Properties of a New Electrolyte Solution for Li-ion Batteries*

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Abstract: Recently, the choice and use of new electrolyte solvents are getting more and more important to improve the reversible capacity and cycle ability of lithium ion batteries. In our experiments, we chose the binary solvents of EC and DMC with different concentrations and used them in the button cells ($LiCoO_2$ cathode and arbonaceous Mesophase Spheres (CMS) anode) to investigate the electrochemical properties of the electrolytes. From the experiments, we concluded that the best composition ratio of 1 mol/L $LiPF_6$ in EC/DMC (3∶7 volume ratio) was shown to improve the carbon electrode reversibility and long-term cycle ability when compared with the other concentrations.

Key words: EC (ethylene carbonate); DMC (dimethyl carbonate); SEI (solid electrolyte interface)
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1 Introduction

Since 1991, the lithium ion battery of Sony Company has appeared on market. More and more researchers paid attention to it. Moreover, most studies have been on developing new electrode materials and new electrolyte for Li-ion batteries. The choice and use of electrolytes are becoming more and more important to improve the capacity and cycling properties of lithium ion batteries.

The theoretical formula of conductivity of solvents is[1]

$$k = \frac{\sum i[(Z_i)2FC_i]}{6\pi\eta\gamma_i} \quad (1)$$

Z_i is the charge number of I ion; C_i is the molar concentration of I ion; F is the Faraday constant; η is the viscosity of the solvent; γ_i is the solvent radius of I ion.

From (1) we can see C_i and η are important factors of the conductivity. We intend to find a solvent with high dielectric constant and low viscosity, but from Tab. 1 we can see the solvent with high dielectric constant always has high viscosity, and the one with low viscosity always has low dielectric constant. In fact, we often choose a solvent with high dielectric constant and the others have low viscosity, and then mix them together to get new binary solvents with higher dielectric constant and lower viscosity. The physiochemical properties of carbonate solvents commonly used in Li-ion batteries were listed in Tab. 1

Tab 1 Physiochemical properties of carbonate solvents commonly used in Li-ion batteries (25 ℃)[2-4]

items	EC	PC	DMC	EMC	DEC
Viscosity/ (10^{-3} Pa·s^{-1})	1.93[1)]	2.5	0.5889	0.6478	0.7534
Dielectric constant ε	89.78[1)]	65	3.1	2.9	2.8
Oxidization potentials /V (*vs.* Li^+/Li)	5.8[2)]	5.8[2)]	5.7[2)]	—	5.5[2)]
AN	—	18.9	3.6	—	2.6
DN	16.4	15.1	8.7	—	8.0
Boling point/℃	238	242	90	108	127
Melting point/℃	37	−49	3	−55	−43

1) At 40℃; 2) On surface of glass carbon under 20℃

2 Experimental

Some solvents have high dielectric constant, such as ethylene carbonate (EC) and propylene carbonate (PC), some solvents have low viscosity, such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethyl carbonate (EMC), we chose the binary solvents of ethylene carbonate (EC/dielectric constant: 89.78, viscosity: 1.93×10^{-3} Pa·s^{-1}) and dimethyl carbonate (DMC/dielectric constant: 3.1, viscosity: 0.5889×10^{-3} Pa·s^{-1}) to investigate the electrochemical behaviors in Li-ion batteries. We make button cells of $LiCoO_2$ cathode materials and Carbonaceous Mesophase Spheres (CMS) anode materials to investigate the electrochemical properties of the electrolytes with different concentration. (Tab. 2)

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Tab 2 Physiochemical properties of the binary solvents of EC and DMC with different concentrations in the experiments (1 mol/L $LiPF_6$)

EC: DMC	1∶1	3∶7	2∶8	7∶3	8∶2
Conductivity/ ($ms \cdot cm^{-1}$)	11.9	11.9	11.4	10.3	9.5
Water/10^{-6}	5.7	9.6	9.2	8.7	8.2
HF/10^{-6}	28.6	21.1	17.9	19.3	22.2
Density/ ($g \cdot cm^{-3}$)	1.281	1.238	1.206	1.336	1.361
No. of APHA	10	20	20	20	30

The button cells were changed at constant current of 0.5 mA to reach 4.2 V over 5 hours and then discharged to 2.5 V. The charge and discharge were repeated 50 times at 25 ℃. After 10 cycles the carbon electrodes were recovered from the button cells and rinsed with DME (1, 2-dimethoxythame) solvent and then dried in vacuum at room temperature to evaporate the DME solvent. Furthermore, the scanning electron microscope (SEM) and fourier infrared ray (FTIR) were applied to analyze the carbon electrodes (Fig. 2, 3).

3 Results and discussion

The most important function of the SEI is to block co—intercalation of the electrolytic solvents into the graphite plane layers so that both solvents reduction and graphite exfoliation are minimized or entirely eliminated. Furthermore, capacity retention and storage life of the Li-ion batteries directly depend on the stability of the SEI[5]. Therefore, the formation of the SEI has been recognized to be an essential process in the manufacture of lithium ion batteries. It is known that formation of the SEI on the surface of graphite must be completed during the initial few cycles. The much lower Coulomb Efficiency (CE) in the second cycle is due to the irreversible reduction of the electrolytic solvents (Fig. 1 EC∶DMC = 3∶7), which would must significantly affected by the catalytic effect of the fresh surface of the carbon electrode. A substantial increase of the CE in the third cycle is probably because of the catalytic effect of the graphite was invalided as a result of the insoluble products covering the catalytic sites during the first and the second cycle, which suppresses solvent co-intercalation and graphite exfoliation. From Fig. 1 we can see the button cell made with electrolyte of EC∶DMC =3∶7 (1 mol/L $LiPF_6$) and EC∶DMC = 1∶1 (1 mol/L $LiPF_6$) had a much lower CE in the second cycle and this would be most significantly affected of the fresh surface of the graphite; and then a substantial increase of CE in the third cycle is probably because the catalytic effect of the graphite was invalided as a result of the insoluble products during the first and second cycle. Which suppresses solvent co-intercalation and graphite exfoliation. The former and the latter all had a SEI on the surface of the graphite, but the former (EC∶DMC = 3∶7) has the better cycle life. Fong, et al[6] have identified that the formation of an efficient SEI is therefore the key for the achievement of a good reversibility of the battery even for prolongated cycling.

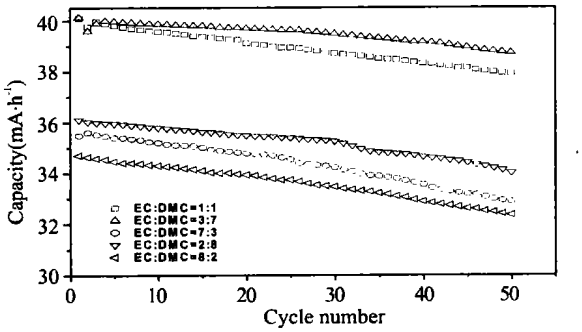

Fig 1 Capacity *vs.* cycle number of button cells ($LiCoO_2$ cathode and CMS anode) with 1 mol/L $LiPF_6$ electrolytes

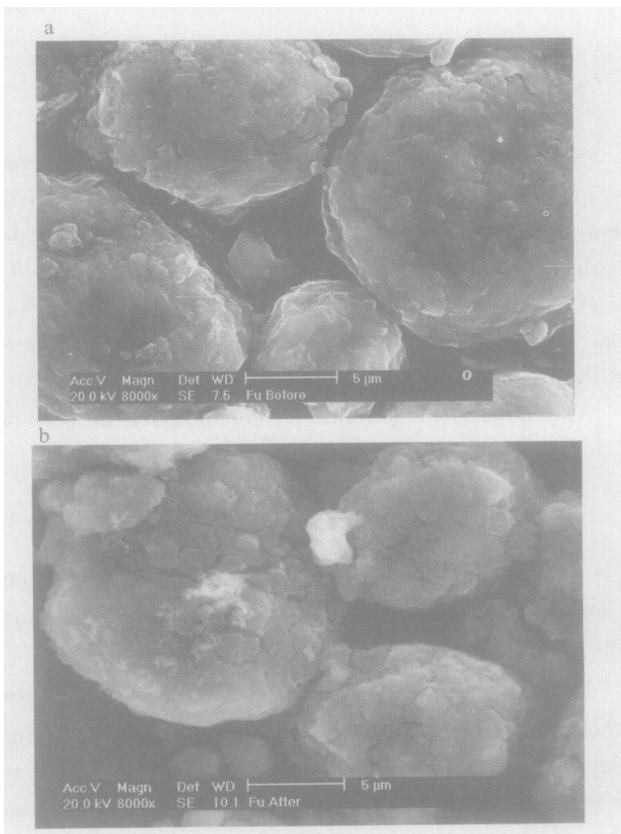

Fig 2 SEM micrographs of graphite anode of buttons cells ($LiCoO_2$ cathode, CMS anode and 1 mol/L $LiPF_6$ EC∶DMC = 3∶7) before cycles(a) and after 10 cycles(b)

Fig. 2b shows a typical SEM graph of the CMS anode after electrochemical experiments. From Fig. 2b we can see the surface of the graphite particle is different from the one prior to the electrochemical experiments (Fig. 2a), and this also can be certified by the FTIR spectra of carbon electrode after 10 cycles (Fig. 3). The most important function of the SEI is to block co-intercalation of the electrolytic solvents into the graphite plane layers so that both

solvent reduction and graphite exfoliation are minimized or entirely eliminated. Aurbach et al[7] have reported that the SEI is mainly composed of the insoluble solid products of solvent reduction, which is completed in the initial few cycles. From the FTIR spectra of the carbon electrode of the button cells made with 1 mol/L $LiPF_6$ (EC∶DMC=3∶7) (Fig. 3), we can see the SEI is mainly composed of the $LiPF_6$ (840, 1 276 cm^{-1}), EC (1 176, 1 498 cm^{-1}), $ROCO_2Li$ (1 071, 1 332, 1 403 and 1 498 cm^{-1}) and Li_2CO_3 (863 cm^{-1}), and these were just in accordance with the results of Wanuk Choi's experiments. These results indicate that the electrolyte and the solvent are decomposed into $ROCO_2Li$ and Li_2CO_3 on the surface of Li insertion. Aurbach et al[7] have reported that the major surface species on carbon electrodes are $ROCO_2Li$ and Li_2CO_3. The former was formed by decomposition of solvent and the latter could be formed either by further reduction of $ROCO_2Li$ in the presence of Li ions, or by reaction of $ROCO_2Li$ with trace water.

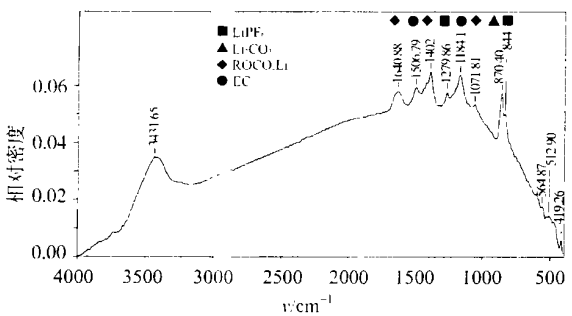

Fig. 3　FTIR spectra of carbon electrode in 1 mol/L $LiPF_6$/EC∶DMC=3∶7 after 10 cycles

From the experiments, we concluded that the best composition ratio of 1 mol/L $LiPF_6$ in EC/DMC (3∶7 volume ratio) was shown to improve the carbon electrode reversibility and long-term cyclebility when compared with the other concentrations.

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一种新型锂离子二次电池用有机电解液的性能研究

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摘　要：为了提高锂离子二次电池的笔容量和循环寿命，研究者们越来越重视有机电解液的使用及选择。实验选择了 EC 和 DMC 二元体系，将其以不同体积配比用于锂离子二次扣式电池中（正极材料为 $LiCoO_2$，负极材料为 CMS，电解质盐为 $LiPF_6$）以研究电解液的电化学性能。通过实验，发现此种电解液的最佳配比为 EC∶DMC=3∶7（1 mol/L $LiPF_6$），此种电解液大大提高了电池的循环性能。

关键词：EC（碳酸二乙酯）；DMC（二甲基碳酸酯）；SEI（固体电解质膜）
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