



# Studies on Solvation of Lithium Ions in Organic Electrolyte Solutions by Electrospray Ionization-Mass Spectroscopy

著者	Fukushima Tsuyoshi, Matsuda Yoshiharu, Hashimoto Hiroyuki, Arakawa Ryuichi
journal or publication title	The Journal of Electrochemical Society
volume	4
number	8
page range	A127-A128
year	2002
URL	<a href="http://hdl.handle.net/10112/6012">http://hdl.handle.net/10112/6012</a>



## Studies on Solvation of Lithium Ions in Organic Electrolyte Solutions by Electrospray Ionization-Mass Spectroscopy

Tsuyoshi Fukushima, Yoshiharu Matsuda,<sup>\*,z</sup> Hiroyuki Hashimoto, and Ryuichi Arakawa

Department of Applied Chemistry, Faculty of Engineering and High-Technology Research Center, Kansai University, Yamate-cho 3-3-35, Suita, Osaka 564-8680, Japan

Solvation of lithium ions in organic electrolyte solutions, ethylene carbonate (EC), propylene carbonate (PC), and  $\gamma$ -butyrolactone (GBL) containing  $\text{LiClO}_4$ , for lithium batteries was studied by electrospray ionization-mass spectroscopy (ESI-MS). The mass spectrograms showed that a lithium ion solvated with two or three solvent molecules.  
© 2001 The Electrochemical Society. [DOI: 10.1149/1.1383428] All rights reserved.

Manuscript submitted January 13, 2001; revised manuscript received April 23, 2001. Available electronically June 19, 2001.

In the course of the research and development of advanced batteries, the selection of the electrolyte solution has been an important factor. The solvent molecules react with the negative and positive electrodes and lithium salts in the electrolyte solutions. The solvent molecules solvated to lithium ions would react preferentially with the electrodes and the chemical species near the electrodes. Therefore, the solvation of lithium ion would concern the film formation on the interface between the electrode and the electrolyte. However, the solvation of lithium ions in the electrolyte solutions of lithium batteries has been reported in a few papers.<sup>1-5</sup> In these previous papers, the main procedure was Raman spectroscopy and solvation numbers of the solvated molecules were discussed. On the other hand, electrospray ionization-mass spectroscopy (ESI-MS) was introduced on the analysis of large biomolecules in 1989.<sup>6</sup> It was then applied on analytical studies of alkali metal cations complexed with 18-crown-6,<sup>7</sup> transition-metal ion complex with solvent,<sup>8</sup> and alkali metal cations-solvent binding.<sup>9</sup> In this work, ESI-MS was used as a first attempt for the evaluation of the solvation number of solvated molecules to lithium ion in organic electrolyte solutions, and reasonable results were obtained.

### Experimental

Sample solutions were prepared containing  $\text{LiClO}_4$  (reagent grade) and EC, PC, or GBL (Lithium battery grade, Ube Industries) in methanol (MeOH) (reagent grade) to decrease the viscosity of the solutions. The diluted solutions were prepared by mixing MeOH containing  $\text{LiClO}_4$  (1 mM  $\text{LiClO}_4/\text{MeOH}$ ) and EC, PC, or GBL and their volumetric ratio was 9:1.

A schematic of ESI-MS instrument is shown in Fig. 1. The instrument was a mass spectrometer (JEOL-D300) furnished with an electrospray ionization interface. Samples dissolved in methanol were introduced at a rate of 0.15 mL/h to an injector with a nozzle conductor connecting to a high voltage dc source. High dc voltage was applied to the nozzle and the samples contained in methanol were positively charged. The lithium ions solvated with EC, PC, or GBL molecules were introduced together with methanol, through a path of which temperature was controlled by heated nitrogen gas, to a skimmer, and methanol vapor was stripped there.

The positively charged sample was then injected into a mass analyzer capable of analyzing samples with mass numbers over 50.

### Results and Discussion

ESI-MS spectra of 1 mM  $\text{LiClO}_4/\text{methanol}$  solution without the aprotic solvent are shown in Fig. 2. The figure shows the spectra of  $[\text{Li}(\text{MeOH})_2]^+$  ( $m/z = 71.1$ ) and  $[\text{Li}(\text{MeOH})_3]^+$  ( $m/z$

$= 103.3$ ). From the results, lithium ion solvates to 2 or 3 methanol molecules in methanol solution dissolving  $\text{LiClO}_4$  without the aprotic solvent, EC, PC, or GBL.

Figure 3 shows ESI-MS spectra of EC and 1 mM  $\text{LiClO}_4/\text{MeOH}$  (1:9 vol) solution. In this figure, the spectra of  $[\text{Li}(\text{EC})_2]^+$  ( $m/z = 183.1$ ) and  $[\text{Li}(\text{EC})_3]^+$  ( $m/z = 271.1$ ) were observed and no other spectra corresponding to  $[\text{Li}(\text{MeOH})_2]^+$  and  $[\text{Li}(\text{MeOH})_3]^+$  shown in Fig. 2 appeared. Therefore, it was assumed that the solvation of methanol to lithium ions was weak or not present in the

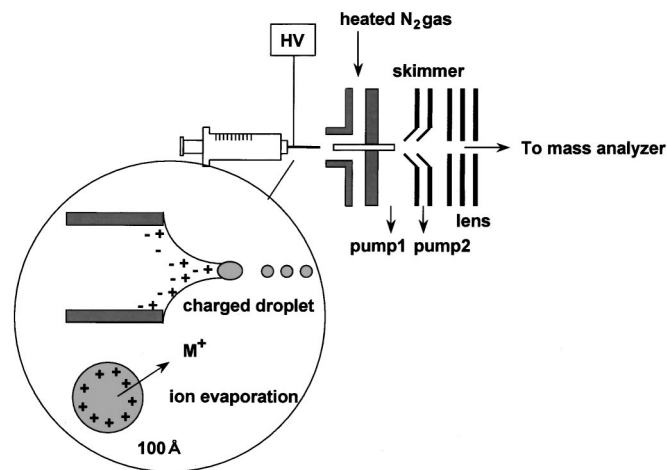


Figure 1. Apparatus of electrospray ionization-mass spectroscopy.

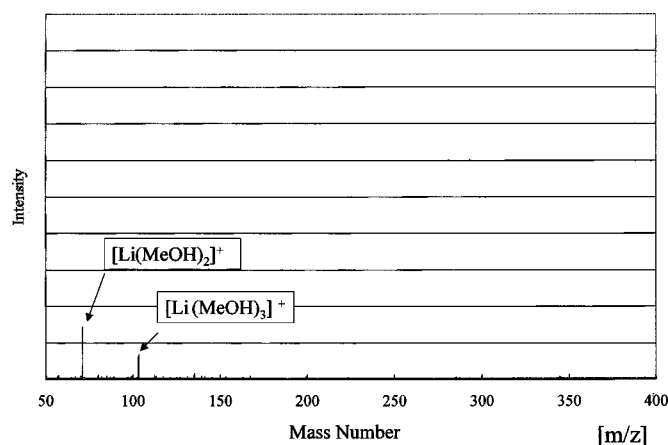


Figure 2. ESI-MS spectra of 1 mM  $\text{LiClO}_4/\text{MeOH}$ .

\* Electrochemical Society Active Member.

<sup>z</sup> E-mail: ymatsuda@ipcku.kansai-u.ac.jp

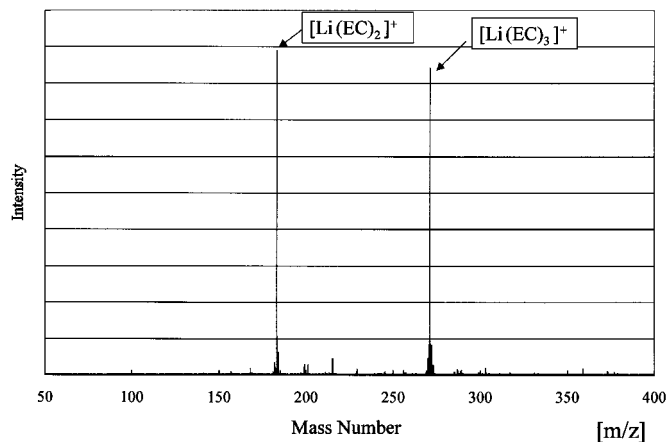


Figure 3. ESI-MS spectra of EC 1 mM LiClO<sub>4</sub>/MeOH (1:9 by volume).

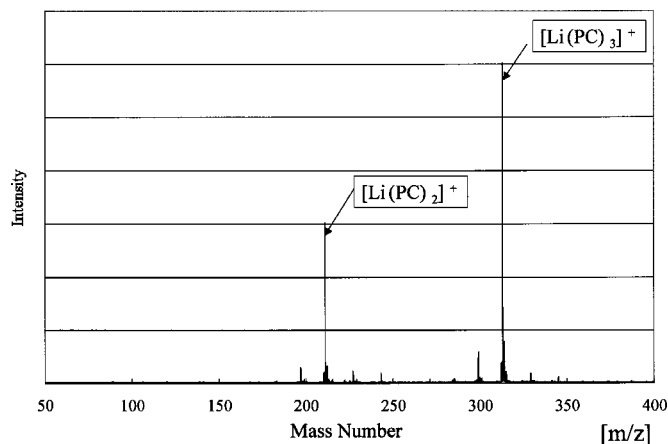


Figure 4. ESI-MS spectra of PC 1 mM LiClO<sub>4</sub>/MeOH (1:9 by volume).

EC-methanol system. This result shows that lithium ions would solvate mainly to two or three EC molecules in this system and the ratio of these ionic species is assumed to be about 1:1, though exact quantitative analysis is difficult.

The ESI-MS spectra of PC and 1 mM LiClO<sub>4</sub>/MeOH (1:9 vol) are shown in Fig. 4. In this figure, two large peaks corresponding to [Li (PC)<sub>2</sub>]<sup>+</sup> ( $m/z = 211.2$ ) and [Li (PC)<sub>3</sub>]<sup>+</sup> ( $m/z = 313.1$ ) were obtained. In a comparison of these two spectra, the peak of [Li (EC)<sub>3</sub>]<sup>+</sup> was higher than that of [Li (EC)<sub>2</sub>]<sup>+</sup>. Therefore the concentration of [Li (PC)<sub>3</sub>]<sup>+</sup> would be higher than that of [Li (PC)<sub>2</sub>]<sup>+</sup>. The results were similar to that in a previous report<sup>1</sup> which showed 3.2 of the solvation number of lithium ion in LiClO<sub>4</sub>/PC. From the consideration on these results, the solvation number obtained by ESI-MS should be reasonable, although the concentration of LiClO<sub>4</sub> and PC was diluted with methanol.

Figure 5 shows ESI-MS spectra of GBL and 1 mM LiClO<sub>4</sub>/MeOH (1:9 vol). The figure shows two high spectra corre-

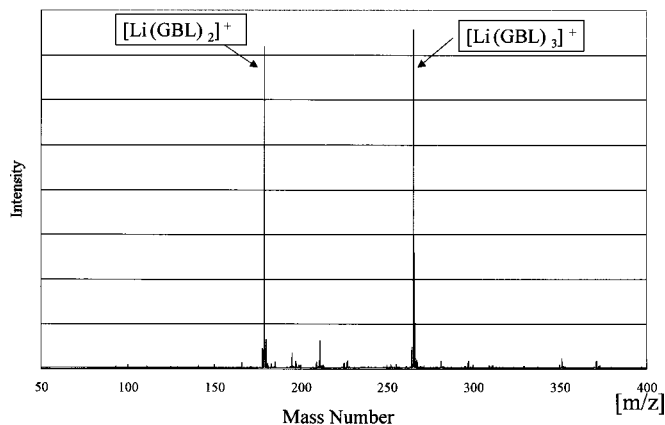


Figure 5. ESI-MS spectra of GBL 1 mM LiClO<sub>4</sub>/MeOH (1:9 by volume).

sponding to [Li (GBL)<sub>2</sub>]<sup>+</sup> ( $m/z = 179.1$ ) and [Li (GBL)<sub>3</sub>]<sup>+</sup> ( $m/z = 265.2$ ). The height of the two peaks are almost the same and these two cationic species are the main species in LiClO<sub>4</sub>/GBL systems and the concentration would be almost 1:1 in a manner similar to that of LiClO<sub>4</sub>/EC in Fig. 3. The coordination number of lithium ion which corresponds to tetrahedral, is four, and the solvation of lithium ion to two or three molecules of EC, PC, or GBL would be possible. As to the mechanism, EC, PC, and GBL would solvate to lithium ion binding of carbonyl groups of these solvent molecules to lithium ion.

### Conclusions

The solvation of lithium ions in EC, PC, and GBL was measured by ESI-MS and a lithium ion solvated to two or three solvent molecules. In LiClO<sub>4</sub>/EC solution, lithium cations solvate mainly as [Li (EC)<sub>2</sub>]<sup>+</sup> and [Li (EC)<sub>3</sub>]<sup>+</sup>, and the concentration of these two species would be almost the same. Main cationic species in LiClO<sub>4</sub>/PC solution are [Li (PC)<sub>2</sub>]<sup>+</sup> and [Li (PC)<sub>3</sub>]<sup>+</sup>, and the concentration of [Li (PC)<sub>3</sub>]<sup>+</sup> is higher than that of [Li (PC)<sub>2</sub>]<sup>+</sup>. In LiClO<sub>4</sub>/GBL, main cationic species are [Li (GBL)<sub>2</sub>]<sup>+</sup> and [Li (GBL)<sub>3</sub>]<sup>+</sup> and the concentration of the two species are almost the same as those in LiClO<sub>4</sub>/EC solution.

### Acknowledgment

The authors thank Ube Industries for donating materials.

Kansai University assisted in meeting the publication costs of this article.

### References

1. Y. Matsuda, H. Nakamura, M. Morita, and Y. Takasu, *J. Electrochem. Soc.*, **128**, 2552 (1981).
2. S. Hyodo and K. Okabayashi, *Electrochim. Acta*, **34**, 1551 (1989).
3. S. Hyodo and K. Okabayashi, *Electrochim. Acta*, **34**, 1557 (1989).
4. B. Klassen, R. Aroca, and M. Nazri, *J. Phys. Chem. B*, **102**, 4795 (1998).
5. M. Morita, Y. Asai, N. Yoshimoto, and M. Ishikawa, *J. Chem. Soc., Faraday Trans.*, **94**, 3451 (1998).
6. J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, and C. M. Whitehouse, *Science*, **246**, 64 (6, Oct. 1989).
7. S. Lee, T. Wytenback, G. von Helden, and M. T. Bowers, *J. Am. Chem. Soc.*, **117**, 10159 (1995).
8. T. G. Spence, T. D. Burns, and L. A. Posey, *J. Phys. Chem. A*, **101**, 139 (1997).
9. M. Strieded, P. Piotrowiak, S. M. Boue, and R. B. Cole, *J. Am. Soc. Mass Spectrom.*, **10**, 254 (1999).