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

Munetaka Takeuchi, Takaaki Sonoda*, Mitsuru Sano**
Kazuya Uezu***, and Kazuharu Yoshizuka***
Fujitsu Limited, Chiba 261-8588, Japan
*Institute of Advanced Material Study, Kyushu University, Fukuoka 816-8580, Japan
**Graduate School of Environmental Studies, Nagoya University, Nagoya 464-8601,Japan
***Faculty of Environmental Engineering, The University of Kitakyushu, Fukuoka 808-0135, Japan

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 inter molecular potentials written in a literature are used [3]. The self-diffusion coefficients increased at higher temperature with the order of diffusion: $PC \geqq BF_4^- \geqq PF_6^- > Li^+$. 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 $30PC/10Li^+/10PF_6^-$ and $30PC/10Li^+/10BF_4^-$ 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.

[1] K. Kondo et al., J. Phys. Chem., 104, 2040 (2000).
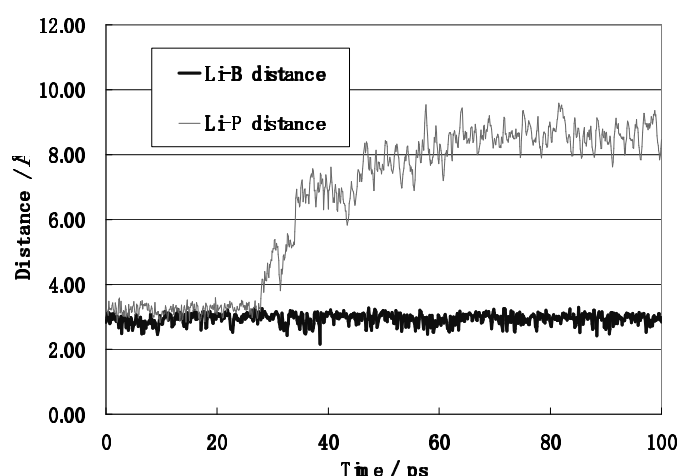[2] J. S. Soetens et al., J. Chem. Phys., A102(1998).
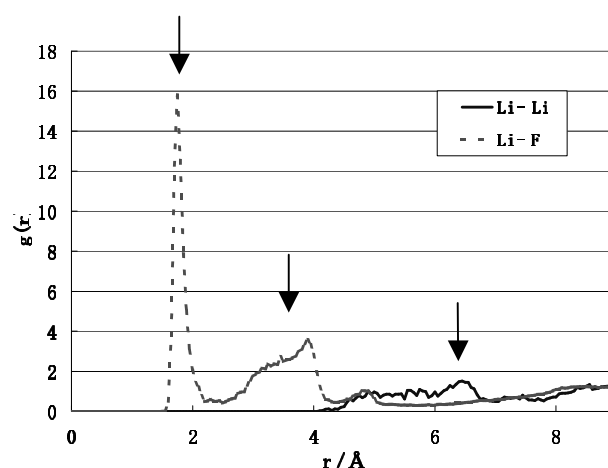
Fig. 1 Evolutions of Li-Anion Distances at 348K

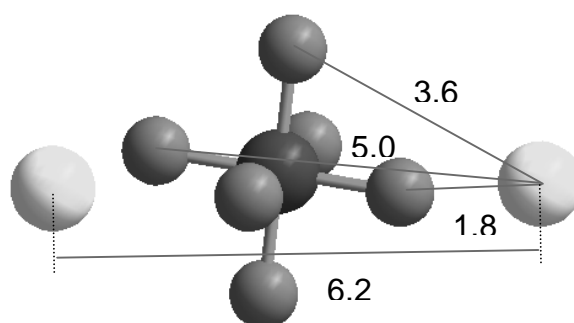Fig. 2 Radial Distribution Function for Li - Li and Li- F in $LiPF_6$ solution.

Fig. 3 The snap shot of triple [trans] Li - PF_6 - Li ion complex derived from MD result in $LiPF_6$ solution.