Specific Transport Properties and Electrochemical Reaction in Solvate Ionic Liquids and Molten Solvates

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Certain molten solvates of Li salts can be regarded as solvate ionic liquids [1]. A typical example is equimolar mixtures of glymes (G3: triglyme and G4: tetraglyme) and Li[TFSA]([TFSA]=[NTf$_2$]) ([Li(glyme)][TFSA]). The amount of free glyme estimated by Raman spectroscopy and MD simulation was found to be a few percent in [Li(glyme)]X with perfluorosulfonylamide-type anions such as [TFSA]$^-$, and thereby could be regarded as solvate ionic liquids [2, 3]. The activity of Li$^+$ in the glyme-Li salt mixtures was also evaluated by measuring the electrode potential of Li/Li$^+$ as a function of concentration [4]. At a higher concentration of Li salt, the amount of free glyme diminished in the solvate ionic liquids, leading to a drastic increase in the electrode potential. Unlike conventional electrolytes, the solvation of Li$^+$ by the glyme forms stable and discrete solvate ions ([Li(glyme)]$^+$) in the solvate ionic liquids. This anomalous Li$^+$ solvation had a great impact on the electrolyte properties and electrode reactions, which enhanced the utility of the molten solvates in advanced lithium batteries. The electrochemical oxidation of [Li(glyme)][TFSA] takes place at the electrode potential of ~4.6 V vs. Li/Li$^+$, while the oxidation of solutions containing excess glyme molecules ([Li(glyme)$_x$][TFSA], $x > 1$) occurs at lower than 4 V [5]. This enhancement of oxidative stability is due to the donation of lone pairs of ether oxygen atoms to the Li$^+$ cation, resulting in the highest occupied molecular orbital (HOMO) energy level lowering of a glyme molecule, which is confirmed by *ab initio* molecular orbital calculations. This anomalous Li$^+$ solvation induces interesting transport properties especially when interfacial electrochemical reactions proceed, which is not Stokes-like transport of solvated ions but something like a hopping transport [5]. Another intriguing aspect of the solvate ionic liquids is unusual solubility. The theoretical capacity of the S cathode is 10 times higher than that of conventional cathode materials used in current Li–ion batteries. However, Li–S batteries suffer from the dissolution of lithium polysulfides, which are formed by the redox reaction at the S cathode. In the equimolar complexes consisting of [Li(glyme)$_1$]$^+$ complex cation and [TFSA]$^-$ anion, both cations and anions are weak coordinating ions with low Lewis acidity and basicity, respectively. The [Li(glyme)][TFSA] molten complexes do not readily dissolve other ionic solutes due to the weak coordinating nature of the cation and anion, which leads to the stable operation of the Li–S battery [6]. An important electrode reaction, which is enabled by the use of molten solvates, is electrochemical Li$^+$ intercalation into graphite electrodes. Li$^+$-intercalated graphite was successfully formed in [Li(G3)$_1$][TFSA] [4]. In contrast, the cointercalation of G3 and Li$^+$ (intercalation of solvate [Li(G3)$_1$]$^+$ cation) into graphite occurred in [Li(G3)$_x$][TFSA] electrolytes containing excess G3 ($x > 1$) [4]. In the solvate ionic liquid, the activity of the free solvent is very low, and consequently, the electrode potentials for the formation of Li$^+$-intercalated graphite could become higher than that for cointercalation, and the cointercalation of G3 could be inhibited in [Li(G3)$_1$][TFSA].

References:
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