

# Solvation of lithium ions in organic electrolytes of primary lithium batteries by electrospray ionization-mass spectroscopy

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## Abstract

Solvation of lithium ions in the organic electrolyte solutions for primary lithium batteries was investigated by electrospray ionization-mass spectroscopy (ESI-MS). In  $\text{LiBF}_4/\gamma$ -butyrolactone (GBL), lithium ions were solvated to GBL molecules in the form  $[\text{Li}(\text{GBL})_2]^+$  or  $[\text{Li}(\text{GBL})_3]^+$ , and in  $\text{LiClO}_4/\text{dimethoxyethane (DME)-propylene carbonate (PC)}$ , lithium ions were solvated mainly to DME and PC in the form  $[\text{Li}(\text{DME})(\text{PC})]^+$ . © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Electrospray ionization-mass spectroscopy; Solvation of lithium ion; Organic electrolyte solutions; Dimethoxyethane; Propylene carbonate

## 1. Introduction

High energy batteries were reviewed by Jasinski in 1967 [1]. Then a primary lithium battery,  $\text{LiLiBF}_4/\gamma$ -butyrolactone (GBL) $(\text{CF})_n$  [2,3], was produced in 1971. Another battery,  $\text{LiLiClO}_4/\text{dimethoxyethane (DME)-propylene carbonate (PC)}|\text{MnO}_2$  [4–7], was commercialized in 1972. Since then these batteries have been used for electric sources of watches, automatic cameras and so on. Although much work concerning with the organic electrolytes have been done [8–11], the details of the solvation in organic solutions for lithium ions in the commercial primary lithium batteries have not been clearly understood. For the evaluation of solvation numbers of ions, the ionic mobility and Stokes' radius of the ions have been commonly used [12]. Laser Raman spectroscopy and conductivity measurement showed that each lithium ion is mainly solvated by two DME molecules in  $\text{LiClO}_4/\text{DME-PC}$  [13]. On the other hand, the conductivity measurement of the DME-PC solutions changing the mixing ratios showed that lithium ion is solvated to both, one DME and one PC molecules [14]. For the measurement of solvation number of ions in organic electrolyte solutions, NMR has been used in some cases [15,16]. Recently, the solvation of lithium ions to solvent molecules in organic electrolyte solutions has been investigated by electrospray ionization-mass spectroscopy (ESI-

MS) [17,18]. ESI-MS was applied first to the analysis of large and fragile polar biomolecules [19]. Then alkali metal cations solvent complexed with 18-crown-6 [20] complex of transition metal ions [21] and solvents and alkali metal cations solvent binding [22] were analyzed using ESI-MS.

In the present work, the solvation of lithium ions to the solvent molecules in the organic electrolyte solutions for primary lithium batteries and relating problems were investigated by means of ESI-MS which gave direct information of the solvated lithium ions, and remarkable results were obtained.

## 2. Experimental

Materials used were lithium salts,  $\text{LiClO}_4$  (reagent grade) and  $\text{LiBF}_4$  (lithium battery grade, Morita Chemical), aprotic solvents, GBL, DME and PC (lithium battery grade, Ube Industries), and methanol (reagent grade). These reagents were used as received. The sample solutions diluted with methanol were prepared by mixing 0.1 ml of GBL, PC or DME and 0.9 ml of 0.1 mM  $\text{LiClO}_4/\text{MeOH}$  or 0.1 mM  $\text{LiBF}_4/\text{MeOH}$ , i.e. in the volume ratio 1 of the aprotic solvent to 9 of the methanol solution. For the mixed aprotic solvent, DME-PC, the sample solution was prepared by mixing 0.05 ml of DME-PC (1:1 (v/v)), 0.9 ml of MeOH and 0.1 ml of 5 mM  $\text{LiClO}_4/\text{MeOH}$ . In methanol containing the aprotic solvents and lithium salt, lithium ions are preferentially solvated by aprotic solvents and not by methanol [17,18].

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The instrument of ESI-MS was a mass spectrometer (JEOL-D300) furnished electrospray ionization interface and the details were shown in a previous paper [17]. The lithium ions solvated to PC, GBL and/or DME molecules were introduced with a large amount of methanol which reduced the viscosity of the sample solutions at a rate of  $2.5 \mu\text{l min}^{-1}$  to the injector whose nozzle equipped a conductor connecting to a high voltage dc source. The lithium ions solvated to PC, GBL and/or DME, and methanol were introduced together to a skimmer whose temperature was controlled by heated nitrogen gas, and methanol was stripped there. Then the solvated lithium ions were injected to a mass analyzer, capable of analyzing samples whose mass numbers were over 50.

### 3. Results and discussion

Fig. 1 shows ESI-MS spectrum of DME–1 mM LiClO<sub>4</sub>/MeOH (1:9 (v/v)) solution. In the sample solution, the concentration of the species is the order of  $\text{Li}^+ \ll \text{DME} \ll \text{MeOH}$ , and the peaks of lithium ions solvated to MeOH were not observed as represented in the previous paper [17,18]. In Fig. 1 intense peak of  $[\text{Li}(\text{DME})_2]^+$  ( $m/z = 187.3$ ) with very weak peak of  $[\text{Li}(\text{DME})]^+$  ( $m/z = 97.1$ ) are observed. Therefore, lithium ions are mainly solvated to two DME molecules. The coordination number of lithium ion has been reported to be between 2 and 8 [23,24] and a lithium ion would commonly coordinate to four oxygen atoms of two DME molecules in LiClO<sub>4</sub>/DME solution.

ESI-MS spectrum of PC–1 mM LiClO<sub>4</sub>/MeOH (1:9 (v/v)) is given in Fig. 2. Two large peaks due to  $[\text{Li}(\text{PC})_3]^+$  and  $[\text{Li}(\text{PC})_2]^+$  appear in the figure and the former peak is larger than the latter one. Similar results were obtained in the previous papers [17,18].

The result by ESI-MS of solvated lithium ions in DME–PC–MeOH–5 mM LiClO<sub>4</sub>/MeOH (0.25:0.25:9:1 (v/v/v/v))

is shown in Fig. 3. As is clear from the figure, there are five significant peaks corresponding to  $[\text{Li}(\text{DME})_2]^+$  ( $m/z = 187.3$ ),  $[\text{Li}(\text{DME})(\text{PC})]^+$  ( $m/z = 199.3$ ),  $[\text{Li}(\text{PC})_2]^+$  ( $m/z = 211.3$ ),  $[\text{Li}(\text{DME})(\text{PC})_2]^+$  ( $m/z = 301.3$ ) and  $[\text{Li}(\text{PC})_3]^+$  ( $m/z = 313.2$ ). Among the five peaks, the peak of  $[\text{Li}(\text{DME})(\text{PC})]^+$  was the largest and this solvated ion species would be the main cationic component in the solution. Although the peak height in the spectrum is not directly proportional to the concentration of the solvated lithium ions, the order of these solvated ions is:

$$\begin{aligned} [\text{Li}(\text{DME})(\text{PC})]^+ &\gg [\text{Li}(\text{DME})(\text{PC})_2]^+ > [\text{Li}(\text{DME})_2]^+ \\ &\geq [\text{Li}(\text{PC})_3]^+ > [\text{Li}(\text{PC})_2]^+ \end{aligned}$$

It has been assumed that in mixed organic electrolyte solutions, the solvent whose donor number is higher would preferentially solvate to cations. Because the donor numbers of DME and PC have been reported to be 24 and 15.1, respectively [11], DME has been showed solvate preferentially to lithium ions. In spite of this assumption, the main solvated lithium ion was  $[\text{Li}(\text{DME})(\text{PC})]^+$  and co-solvation of DME and PC was observed.

In previous papers [13,14], it was reported that lithium ions solvate one, two or three solvent molecules in the solutions consisted of DME–PC and LiClO<sub>4</sub>. By means of Laser Raman spectrometry and conductivity measurement the solvation of one DME molecule to lithium ions has been certified, but the other co-solvated molecules have not been identified. In the present work, ESI-MS gives directly the information on the solvation of lithium ions and it is suggested that the main solvated lithium ion is  $[\text{Li}(\text{DME})(\text{PC})]^+$ . These results correspond to that in the previous papers and give more detailed structure. The solvated lithium ion in the form of  $[\text{Li}(\text{DME})(\text{PC})]^+$  would be stereographically stable.

For the solvated lithium ions in GBL–1 mM LiBF<sub>4</sub>/MeOH (1:9 (v/v)), the ESI-MS spectra are shown in

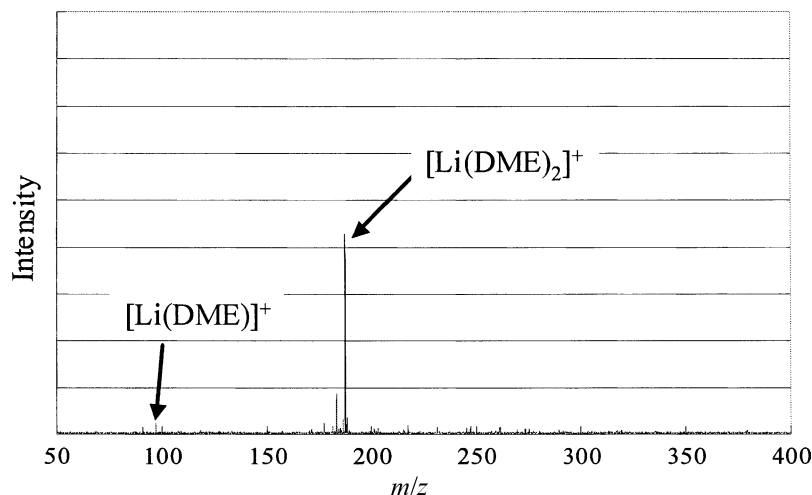


Fig. 1. ESI-MS spectra of DME–1 mM LiClO<sub>4</sub>/MeOH (1:9 (v/v)).

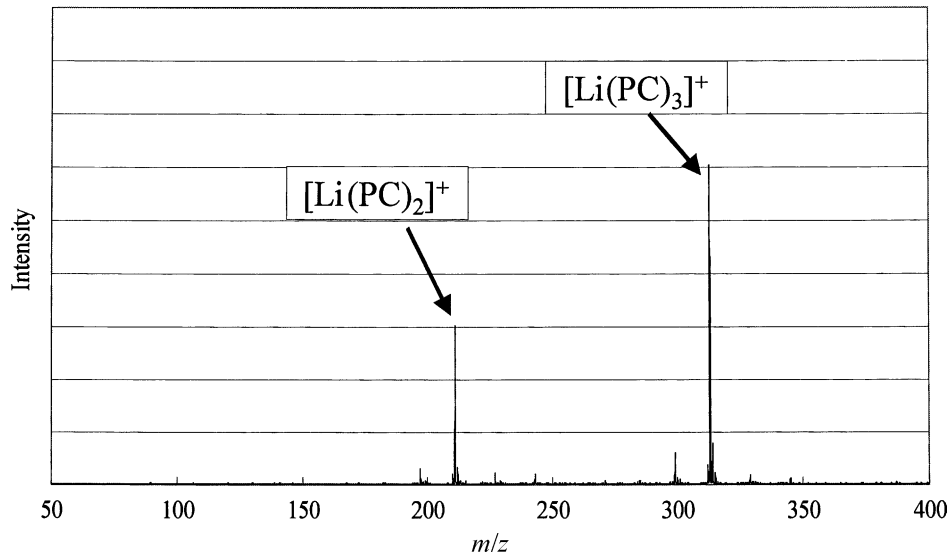


Fig. 2. ESI-MS spectra of PC-1 mM LiClO<sub>4</sub>/MeOH (1:9 (v/v)).

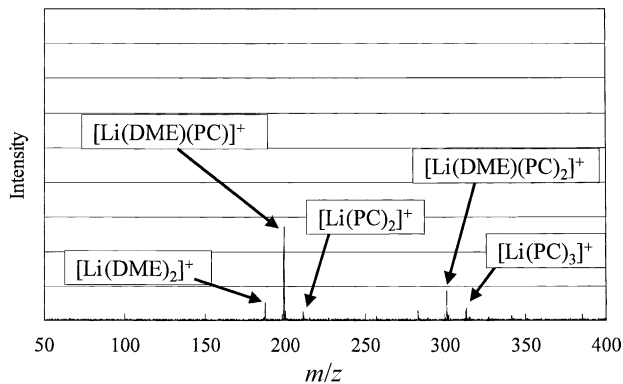


Fig. 3. ESI-MS spectra of PC-DME-MeOH-5 mM LiClO<sub>4</sub>/MeOH (0.25:0.25:9:1 (v/v/v)).

Fig. 4. In the figure, two large peaks due to [Li(GBL)<sub>2</sub>]<sup>+</sup> and [Li(GBL)<sub>3</sub>]<sup>+</sup> are apparent, and the heights of both peaks are similar. Therefore, lithium ions in this solution solvate probably to two or three GBL molecules.

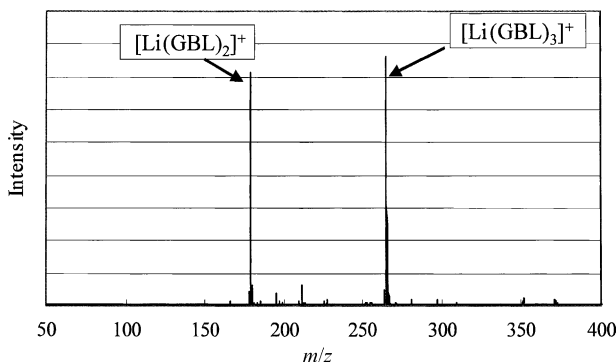


Fig. 4. ESI-MS spectra of GBL-1 mM LiBF<sub>4</sub>/MeOH (1:9 (v/v)).

#### 4. Conclusions

Solvation of lithium ions in the organic electrolyte solutions was directly measured by means of ESI-MS. Solvation of lithium ions in the organic electrolyte solutions, LiBF<sub>4</sub>/GBL and LiClO<sub>4</sub>/DME-PC, was investigated by ESI-MS. As the result, lithium ions are solvated to two or three GBL molecules in LiBF<sub>4</sub>/GBL. In LiClO<sub>4</sub>/DME-PC, lithium ions are solvated mainly to DME and PC in the form of [Li(DME)(PC)]<sup>+</sup> and a little amount of lithium ions are solvated yielding [Li(DME)<sub>2</sub>]<sup>+</sup>, [Li(PC)<sub>2</sub>]<sup>+</sup>, [Li(DME)(PC)<sub>2</sub>]<sup>+</sup> and [Li(PC)<sub>3</sub>]<sup>+</sup>.

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