

Solvation Structure of Electrolyte : Environment of Alkyl Group in Concentrated Linear Carbonate

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Abstract

Lithium ion battery(LIB) is indispensable material in daily life for the portable energy storage devices. For this reason, various studies of LIB have been steadily done specially in the efficiency of this battery. In this investigation, We focus on electrolytes, which is a major component of LIB system, used for transporting Li ion between cathode and anode. There are many researches how electrolytes, in general carbonates, form solvation structure and this structure is involved in the mobility of Li ion. Most of these researches are concerned about interaction of Li ion with carbonyl oxygen, but we are interested in alkyl chain interaction with something. We carefully propose that the environment of alkyl chain has an effect on the solvation structure and macroscopic properties.

Introduction

Conductivity, one of the major property of electrolytes, is standard of the efficiency of battery. This property is related to other physical property, dielectric constant and viscosity which indicate the solubility and mobility of Li ion. those property has been enough to explain the efficiency of LIB.

	Electrolyte	Structure	Dielectric constant	Viscosity (mPa)
Cyclic carbonate	Ethylene Carbonate(EC)		89.78	1.9
	Propylene Carbonate(PC)		64.92	2.53
Linear carbonate	Dimethyl Carbonate(DMC)		3.107	3.107
	Diethyl Carbonate(DEC)		2.805	2.805

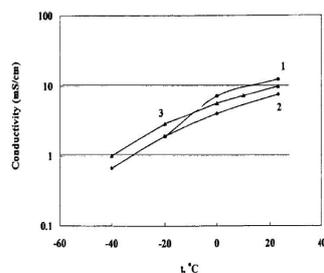


Table 1. Physical properties of Electrolyte solvents

Figure 1. Ionic conductivity of electrolytes containing 1.0M LiPF₆ in (1) EC/DMC(3:7) (2) EC/DEC(3:7) (3) EC/DMC/DEC(1:1:1)

However, In linear carbonates, although the difference of dielectric constant and viscosity is small compared with cyclic carbonate, DMC has much larger conductivity than DEC. This result can't be explained by those macroscopic property. Thus, We think that this result is associated with microscopic property like solvation structure.

Experiment & Results

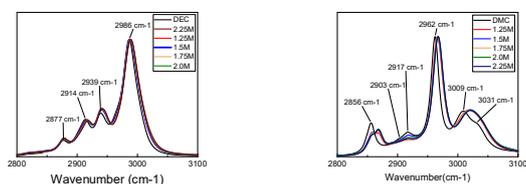


Figure 2. The FT-IR spectra of ethyl and methyl symmetric stretch of DEC and DMC

Above all, we make various concentration solution of DMC and DEC, setting maximum ionic conductivity of DMC(1.75 M) and DEC(1.5 M) as a standard, using LiPF₆ to Li Ion source. In this spectra, we can observe dynamic changes of CH₃ stretch of DMC than those of DEC. So we check out which change can occur in alkyl chain.

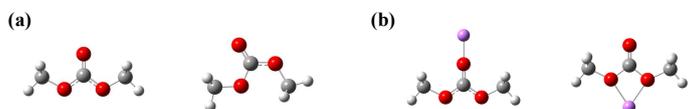


Figure 3. (a) Two conformers of DMC. (Left) cis-cis form (Right) cis-trans form.

(b) Two Li ion --- DMC dimer structures. Li ion in DMC solution can interact with (Left) carbonyl oxygen atom, or (Right) with two ester ether oxygen atoms of DMC molecule.

DMC and DEC have two conformers, cis-cis and cis-trans form (figure 3). We suggest that the change of CH₃ stretch is caused by exchange of those two conformers. Then, the investigation of possibility of free rotation on ester ether bond is necessary.

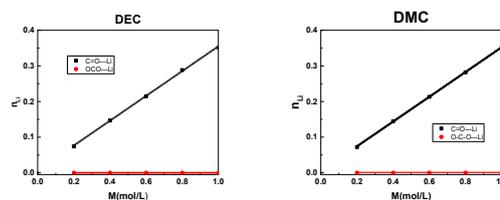


Figure 4. (a) coordination number of C=O---Li and O-C-O---Li Classical MD Simulation

First, we research the presence of Li ion interaction with two ester ether which hinder the free rotation of ester ether. Though the Classical Molecular Dynamic simulation, we can confirm this interaction is much less enough to ignore.

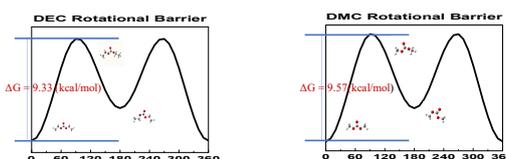


Figure 5. Rotational Barrier of ester ether bond of DEC and DMC

Second, we check out the possibility of the free rotation at room temperature. Quantum Mechanics computation reveals that the free rotation is possible, because the environments of room temperature are able to jump the barrier about 10 kcal/mol.

Conclusion

There are differences of CH₃ stretch between DEC and DMC. We are still investigating this reason to collecting data through various experiment using spectroscopy and MD & QM simulation.

Reference

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- Amines ; Synthesis properties and Applications

Acknowledge

This work was supported by the Institute for Basic Science (IBS) R023-D1