Study on the Characteristic of Lithium Battery Electrolyte Solution by Molecular Dynamics

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In our previous studies the measurements of conductivity, viscosity, self-diffusion coefficients, and the number of solvated molecules of LiPF\(_6\) and LiBF\(_4\) in PC and EC/DMC/DME mixed solvent systems have proved that 1) irrespective of its increased anion size the conductivity of the electrolyte LiPF\(_6\) solution becomes higher with increased dissociation of the lithium salt, 2) the LiPF\(_6\) solution shows its high ion dissociation even in concentrated solution compared with the LiBF\(_4\) solution etc. [1].

In this study we demonstrate our results of MD simulation and MO calculation of three kinds of model systems of LiPF\(_6\) and LiBF\(_4\) electrolyte solutions in PC solvent to investigate their dynamic ions behavior.

[Model I]

As a model of freely dissociated ions without ion-pair formation MD simulation of the solutions of five numbers of lithium ions, BF\(_4^-\) ions, and PF\(_6^-\) ions in 214 PC molecules was performed with NTP conditions at 298K, 323K, and 348K with 0.5-fs interval for 100-300 ps with Fujitsu WinMASPHYC (Materials Explorer), where PC, BF\(_4^-\), and PF\(_6^-\) are treated as rigid bodies and intermolecular potentials written in a literature are used [3].

The self-diffusion coefficients increased at higher temperature with the order of diffusion: PC \(\geq\) BF\(_4^-\) \(\geq\) PF\(_6^-\) \(>\) Li\(^+\). Lithium ion is solvated with four PC molecules.

[Model II]

For investigating ion-pair formation the dissociation of one molecule of LiBF\(_4\) and LiPF\(_6\) as ion pair in 30 PC molecules was monitored at 298K and 398K by MD simulation. The MD simulation at 348K showed the dissociation of LiPF\(_6\) ion pair at 30 ps while LiBF\(_4\) ion pair showed no dissociation. (See. Fig. 1)

[Model III]

To investigate the multiple ion cluster structures in a model system of concentrated solutions, radial distribution function and running integral by MD simulation are analyzed in two model systems of 30PC/10LiPF\(_6\) and 30PC/10LiBF\(_4\) at 298K. Two types of direct triple ions of Li\(^+\) and anion A (BF\(_4^-\) and PF\(_6^-\)) such as A-Li-A (Type I) and Li-A-Li (Type II) are observed. Hexa-coordinated PF\(_6^-\) shows two types of Type II direct triple ions (Li: PF\(_6^-\)-Li with linear (180 degree) F-P-F angle and bent(90 degree) F-P-F angle) while tetra-coordinated BF\(_4^-\) shows only bent(109 degree) F-B-F angle. (See. Fig. 2, 3)

[MO calculation]

Quantum mechanical MO calculations on LiBF\(_4\) and LiPF\(_6\) and their clusters with solvated EC and PC molecules are performed to investigate the electronic structures of these slats in concentrated non-aqueous solution.


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Fig. 1 Evolutions of Li-Anion Distances at 348K

![Fig. 1](image1)

Fig. 2 Radial Distribution Function for Li- Li and Li- F in LiPF\(_6\) solution.

![Fig. 2](image2)

Fig. 3 The snapshot of triple [trans] Li- PF\(_6^-\)-Li ion complex derived from MD result in LiPF\(_6\) solution.