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# Local structure of $Li^+$ in concentrated $LiPF_6$–dimethyl carbonate solutions

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ABSTRACT

Neutron diffraction measurements have been carried out at 25 °C for 9.6 mol% $^*LiPF_6$-deutrerated dimethyl carbonate (DMC-$d_6$) solutions in which the isotopic ratio of $^6Li/^7Li$ was changed. Local structure of $Li^+$ in the solution was derived from the least squares fitting analysis of observed difference function, $\Delta_{Li}(Q)$. It was revealed that $Li^+$ is surrounded by ca. 3 DMC molecules and ca. 1 $PF_6^-$ with intermolecular distances of $r(Li^+\cdots O(DMC)) = 2.08 \pm 0.02$ Å and $r(Li^+\cdots F(PF_6^-)) = 2.03 \pm 0.06$ Å, respectively. Raman experimental study and DFT calculations agree well with neutron structure analysis.

## 1. Introduction

In recent years, the solvation structure of $Li^+$ in non-aqueous solutions attracts much attention in relation with electrolytes used for lithium ion secondary batteries. Especially, formation of the contact ion pair and aggregation of ions in highly concentrated non-aqueous solutions receives considerable attraction in close connection with fast-charging and high-voltage advanced batteries [1]. Combination of $LiPF_6$ and carbonate solvents has mostly been employed as electrolyte solutions because of high solubility of Li salt and good electrical conductivity [2]. Mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) is often employed as a solvent in practical use to keep a wider liquid range of electrolyte solution and favorable transport property of $Li^+$. In order to obtain deeper insights for the transport mechanism of $Li^+$ in non-aqueous electrolyte solutions, it is necessary to determine the local structure around $Li^+$. According to IR and Raman spectroscopic studies on $LiAsF_6$–DMC solutions, the conformational equilibrium of DMC molecule ("cis–cis" and "cis–trans") is modified by solvating $Li^+$ [3]. The ratio of these conformers in dilute $LiBF_4$–DMC solution has been estimated to "cis–cis"/"cis–trans" ≈ 2/1 from a molecular dynamics (MD) simulation study [4]. More recent MD studies have revealed that the number of DMC molecules in the first solvation shell of $Li^+$ is 2.7 [5] and 2.3 [6] in 9.1 and 7 mol% $LiPF_6$ solutions in DMC, respectively. The number of $PF_6^-$ in the first solvation shell of $Li^+$ in these solutions is estimated to be 1.7 [5] and 2.1 [6], respectively, which implies $Li^+\cdots PF_6^-$ contact ion pairs are commonly produced. The solvation number of $Li^+$ in 1.5 M $LiPF_6$ solution in EC + DMC mixed solvent was obtained to be 3.9 from recent Raman spectroscopic study [7], suggesting tetrahedral coordination of $Li^+$ in the carbonate solution. On the other hand, a much larger number of DMC molecules (8.19) associated with $Li^+$ in 1.0 M $LiPF_6$ solution in DMC was reported from $^{17}O$ NMR chemical shift of carbonyl oxygen atom within the DMC molecule [8]. In order to determine the solvation number of $Li^+$ in the solution, neutron diffraction with $^6Li/^7Li$ isotopic substitution method is one of the most effective experimental techniques to obtain direct information on the solvation structure of $Li^+$. The $^6Li/^7Li$ isotopic substitution method was first applied for investigation of the hydration shell of $Li^+$ in aqueous solutions [9–13]. This method was then adopted for non-aqueous systems. The environmental structure around $Li^+$ in highly concentrated methanolic LiBr and LiI solutions has been reported [14]. The solvation structure of LiBr in concentrated acetone solution has revealed that the first solvation shell of $Li^+$ involves, on the average, ca. three carbonyl oxygen atoms of acetone molecules and ca. one $Br^-$ with interatomic distances of $r_{LiO} = 2.24 \pm 0.02$ Å and $r_{LiBr} = 2.86 \pm 0.02$ Å, respectively [15]. More recently, the $^6Li/^7Li$ substitution method has been applied to investigate solvation structure of $Li^+$ in concentrated propylene carbonate (PC) solution [16]. The first solvation shell of $Li^+$ in the 10 mol% $LiPF_6$–PC solution involves $4.5 \pm 0.1$ carbonyl oxygen atoms of PC molecules with interatomic distance of $r_{LiO} = 2.04 \pm 0.01$ Å. It has been found that no $PF_6^-$ is involved in the first solvation shell of $Li^+$ [16]. Special attention is now given to the solvation structure of $Li^+$ in the linear carbonate such as dimethyl carbonate, since an addition of DMC to the PC solution gives the electrolyte solution more favorable physical properties (lower melting point, lower viscosity, etc.). However, structural properties concerning the local structure of $Li^+$ in the linear carbonate solvent has not yet been obtained experimentally.

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In the present paper, we describe the results of neutron diffraction experiments on concentrated 9.6 mol% $LiPF_6$ solutions in DMC. Detailed structural properties of the first solvation shell of $Li^+$ was derived from the least squares fitting analysis of observed difference function obtained from the difference between scattering cross sections for the solutions with different $^6Li/^7Li$ compositions. DMC solvation number around the $Li^+$ in $LiClO_4$–DMC solution was also evaluated by Raman spectra to ensure neutron structure analysis. Subsequently, DFT calculations were performed to yield further insight into the $Li^+$ solvation by DMC.

## 2. Materials and methods

### 2.1. Materials

$^6$Li-enriched $^6Li_2CO_3$ (95.6% $^6$Li, Tomiyama Chemical Co. Ltd.) and natural $^{nat}Li_2CO_3$ (92.5% $^7$Li, natural abundance) were respectively converted to $^6$LiCl and $^{nat}$LiCl by reacting with HCl in the aqueous solution. The product solution was dried under vacuum to obtain anhydrous $^*$LiCl ($^*$Li: $^6$Li, $^{nat}$Li). Enriched $^*$LiCl was reacted with $AgPF_6$ in acetonitrile solution. After filtering precipitated AgCl, the filtrate was evaporated to dryness under reduced pressure to obtain anhydrous $^*LiPF_6$.

Required amounts of enriched $^*LiPF_6$ was dissolved into fully deuterated dimethyl carbonate (DMC-$d_6$, 99% D, CIL Inc.) to prepare 9.6 mol% $^*LiPF_6$ solutions in DMC-$d_6$. Density of sample was measured by a vibration tube densimeter (Kyoto Electronic, DA-310) at 25 °C. Sample solutions were sealed into cylindrical fused quartz cell with inner diameter of 12 mm and 1.0 mm in wall thickness. The sample parameters are listed in Table 1.

### 2.2. Neutron diffraction measurements

Neutron diffraction measurements were carried out at 25 °C using the ISSP diffractometer 4G (GPTAS) installed at the JRR-3M research reactor operated at 20 MW in the Japan Atomic Energy Agency (JAEA), Tokai, Japan. The incident neutron wavelength $\lambda = 1.281(3)$ Å, was determined by Bragg reflections from KCl powder. Beam collimations were 40′–80′–80′ going from the reactor to the detector. The aperture of the collimated beam was 20 mm in width and 40 mm in height. Scattered neutrons were collected over the angular range of $3.0 \le 2\theta \le 118.0°$, corresponding to $0.26 \le Q \le 8.41$ Å$^{-1}$ ($Q = 4\pi\sin\theta/\lambda$). Angular step intervals were chosen to be $\Delta 2\theta = 0.5°$ in the range of $3.0 \le 2\theta \le 40.0°$ and $\Delta 2\theta = 1.0°$ in the range of $41.0 \le 2\theta \le 118.0°$, respectively. The preset times were 220 s and 140 s for $^6LiPF_6$ and $^{nat}LiPF_6$ solutions, respectively. Scattering measurements were carried out for the vanadium rod (10 mm in diameter), empty cell, and instrumental background.

### 2.3. Data reduction

Observed scattering intensities from the sample solutions were corrected for instrumental background, absorption [17], and multiple scattering [18]. The observed count rate for sample solution was converted to the absolute scale by the use of corrected scattering intensities from the vanadium rod. Details of data correction and normalization procedures are given elsewhere [19,20].

**Table 1**
Isotopic composition, average scattering length, $b_{Li}$, of lithium ion, total cross section, and number density of samples in the stoichiometric unit $(^*LiPF_6)_{0.096}(DMC\text{-}d_6)_{0.904}$, $\sigma_t$ and $\rho$, respectively.

| Sample | $^6$Li/% | $^7$Li/% | $b_{Li}/10^{-12}$ cm | $\sigma_t$ /barns[a] | $\rho$/Å$^{-3}$ |
|---|---|---|---|---|---|
| $(^6LiPF_6)_{0.096}(DMC\text{-}d_6)_{0.904}$ | 95.6 | 4.4 | 0.182 | 116.866 | 0.007942 |
| $(^{nat}LiPF_6)_{0.096}(DMC\text{-}d_6)_{0.904}$ | 7.5 | 92.5 | −0.190 | 60.311 | |

[a] For incident neutron wavelength of 1.281 Å.

The first-order difference function [21–23], $\Delta_{Li}(Q)$, was obtained as the numerical difference in normalized scattering cross sections for sample solutions with different $^6Li/^7Li$ ratios. Difference function scaled at the stoichiometric unit, $(^*LiPF_6)_x(DMC\text{-}d_6)_{1-x}$, is expressed as the weighted sum of six partial structure factors relating Li atom.

$$\begin{aligned}\Delta_{Li}(Q) &= (d\sigma/d\Omega)(\text{for}\,^6\text{Li sample}) - (d\sigma/d\Omega)(\text{for}\,^{nat}\text{Li sample})\\ &= A[a_{LiO}(Q)-1] + B[a_{LiD}(Q)-1] + C[a_{LiC}(Q)-1] + D[a_{LiP}(Q)-1]\\ &\quad + E[a_{LiF}(Q)-1] + F[a_{LiLi}(Q)-1],\end{aligned} \tag{1}$$

where, $A = 6x(1-x)(b_{6Li}-b_{natLi})b_O$, $B = 12x(1-x)(b_{6Li}-b_{natLi})b_D$, $C = 6x(1-x)(b_{6Li}-b_{natLi})b_C$, $D = 2x^2(b_{6Li}-b_{natLi})b_P$, $E = 12x^2(b_{6Li}-b_{natLi})b_F$, and $F = x^2({b_{6Li}}^2-{b_{natLi}}^2)$. The distribution function around the $Li^+$, $G_{Li}(r)$, was obtained by the Fourier transform of observed $\Delta_{Li}(Q)$,

$$\begin{aligned}G_{Li}(r) &= 1 + (A+B+C+D+E+F)^{-1}(2\pi^2\rho r)^{-1}\int_0^{Q_{max}} Q\Delta_{Li}(Q)\sin(Qr)dQ\\ &= [Ag_{LiO}(r) + Bg_{LiD}(r) + Cg_{LiC}(r) + Dg_{LiP}(r) + Eg_{LiF}(r) + Fg_{LiLi}(r)]\\ &\quad \times (A+B+C+D+E+F)^{-1}.\end{aligned} \tag{2}$$

The upper limit of the integral, $Q_{max}$, was set to be 8.41 Å$^{-1}$.

Intermolecular parameters concerning the nearest neighbor $Li^+\cdots$DMC and $Li^+\cdots PF_6^-$ interactions were determined through the least squares fitting for observed $\Delta_{Li}(Q)$, employing the model function $\Delta_{Li}^{model}(Q)$, involving both the short- and long-range contributions [24–26].

$$\begin{aligned}{\Delta_{Li}}^{model}(Q) = {} & \Sigma 2x n_{Li\alpha}(b_{6Li}-b_{natLi})b_\alpha \exp\left(-{l_{Li\alpha}}^2Q^2/2\right)\sin(Qr_{Li\alpha})/(Qr_{Li\alpha})\\ & + 4\pi\rho(A+B+C+D+E+F)\exp\left(-{l_0}^2Q^2/2\right)\\ & [Qr_0\cos(Qr_0) - \sin(Qr_0)]Q^{-3}.\end{aligned} \tag{3}$$

where, $n_{Li\alpha}$ denotes the coordination number of α atom around $Li^+$. Parameters, $l_{Li\alpha}$ and $r_{Li\alpha}$, are the root-mean-square displacement and internuclear distance for $Li^+\cdots\alpha$ pair, respectively. The long-range parameter, $r_0$, corresponds the distance beyond which a continuous distribution of atoms around $Li^+$ can be assumed. The parameter, $l_0$, describes the sharpness of the boundary at $r_0$. Structural parameters, $n_{Li\alpha}$, $l_{Li\alpha}$, $r_{Li\alpha}$, $l_0$ and $r_0$ are respectively determined from the least squares fit to the observed $\Delta_{Li}(Q)$. The fitting procedure was performed in the range of $0.26 \le Q \le 8.41$ Å$^{-1}$ with the SALS program [27], assuming that the statistical uncertainties distribute uniformly. In the present analysis, interatomic distances within DMC molecule was fixed to those reported from gas phase electron diffraction study [28]. The geometry of $PF_6^-$ was assumed to be octahedral, with the average P–F distance of 1.597 Å [29].

### 2.4. Raman sample preparation and measurement

For Raman spectra measurements, $LiClO_4$ salt was prepared by treating $Li_2CO_3$ with $HClO_4$ in an aqueous solution, followed by repeated evaporation to remove $HClO_4$ and solvent $H_2O$. Residual $HClO_4$ was checked to be negligible by a pH measurement. Thus obtained $LiCO_4$ salt was dried at 200 °C in a glass tube vacuum oven during a few days. DMC was stored with a molecular sieve 3A during several weeks to reduce water content. Sample solutions were prepared in the glove box of an Ar gas atmosphere with a water content kept less than 1 ppm. Finally, water content of thus prepared sample solutions were checked by the Karl Fischer titration. Raman spectra were measured by using a JASCO NR-1100 Raman spectrometer with the optical resolution of 2.5 cm$^{-1}$.