

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

Yoshiharu Matsuda, Tsuyoshi Fukushima, 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

## Introduction

In mixed organic solvents containing lithium salts, the solvation of lithium ions is an important problem in lithium battery technology. The solvent molecules solvated to lithium ions would react preferentially with the electrodes and the chemical species near the electrodes. Therefore the solvated molecules to 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. The authors<sup>6</sup>) reported the solvation of lithium ions in organic solvents measured by electrospray ionization-mass spectroscopy (ESI-MS). In the present work the solvation of lithium ions in mixed organic electrolyte solutions was studied by means of ESI-MS and very interesting results were obtained.

## Experimental

Sample solutions were prepared dissolving LiClO<sub>4</sub> (reagent grade) and binary solvents of ethylene carbonate (EC) and propylene carbonate (PC), dimethyl carbonate (DMC) or diethyl carbonate (DEC) (Lithium battery grade, Ube Industries) in methanol (MeOH) (reagent grade) to decrease the viscosity of the solutions.

The instrument was a mass spectrometer (JEOL-D300) furnished electrospray ionization interface as shown in a previous report<sup>6</sup>). Samples dissolved in methanol were introduced at a rate of 0.15ml/h to the injector whose needle equipped a conductor connecting to a high voltage DC source. High DC voltage was applied on the needle and the samples dissolved in methanol were positively charged. The lithium ions solvated with solvent molecules were introduced together with the solvent was striped there. Then the positively charged sample was injected to mass analyzer. The mass analyzer was capable of analyzing for the samples whose mass numbers were over 50.

## Results and Discussion

ESI-MS spectra of the solvated lithium ions in EC- DMC-

MeOH- 5mM LiClO<sub>4</sub>/ MeOH (0.25: 0.25: 9.00: 1.00 vol.) are shown in Fig.1. Major solvated lithium ion was [Li(EC)<sub>2</sub>]<sup>+</sup> and other solvated species were [Li(EC)<sub>3</sub>]<sup>+</sup> and a small amount of [Li(EC)]<sup>+</sup>. In this case, lithium ions solvate preferentially to EC. Similar results were obtained in the case of 5mM LiClO<sub>4</sub>/ EC- DEC (1:1 vol.) and MeOH (1:9 vol.) solution. However a small peak of [Li(EC)(DEC)]<sup>+</sup> was observed. In the ESI-MS spectra of 5mM LiClO<sub>4</sub>/ EC- PC- MeOH (0.5: 1.0: 9.0 vol.), main peak was due to [Li(PC)<sub>2</sub>]<sup>+</sup> and as the other species [Li(EC)(PC)]<sup>+</sup>, [Li(PC)<sub>3</sub>]<sup>+</sup>, [Li(EC)(PC)<sub>2</sub>]<sup>+</sup>, [Li(EC)<sub>2</sub>(PC)]<sup>+</sup> and [Li(EC)<sub>2</sub>]<sup>+</sup> were detected. The details will be discussed.

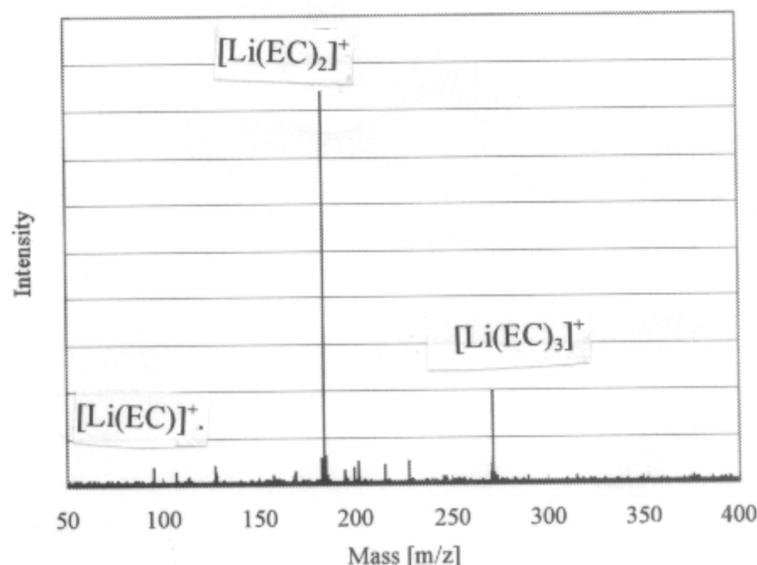


Fig.1 ESI-MS spectrum of EC- DMC- MeOH- 5mM LiClO<sub>4</sub>/ MeOH (0.25: 0.25: 9.00: 1.00 vol.)

## Reference

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