

## Relationship between carbonaceous materials and electrolyte in secondary lithium-ion batteries

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### Abstract

We have examined the initial charge characteristics of the following prototype battery: (i) positive electrode:  $\text{LiCoO}_2$ ; (ii) negative electrode: meso-carbon micro-beads (MCMB) with heat treatment at 2800 °C; (iii) electrolyte: mixture of ethylene carbonate (EC) and other solvent(s), and mixture of EC+diethyl carbonate (DEC) and other solvents dissolved with  $\text{LiPF}_6$ , and (iv) battery: cylinder-type battery, in which positive and negative electrodes are spirally wound. We found that electrolytes which contain methyl acetate (MA), methyl propionate (MP) and ethyl propionate (EP) showed good performances. In general, when the distance between carbon layers  $d(002)$  value became smaller, the charge/discharge capacity became higher when the carbon electrode was charged to 0 V versus metallic Li electrode. We prepared a cylinder-prototype battery by using 1.5 M  $\text{LiPF}_6/\text{EC}+\text{DEC}+\text{MP}$  as electrolyte and examined its stability at conditions of regular use and found, when it was charged and stored at high temperature, the ester-exchange reaction product of the electrolyte occurred and methane gas at the negative electrode and gas mainly carbon monoxide (CO) and carbon dioxide ( $\text{CO}_2$ ) at the positive electrode were formed. In the case of an electrolyte with mixed solvents, it was assumed that the ester-exchange reaction and gas-evolution reaction by oxidation/reduction may have taken place.

*Keywords:* Carbonaceous materials; Electrolytes; Secondary lithium batteries

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### 1. Introduction

Secondary lithium-ion batteries using  $\text{LiCoO}_2$  as positive electrode and carbon as negative electrode show higher energy density than the conventional batteries such as Ni/Cd and Ni/MH batteries. Therefore, secondary lithium-ion batteries have been developed by various organizations nowadays. Since the crystal structure of carbonaceous materials, as a negative electrode, involves quite different characteristics, many researches have been conducted on this subject.

Table 1 shows results of recent research on different kinds of carbonaceous materials [1–9]. Performances have been evaluated with use of test cells with two or three electrodes and metallic lithium as counter electrode. The electrolytes and test conditions were specified by each researcher. When carbonaceous material with a high degree of crystallization was used in the electrolyte containing propylene carbonate (PC), PC is decomposed during charging and as a result, the graphitized electrode

cannot be charged sufficiently. The capacity at the initial charge and discharge (IIC = initial irreversible capacity) was significantly different by the combination of the carbonaceous material and the electrolyte. IIC is a very important factor for the design of the capacity of both the positive and negative electrodes of a lithium-ion secondary battery, since this battery is activated (initially charged) in a cell. The amount of gas formed at the initial stage and during charge/discharge and storage is an important factor for the design of the battery, including safety issue.

In order to find a stable electrolyte with a small IIC and capable of a good charge/discharge when carbonaceous material of graphite group is used, we have examined various electrolytes in a cylinder-type battery with spirally wound electrodes, in which both the amount of the electrolyte and the capacity of positive electrode are limited to small values and the conditions of regular use can be simulated. We also examined various carbonaceous materials in a coin-type battery with metallic lithium as the counter electrode.

Table 1  
Characteristics of carbon electrodes for lithium-ion secondary batteries

Classification	Ref. No.	Test cell	Electrolyte	Current density (mA cm <sup>-2</sup> )	Discharge capacity (mAh g <sup>-1</sup> )	Efficiency (%)
Graphite	[1]	3E-system <sup>a</sup>	1 M LiPF <sub>6</sub> -EC		370	1st cycle 92
	[2]	Coin battery	1 M LiPF <sub>6</sub> -EC+DEC(1:1)	0.13	192	1st cycle 83
Coke	[3]	2E-system <sup>b</sup>		0.53	220–250	
	[1]	3E-system	1 M LiPF <sub>6</sub> -PC	0.2	180–240	
Carbon fibre	[4]	2E-system	1 M LiClO <sub>4</sub> -PC+DME(1:1)	0.35	83	5th cycle > 90
	[5]	3E-system	1.5 M LiClO <sub>4</sub> -PC		160	
	[6]	3E-system	1 M LiClO <sub>4</sub> -AN+EC(3:1)	2.0	160	
	[7]	3E-system	1 M LiClO <sub>4</sub> -EC+DMC		290	1st cycle 93
	[8]	2E-system	1 M LiPF <sub>6</sub> -PC	0.5	180–270	1st cycle 70–82
	[9]	Coin battery	1 M LiPF <sub>6</sub> -EC+DEC(1:1)	0.3	246	
Meso-carbon microbeads	[8]	2E-system	1 M LiPF <sub>6</sub> -PC	0.5	250–270	1st cycle 70–82
	[6]	3E-system	1 M LiClO <sub>4</sub> -AN+EC(3:1)	2.0	250	

<sup>a</sup> 3E: Three-electrode system.

<sup>b</sup> 2E: Two-electrode system.

## 2. Experimental

### 2.1. Investigation of the most suitable electrolyte

LiCoO<sub>2</sub>, acetylene black as an electric conductor and fluoride resin as a binder were mixed together. The positive electrode was prepared by coating the above mixture on both sides of an aluminium foil of 30 μm thickness. The total thickness of the positive electrode, thus prepared, was 200 μm. A porous membrane of polyethylene of 25 μm thickness was used as a separator. Various mixtures of EC with other solvent(s) and of EC+DEC with other solvents were tested in the prototype cylindrical battery of 'A'-size, in which the electrodes were spirally wound together. Charge characteristics for activation (initial charge), IIC and low-temperature characteristics were mainly examined and the most suitable electrolyte has been tested. The battery was charged at a constant current of rate of 0.2 C (140 mA) at 20 °C with a cutoff voltage of 4.1 V.

### 2.2. Investigation of suitable carbonaceous materials

We found that the mixture of EC+DEC (2:8) remained stable during charging at room temperature. Therefore, we used the electrolyte made of this solvent and metallic lithium of a much higher capacity than the positive as negative electrode, and evaluated various carbonaceous materials in a coin-type battery of R2016 size. We repeated the charge/discharge at a current density of 0.16 mA cm<sup>-2</sup> at 20 °C in the range 0–1.5 V and measured the charge/discharge capacity (mAh g<sup>-1</sup>) and IIC (mAh g<sup>-1</sup>) for each carbonaceous material.

### 2.3. Characteristics of prototype battery

We prepared a prototype cylindrical battery as follows and evaluated its characteristics: (i) positive electrode and negative electrode: same as those in Section 2.1., and (ii) electrolyte: 1.5 M LiPF<sub>6</sub>-EC+DEC+MP (1:2:2).

We mainly examined the low-temperature characteristics at -10 °C, which is closely related to the property of the electrolyte and the stability of the electrolyte after storage of 20 days at 60 °C after the battery being charged. Charge conditions, were the same as those conditions in Section 2.1.

## 3. Results and discussion

Typical initial charge curves of various kinds of electrolyte are shown in Fig. 1. Electrical conductivity and IIC of these electrolytes are shown in Table 2. As shown in Fig. 1, comparison of each electrolyte with our standard electrolyte, which is EC+DEC (1:1), can be regarded as the most stable during charging; it is summarized as follows:

(i) PC+DEC (1:1): PC should react with carbon as the electrode, therefore a battery cannot be charged;

(ii) EC+PC+DEC (1:1:2): a plateau was observed around 3.2 V which indicates that PC reacted with carbon;

(iii) EC+DEC+THF (1:2:2) and EC+DEC+DME (1:2:2): the charging curves showed that the reaction with electrolyte has occurred, and

(iv) EC+DEC+MA (1:2:2) and EC+DEC+MP (1:2:2): a chain ester has been added. The curves showed the same characteristics as using the standard electrolyte. The electrolyte containing EC should be used for

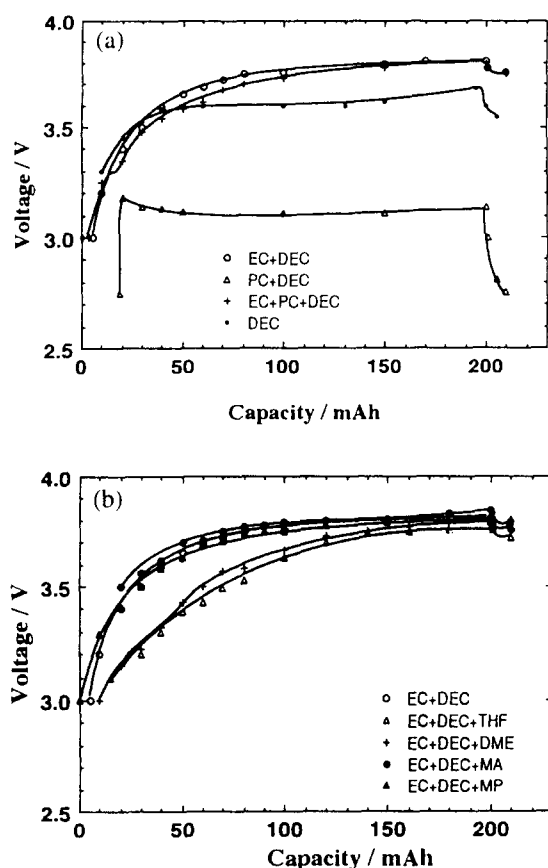


Fig. 1. Typical initial charge curves of various electrolytes 1 M  $\text{LiPF}_6$ -EC+DEC(1:1); PC+DEC(1:1); EC+PC+DEC(1:1:2); EC+DEC+THF(1:2:2); EC+DEC+DME(1:2:2); EC+DEC+MA(1:2:2); and EC+DEC+MP(1:2:2).

Table 2  
Electrical conductivity and IIC of various electrolytes: solute: 1 M  $\text{LiPF}_6$

Electrolyte	Electrical conductivity at $-10^\circ\text{C}$ ( $\text{mS cm}^{-1}$ )	IIC (mAh)
EC+DEC(1:1)	deposit	70
PC+DEC(1:1)	2.5	>200
EC+EMC(1:4)	3.4	70
EC+PC+DEC(1:1:2)	3.5	96
GBL+DEC(1:1)	6.8	>200
EC+DEC+THF(1:2:2)	6.5	155
EC+DEC+DME(1:2:2)	9.6	127
EC+n-PrA(1:4)	7.3	68
EC+DEC+MA(1:2:2)	7.6	83
EC+DEC+EA(1:2:2)	4.4	80
EC+iso-PrA(1:4)	5.0	62
EC+n-BA(1:4)	deposit	79
EC+DEC+MP(1:2:2)	5.2	82
EC+DEC+EP(1:2:2)	4.1	80

the battery systems which uses highly graphitized carbon as negative electrode. EC+EMC, EC+DEC+MA, EC+DEC+EA (ethyl acetate), EC+DEC+n-PrA (normal propyl acetate), EC+DEC+iso-PrA (iso-pro-

pyl acetate), EC+DEC+MP and EC+DEC+EP can be considered to be promising electrolytes regarding the IIC, electrical conductivity and initial charge curves.

Fig. 2 shows the relationship between  $d(002)$  and charge/discharge capacity. When  $d(002)$  became smaller, discharge capacity became higher. The charge/discharge capacity of carbonaceous materials, whose value is close to that of graphite (about  $0.336\text{ nm}$ ), varied from 250 to  $400\text{ mAh g}^{-1}$ . The relationship between  $d(002)$  and IIC is shown Fig. 3. The value of IIC tended towards small values when the range of  $d(002)$  was over  $0.34\text{ nm}$ . The values of IIC and charge/discharge capacity cannot be derived from  $d(002)$ . Moreover, it seems necessary to investigate the structure and texture of the carbonaceous materials.

We evaluated especially the storage and discharge characteristics at low temperature using 'A'-size battery with EC+DEC+MP as the electrolyte and MCMB as the negative material. About 90% of the retention capacity at 1C rate of discharge at  $-10^\circ\text{C}$  versus capacity at 1C rate discharge at  $20^\circ\text{C}$  has been obtained as well as excellent storage characteristics after a 20 day storage at  $60^\circ\text{C}$  of which was only 10% self-discharge.

We observed also a little amount of gas in a battery after storage. Various kinds of carbonaceous material

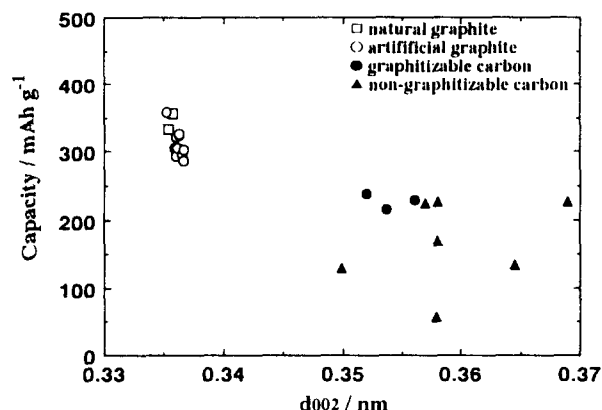


Fig. 2.  $d(002)$  vs. charge/discharge capacity.

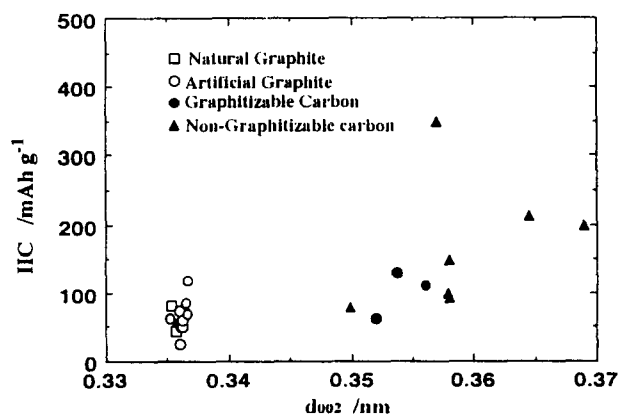


Fig. 3.  $d(002)$  vs. initial irreversible capacity (IIC).

were used as negative material to study the gas evolution. The amount of gas was proportional to the specific surface area regardless the kind of highly graphitized carbonaceous material as shown in Fig. 4. In these carbonaceous materials, the amount of gas when using MCMB was less than that of any other carbon. Table 3 shows the composition of the gas in a battery using MCMB. The composition of the gas mainly consisted of methane ( $\text{CH}_4$ ) and  $\text{CO}$ . Also,  $\text{CH}_4$  and  $\text{CO}$  gas were observed from a cell which consisted of MCMB after charging and using 1.5 M  $\text{LiPF}_6\text{-EC+DEC+MP}$  as electrolyte after a 10 day storage at 85 °C. It was considered that  $\text{CH}_4$  was evolved by the reaction of the electrolyte with the charged carbon.

Further, some changes in the electrolyte itself has been revealed by gas chromatography, see Figs. 5 and 6. Chemical products such as ethyl propionate (EP), ethylmethyl carbonate (EMC) and dimethyl carbonate (DMC) were detected in a  $\text{LiCoO}_2$  cell after charging and after a 10 day storage at 85 °C. These chemical products may have been produced by the ester-exchange reaction of DEC and MP. Although the mechanism of the gas reaction was unknown, it was assumed that  $\text{CH}_4$  is formed from the electrochemical reaction of

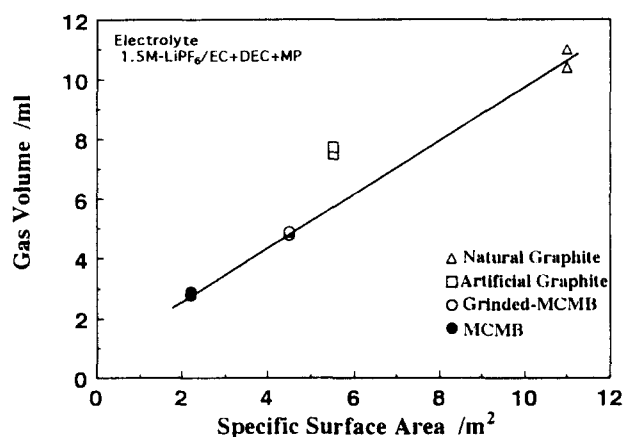


Fig. 4. Specific surface area of several carbonaceous materials vs. gas volume in 'A'-size cells after a 3 day storage at 85 °C.

Table 3

The gas composition in a cell after 20 day storage at 60 °C: 1.5 M  $\text{LiPF}_6\text{-EC+DEC+MP}$

Battery	Positive electrode		Negative electrode		
Total gas volume (ml)	2.3	(+)3.5	(-)3.6		
$\text{N}_2$ (%)	43.5	$\text{N}_2$ (%)	74.0	$\text{N}_2$ (%)	52.0
$\text{O}_2$ (%)	6.5	$\text{O}_2$ (%)	5.8	$\text{O}_2$ (%)	4.0
$\text{CH}_4$ (%)	30.4	$\text{CH}_4$ (%)	1.4	$\text{CH}_4$ (%)	19.8
$\text{CO}$ (%)	15.2	$\text{CO}$ (%)	10.0	$\text{CO}$ (%)	22.8
$\text{CO}_2$ (%)	2.2	$\text{CO}_2$ (%)	8.6	$\text{CO}_2$ (%)	1.4
Others (%)	2.2				

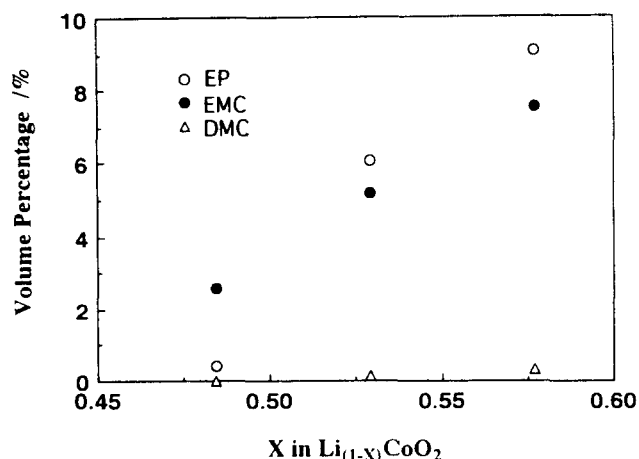


Fig. 5. Generation of EP, EMC and DMC in 1.5 M  $\text{LiPF}_6\text{-EC+DEC+MP}$  with  $\text{LiCoO}_2$  in several charging states for 10 days at 85 °C.

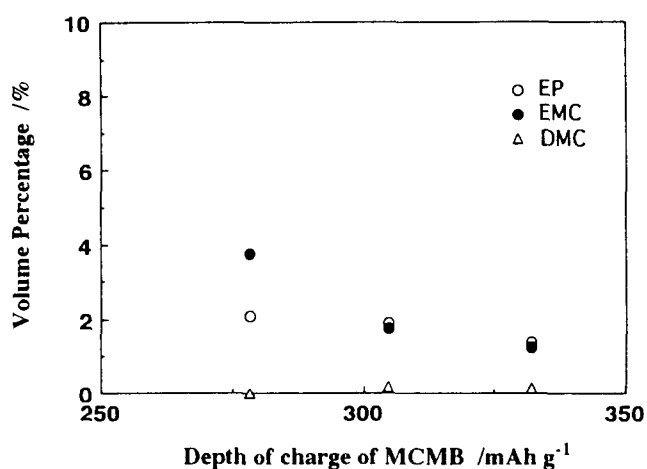


Fig. 6. Generation of EP, EMC and DMC in 1.5 M  $\text{LiPF}_6\text{-EC+DEC+MP}$  with MCMB of several charging states for 10 days at 85 °C.

MP and Li in graphite intercalated compound (GIC), occurring at the surface of carbonaceous material.

#### 4. Conclusions

An electrolyte containing EC should be used for battery systems which use highly graphitized carbon as negative material. EC+EMC, EC+DEC+ chain ester such as MA, EA, n-PrA, iso-PrA, MP and EP were used as electrolytes in this study. An 'A'-size battery with EC+DEC+MP and highly graphitized MCMB was evaluated. In this battery system, an ester-exchange reaction with DEC and MP on the side of the positive electrode occurred, and the existence of gas evolution at the negative electrode was observed.

MCMB has a small specific surface area in highly graphitized carbonaceous materials and chemical products, such as EP and EMC, were considered as suitable electrolytes in this study; MCMB showed an excellent

performance in 'A'-size batteries with a small amount of gas formed during storage.

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