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

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Solvation of lithium ions in mixed organic electrolyte solutions for secondary lithium batteries was investigated by electrospray ionization mass spectroscopy. The electrolyte solutions were mixed binary solutions of diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), γ -butyrolactone (GBL), and propylene carbonate (PC) containing LiClO₄. Lithium ions solvated mainly to two solvent molecules. The order of the inclination of the solvent molecules solvating to lithium ions is PC > EC \approx GBL \gg DEC > DMC.

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In the studies of secondary lithium batteries, solvation of lithium ions in mixed organic electrolyte solutions has been an important problem in view of the development of advanced batteries. The formation of ion-permeable film at the interface between the negative electrodes and electrolyte solutions of secondary lithium batteries has been reported.¹⁻⁴ In such process, the solvent molecules react with the negative electrode and also probably react with the positive electrode. In mixed organic electrolyte solutions, solvent molecules which are solvated preferentially to lithium ions would react with the electrodes and the chemical species near the electrodes. Therefore, the solvated molecules to lithium ions would concern the film formation at the interface between the electrode and the electrolyte and affect the composition of the film formed.⁴

As to the solvation of lithium ions in the organic electrolyte solutions some papers have been reported. In these previous papers,⁵⁻¹² Raman spectroscopy, nuclear magnetic resonance, and conductivity measurement varying the composition of the solutions were applied to study the solvation. The results were somewhat different for the mixed solvent systems depending on the measuring methods. Electrospray ionization-mass spectroscopy (ESI-MS) emerged as a powerful technique for producing intact ions *in vacuo* from large and complex species in solution and was first applied to mass spectrometric analysis to large and fragile polar biomolecules in the gas phase.¹³ In the paper,¹³ nonvolatile small molecules and large biomolecules were diluted at concentrations from 2 to 100 ppm in 50:50 methanol:water. Then it spread to analytical studies of alkali metal cations solvent complexed with 18-crown-6,¹⁴ transition-metal ion complexed with solvent,¹⁵ and alkali metal cations/solvent binding.¹⁶ In a previous paper,¹⁷ ESI-MS was first introduced into the estimation of solvation number of solvents to lithium ion in single aprotic solvents containing lithium salts. At the present time, ESI-MS is used widely in the investigation of ionic species of molecular weight of *ca.* 50.

In view of preferential solvation of solvent molecules to a cation in mixed organic electrolyte solutions, the donor number of the solvent has been considered to be a measure of solvent/cation interaction,¹⁸⁻²¹ but the solvation of lithium ions in mixed organic electrolyte solutions has not been studied actively. In the present work, the solvation of lithium ions in mixed organic electrolyte solutions in which the structure of solvated lithium ions had not been investigated was studied by means of ESI-MS to clarify the solvation of lithium ions in the electrolyte solution of secondary lithium batteries and very interesting results were obtained.

Experimental

Sample solutions were prepared using LiClO₄ (reagent grade), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylene carbonate (EC), γ -butyrolactone (GBL), propylene carbonate (PC), (lithium battery grade, Ube Industries), and methanol (MeOH) (reagent grade). The dilute solutions were prepared by mixing the binary mixed aprotic solvent containing 0.5×10^{-6} mol/L LiClO₄ and methanol in the volumetric ratio of 1:20, because a low viscous solution is necessary for passing the solution through the feeding nozzle of electrospray ionization mass spectrometer.

The details of ESI-MS have been presented in a previous paper.¹⁷ The instrument was a mass spectrometer (JEOL-D300) furnished with an electrospray ionization interface. Samples diluted with methanol were introduced at a rate of 2.5 μ L/min to the injector whose nozzle was equipped with a conductor connecting to a high voltage direct current (dc) source. High dc voltage applied on the nozzle and the samples contained in methanol were positively charged. The lithium ions solvated to the aprotic solvent molecules were introduced together with methanol, through a path of which temperature was controlled by heated nitrogen gas, to a skimmer, and methanol and free aprotic solvents were stripped there. Then the solvated lithium ions were injected into the mass analyzer.

Results and Discussion

Among the organic electrolyte solutions of commercial secondary batteries mixed DEC-EC and DMC-EC with LiPF₆ are common solutions.^{21,22} However, the details of the solvation of lithium ions to these solvent molecules have not been clarified. In Fig. 1, ESI-MS spectra of mixed solution of 0.5 mol/L LiClO₄/DEC-EC (1:1 vol) and methanol (1:20 vol) are represented. The solvation of lithium ions in this solution is assumed to be similar to that in LiPF₆/DEC-EC (1:1 vol)-methanol (1:20 vol). In the solution, the mol ratio of Li⁺:DEC-EC: methanol was larger ratio than 10^{-6} : 10^{-4} : 10^{-2} . As represented in the paper,¹⁷ lithium ions solvate preferentially to EC and/or DEC in the mixed solution with methanol. As mentioned in the Introduction,¹³ test ionic species which had been contained in a large amount of solvent were analyzed in the gas phase. This procedure has been commonly used in ESI-MS.

The solvation of alkali metal cations to solvents dimethylacetamide or dimethylformamide was investigated using 4 mM alkali metal halide solution of eqimolar MeOH/EtOH/*n*-PrOH.²³ Also formation of alkali metal halide cluster ions from the methanol solution,²⁴ chloride adduct ions of organic compounds methanol-chloroform (19:1),²⁵ and the effect of magnesium ion in the analysis of carboxylated compounds diluted in a large amount of water have been reported.²⁶ Referring to these papers, methanol and free aprotic solvents were eliminated by vaporization in the skimmer of the ESI-MS instrument and the ESI-MS spectra showed the structure of solvated lithium species directly.

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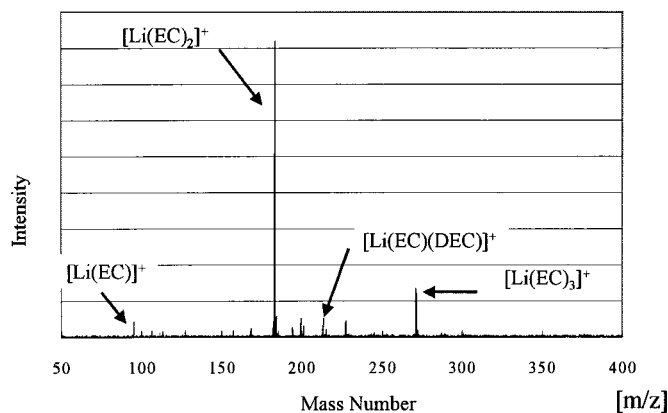


Figure 1. ESI-MS spectra of 0.5 mol/L $\text{LiClO}_4/\text{EC-DEC}$ (1:1 vol) and methanol (1:20 vol).

Figure 1 represents ESI-MS spectra of the mixed solution of 0.5 mol/L $\text{LiClO}_4/\text{DEC-EC}$ (1:1 vol) and methanol (1:20 vol). The figure shows a large peak owing to $[\text{Li}(\text{EC})_2]^+$ and small peaks owing to $[\text{Li}(\text{EC})_3]^+$, $[\text{Li}(\text{EC})(\text{DEC})]^+$, and $[\text{Li}(\text{EC})]^+$. From the results, lithium ions solvate mainly to two EC molecules and in part to three EC molecules, one EC and one DEC molecule together, and one EC molecule.

In previous papers, the donor number (DN) of a solvent has been used to describe the nucleophilic behavior and the solvent whose DN is higher would solvate preferentially to a cation in a solution of mixed solvent.¹⁸⁻²¹ However, the solvation of cations in a EC-DEC system has not been reported. The donor numbers of EC, DEC, and methanol are 16.4, 15.1, and 19.2, respectively,²⁰ and the difference of that between EC and DEC is very small. The results by ESI-MS show that the distribution of the solvated ions do not relate closely to the donor numbers of the solvents. Lithium ions were solvated preferentially to EC, and main solvated species were $[\text{Li}(\text{EC})_2]^+$. At the same time small peaks of $[\text{Li}(\text{EC})_3]^+$, $[\text{Li}(\text{EC})]^+$, and $[\text{Li}(\text{EC})(\text{DEC})]^+$ were observed in the spectra.

These results do not compare with that by any other methods because the data of the solvation of lithium ions in the solutions used in the present work have not been reported. However, in the studies of the electrolyte solutions of primary lithium batteries, the solution of lithium ions in a dimethoxyethane (DME)-PC system was investigated and $[\text{Li}(\text{PC})_2]^+$ and $[\text{Li}(\text{DME})(\text{PC})]^+$ were measured by means of laser Raman spectroscopy⁵ and conductivity measurement varying the composition of the solutions,¹¹ respectively. In

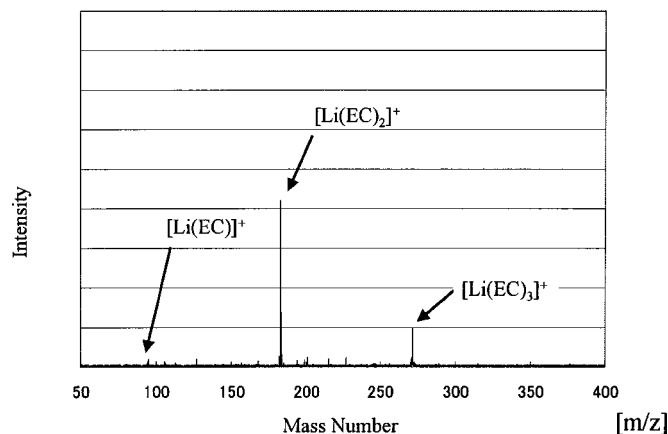


Figure 2. ESI-MS spectra of 0.5 mol/L $\text{LiClO}_4/\text{EC-DMC}$ (1:1 vol) and methanol (1:20 vol).

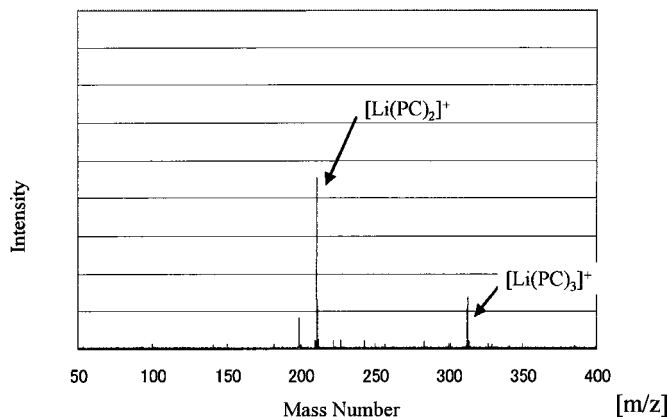


Figure 3. ESI-MS spectra of 0.5 mol/L $\text{LiClO}_4/\text{PC-DEC}$ (1:1 vol) and methanol (1:20 vol).

the previous work using ESI-MS, it was clarified that the main ionic species were $[\text{Li}(\text{DME})(\text{PC})]^+$ in $\text{LiClO}_4/\text{DME-PC}$.²⁷ These results by ESI-MS agree with that by conductivity measurement. On the other hand, as ESI-MS have been used in the investigation of the solvation of many kind of ions, the results shown in Fig. 1 would be expected to suggest directly the solvation of lithium ions. The difference of steric effects²⁷ of EC and DEC on the solvation to lithium ions would cause the different behavior. The solvation though carbonyl groups of EC and DEC, and oxygens in ether bonds of DEC would coordinate to lithium ions. Because the results in the present work were obtained using solutions diluted with large amounts of methanol, the ionic association in $\text{LiClO}_4/\text{DEC-EC}$ was not clarified and also the solvation of lithium ions might be influenced changing electrolytic salts.²⁸ However, the spectra would indicate some direct information of the solvation of lithium ions in the mixed organic solvents.²⁹

ESI-MS spectra of the mixed solution of 0.5 mol/L $\text{LiClO}_4/\text{DMC-EC}$ (1:1 vol) and methanol (1:20 vol) are shown in Fig. 2. In the figure, a large peak corresponding to $[\text{Li}(\text{EC})_2]^+$ and a small peak owing to $[\text{Li}(\text{EC})_3]^+$, and a fine peak, are observed. In the case of this solution, no DMC molecule solvated to lithium ions. The results of Fig. 1 and 2 show that each lithium ion solvates mainly to two EC molecules.

Figure 3 and 4 show ESI-MS spectra of the mixed solutions of 0.5 mol/L $\text{LiClO}_4/\text{DEC-PC}$ (1:1 vol) and DMC-PC (1:1 vol), respectively. Similar results to that used DEC-EC and DMC-EC as the aprotic solvents in Fig. 1 and 2 were obtained. In the ESI-MS spectra of PC-DEC system, a large peak of $[\text{Li}(\text{PC})_2]^+$ and a small peak

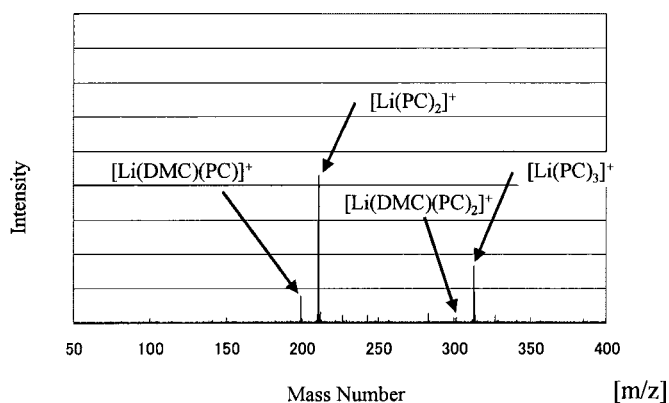


Figure 4. ESI-MS spectra of 0.5 mol/L $\text{LiClO}_4/\text{PC-DMC}$ (1:1 vol) and methanol (1:20 vol).

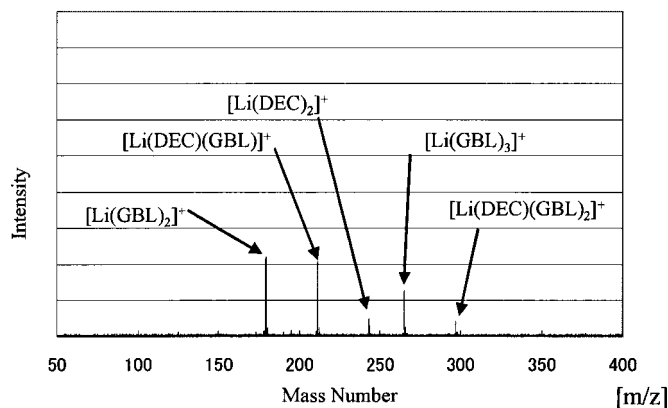


Figure 5. ESI-MS spectra of 0.5 mol/L LiClO_4 /GBL-DEC (1:1 vol) and methanol (1:20 vol).

of $[\text{Li}(\text{PC})_3]^+$ are observed. However in the case of the PC-DMC system as shown in Fig. 4, a large main peak of $[\text{Li}(\text{PC})_2]^+$ and small peaks of $[\text{Li}(\text{PC})_3]^+$, $[\text{Li}(\text{DMC})(\text{PC})]^+$, and $[\text{Li}(\text{DMC})_2(\text{PC})]^+$ are obtained.

The DN of PC is 15.1 which is near the value of EC, 16.4. Therefore some different behavior in the results of the solvation of lithium ions in DEC-EC and DEC-PC system would be caused by the different steric effect of EC and PC to lithium ions.

The ESI-MS spectra of the mixed solution of 0.5 mmol/L LiClO_4 /GBL-DEC (1:1 vol) and methanol (1:20 vol) are somewhat complicated. In the spectra shown in Fig. 5, two large peaks corresponding to $[\text{Li}(\text{GBL})_2]^+$ and $[\text{Li}(\text{GBL})(\text{DEC})]^+$, a middle peak owing to $[\text{Li}(\text{GBL})_3]^+$, two small peaks due to $[\text{Li}(\text{DEC})_2]^+$ and $[\text{Li}(\text{GBL})_2(\text{DEC})]^+$ and a trace peak of $[\text{Li}(\text{DEC})]^+$ are observed. The height of these peaks would approximately reflect on the relationships of the concentration of solvated kinds of lithium ions.

The ESI-MS spectra of LiClO_4 /DMC-GBL (1:1 vol) and methanol (1:20 vol) are shown in Fig. 6. In the figure, a large peak of $[\text{Li}(\text{GBL})_2]^+$ and a small peak of $[\text{Li}(\text{GBL})_3]^+$ are observed. The spectra in Fig. 6 are simpler than that of LiClO_4 /DMC-GBL in Fig. 5. The cause of this different behavior would be the difference of electric property of the carbonyl group in DMC and EC corresponding to the substitution by methyl group.

The mixed organic solvent of EC-PC has been presumed to be suitable for the electrolyte solution of secondary lithium metal batteries. Figure 7 represents the spectra of LiClO_4 /EC-PC (1:1 vol) and MeOH (1:20 vol). In the figure a large peak corresponding to

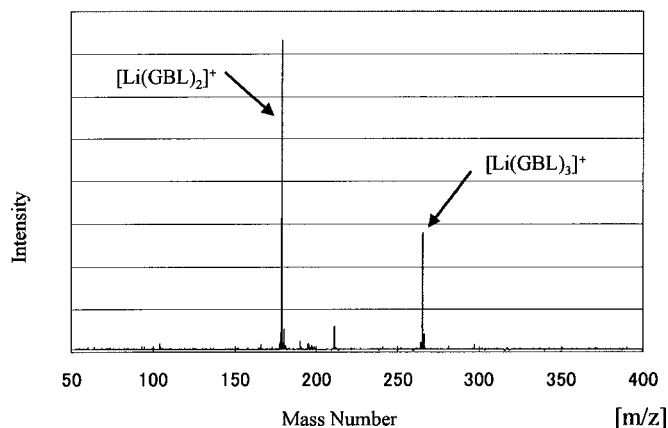


Figure 6. ESI-MS spectra of 0.5 mol/L LiClO_4 /DMC-GBL (1:1 vol) and methanol (1:20 vol).

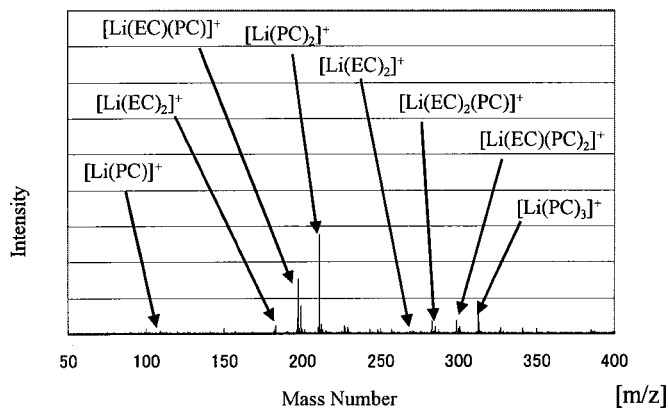


Figure 7. ESI-MS spectra of 0.5 mol/L LiClO_4 /EC-PC (1:1 vol) and methanol (1:20 vol).

$[\text{Li}(\text{PC})_2]^+$ and a mediate peak of $[\text{Li}(\text{EC})(\text{PC})]^+$ are observed with small peaks due to $[\text{Li}(\text{PC})]^+$, $[\text{Li}(\text{EC})_2]^+$, $[\text{Li}(\text{EC})_2(\text{PC})]^+$, $[\text{Li}(\text{EC})(\text{PC})_2]^+$, and $[\text{Li}(\text{PC})_3]^+$. The results suggest that lithium ions solvate mainly to two solvent molecules of the solvents and a little amount of lithium ions solvate to three or one solvent molecules. In a previous paper,¹⁷ lithium ions solvated to two or three molecules in single EC, PC, and GBL. However, lithium ions solvated to two solvent molecules in the mixed organic electrolyte solutions in the represent work. Therefore some interaction would occur between two different solvent molecules. In comparison of EC and PC, lithium ions prefer to solvate to PC than EC because the addition of a methyl group induces the increase of negative electric charge density on the oxygen of carbonyl group resulting stronger solvation to lithium ion.

The ESI-MS spectra of LiClO_4 /GBL-EC (1:1 vol) and LiClO_4 /GBL-PC (1:1 vol) and MeOH (1:20 vol) are shown in Fig. 8 and 9, respectively. A large peak corresponding to $[\text{Li}(\text{EC})(\text{GBL})]^+$ is observed in Fig. 8. Furthermore, two mediate peaks due to $[\text{Li}(\text{GBL})_2]^+$ and $[\text{Li}(\text{EC})_2]^+$ and other four small peaks identified to $[\text{Li}(\text{GBL})_3]^+$, $[\text{Li}(\text{EC})(\text{GBL})_2]^+$, $[\text{Li}(\text{EC})_2(\text{GBL})]^+$, and $[\text{Li}(\text{EC})_3]^+$ are represented in the figure. Comparing these spectra and the results shown in Fig. 7, the inclination of EC and GBL for solvation to lithium ions are similar. In Fig. 9, two large peaks due to $[\text{Li}(\text{PC})_2]^+$ and $[\text{Li}(\text{GBL})(\text{PC})]^+$ and three mediate peaks connecting to $[\text{Li}(\text{PC})_3]^+$, $[\text{Li}(\text{GBL})(\text{PC})_2]^+$, and $[\text{Li}(\text{GBL})_2(\text{PC})]^+$ are apparent with a small peak owing to $[\text{Li}(\text{GBL})_2]^+$. PC would have stronger inclination solvating to lithium ion than GBL.

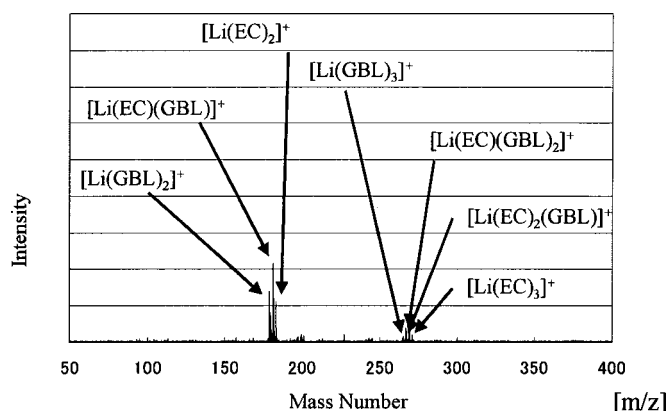


Figure 8. ESI-MS spectra of 0.5 mol/L LiClO_4 /EC-GBL (1:1 vol) and methanol (1:20 vol).

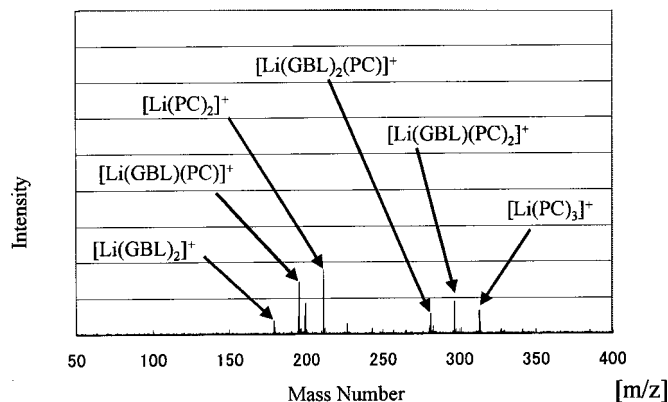


Figure 9. ESI-MS spectra of 0.5 mol/L LiClO_4 /GBL-PC (1:1 vol) and methanol (1:20 vol).

Conclusions

The solvation of lithium ions in mixed organic solvents, DEC-EC, DMC-EC, DEC-PC, DMC-PC, DEC-GBL, DMC-GBL, EC-PC, EC-GBL, and PC-GBL, was investigated by ESI-MS using the diluted solutions with MeOH. MeOH was evaporated and eliminated through the analysis, and the spectra of solvated lithium ions were directly obtained. Throughout the experiment of the ESI-MS lithium ions solvated to one, two, or three solvent molecules of EC, DEC, DMC, GBL, and/ or PC. Lithium ions seem to solvate mainly to two solvent molecules in the mixed organic electrolyte solutions. The inclination of solvent molecules solvating to lithium ions would connect to the negative charge density on the oxygen atom of carbonyl group of the solvent molecule and the steric effect. For the solvents, the order of the inclination solvating to lithium ions is $\text{PC} > \text{EC} \approx \text{GBL} \gg \text{DEC} > \text{DMC}$

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