

Compatibility of high-concentrated solvate ionic liquids and low-viscosity dilute solvent

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Significant improvement for stability of electrolyte solution has been reported by high-salt concentration (ether series^[1]/acetonitrile^[2]) owing to strong interaction between Li salt and solvent molecule. However, high-concentration electrolyte exhibits large viscosity. And the electrolyte systems has risks of rate performance for high rate charge/discharge operations. Therefore, in order to obtain low viscosity electrolyte, we proposed to add low viscosity dilute solvent into electrolyte^[3]. Most important demands for dilute solvent are,

1. Improvement of rate performances for batteries by low viscosity of electrolyte solution
2. Stabilization of solvated structure between Li salt and solvent molecule with/without dilute solvent. In this study, we investigated physicochemical effects for understanding compatibility of two effective approaches of super-concentrated Li salt electrolyte and non-interactive dilute solvent.

Solvate ionic liquid (SIL) sample, [Li(G4)₁]TFSA and (G4: CH₃-O-(C₂H₄O)₄-CH₃, TFSA: N(SO₂CF₃)₂) was prepared in Ar-filled glovebox. Molar ratio of [Li(G4)₁]TFSA was G4:LiTFSA=1:1.

We added given amount of 1,1,2,2,- tetrafluoroethyl-2,2,3,3-tetrafluoropropylether (HFE) dilute solvent into SIL. Fig.1(a) showed the temperature dependences of the density from 10 to 80°C (ρ) for SIL/HFE mixtures. ρ values of HFE were larger than that of SIL ones owing to the difference of fluorine density between SIL and HFE. At this time, we assumed SIL as one molecule, excess densities (E_p) were expressed as following,

$$E_p = \rho - (x\rho_{\text{SIL}} + (1-x)\rho_{\text{HFE}})$$

Where x , ρ_{SIL} and ρ_{HFE} are mole fraction of SIL, ρ of neat SIL and HFE, respectively.

Fig.1(b) shows mole fraction dependences of E_p for SIL-HFE mixtures. E_p always shows a negative value in the temperature range below 30°C. Therefore, by mixing SIL and HFE, and suggested that the density decreasing. This result correlated with spectroscopic method that coordination structure of SIL and G4 doesn't change significant in dilute HFE^[4]. In the presentation, we will report on additional results of non-equimolar SIL that contains excess amount of Li salt that has better oxidation stability.

References:

[1]K. Yoshida et al, *J. Am. Chem. Soc.* **2011**, 133, 13121. [2]Y. Yamada et al, *J. Am. Chem. Soc.* **2014**, 136, 5039. [3]K. Dokko et al, *J. Electrochem. Soc.* **2013**, 160, A1304. [4]S. Saito et al, *J. Phys. Chem. B* **2016**, 120, 3378.

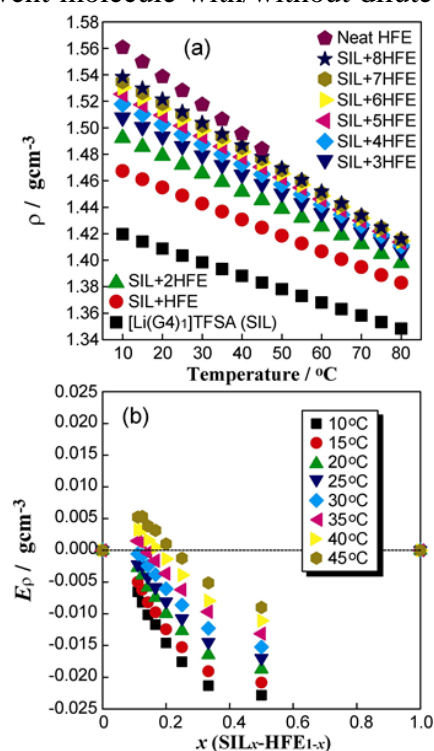


Fig. 1 Temperature dependences of densities (a), and composition dependences of excess densities (b) for SIL-HFE mixtures.