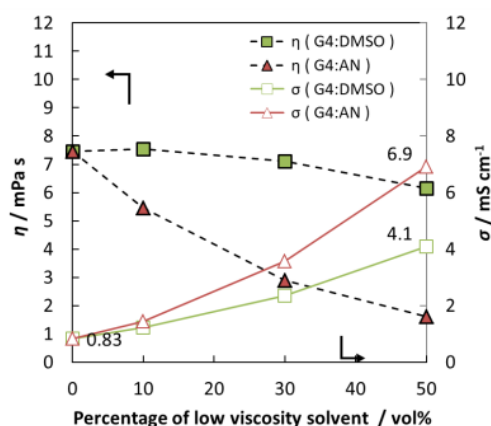**Fig. 1.** η and σ values of 1.0 M LiTfO/G4+X (X = DMSO, AN) at 30ºC.

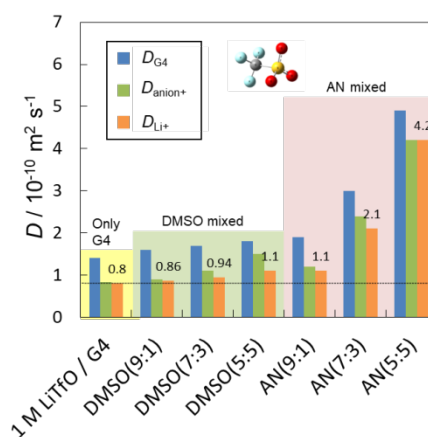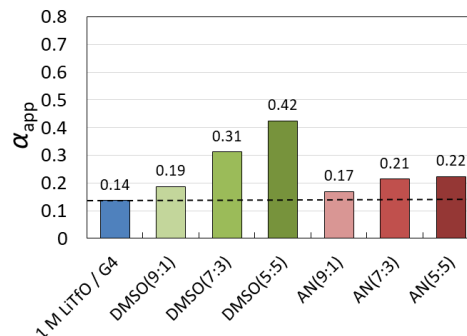**Fig. 2.** D values of 1.0 M LiTfO/G4+X (X = DMSO, AN) at 30ºC.

Fig. 3. α_{app} values of 1.0 M LiTfO/G4+X (X = DMSO, AN) at 30ºC.