Solvation Structure of Lithium Ion in Concentrated Dimethylcarbonate Solutions

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Neutron diffraction measurements were carried out on 9.6 mol% *LiPF6?deuterated dimethylcarbonate (DMC-d6) solutions with different 6Li/7Li isotopic compositions in order to obtain direct information on solvation structure around the lithium ion in non-aqueous solutions employed for high-performance lithium ion batteries. Sample solutions, (6LiPF6)0.096(DMC-d6)0.904 and (7LiPF6)0.096(DMC-d6)0.904, were sealed in fused quartz cell (12 mm in inner diameter and 1 mm in thickness). Neutron diffraction measurements were carried out at 25 ° C using the 4G (GPTAS) spectrometer installed at the JRR-3M research reactor with incident neutron wavelength of = 1.281(1) A. Scattered neutrons were collected over the angular range of 3.0 < 2 < 118°. After corrections for background, absorption, incoherent and multiple scattering, observed count rate was converted to the absolute scattering cross section. The first-order difference function [1] involving information on solvation shell around Li+,

Li(Q), was derived from a difference in scattering cross sections observed for the two samples. The distribution function, GLi(r), around Li+ was obtained from the Fourier transform of the observed Li(Q), which is shown in Fig. 1.

The first peak observed at around r = 2 A is attributable to the sum of contributions from the nearest neighbor Li+…O(DMC) and Li+…F(PF6-) interatomic interactions. Structural parameters concerning the solvation shell of the Li+ were determined from the least squares fitting analysis of the observed difference function in the Q-space. In the fitting procedure, intramolec-

ular structural parameters of DMC were taken from those reported from the gas-phase electron diffraction study [2]. The cis-cis and cis-trans conformations of DMC were taken into account for the fitting analysis. Contribution from the direct ion pair, Li+…PF6- was also added in the model function.

The results of the least squares fitting analysis indicate that the Li+ is surrounded by, on the average, 1.7 DMC(in cis-cis conformation), 1.1 DMC(cis-trans) molecules with the nearest neighbor Li+…O(DMC) distance of 2.08 A. It was also revealed that 1.1 PF6- is involved in the first solvation shell of the Li+ with the nearest neighbor Li+…F(PF6-) distance of 2.03 A.

References
[1] J. E. Endervy, G. W. Neilson, " Water, A comprehensive Treatise ", Plenum Press, New York (1979), Vol. 6, p. 1.
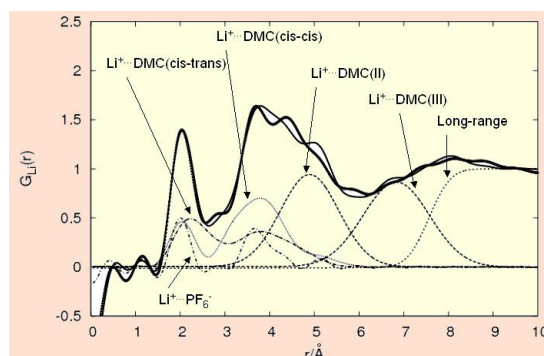[2] F. C. Mijlhoff, J. Mol. Struct., 36, 334 (1977).

Fig. 1. Fig. 1 Distribution function around lithium ion in 9.6 mol% LiPF6-DMC solutions.