

# The Initial Irreversible Capacity of the First Doping/Undoping of Lithium into Carbon

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## Abstract

The initial irreversible capacity,  $Q_{is}$ , is one of the parameters to express the material balancing of the cathode to anode. We introduced new terms, which are the initial intercalation Ah efficiency (IIE) and the initial irreversible specific capacity at the surface ( $Q_{is}$ ), to express precisely the irreversibility of an electrode/electrolyte system. Two terms depended on kinds of active-materials and compositions of the electrode, but did not change with charging state. MPCF had the highest value of IIE and the lowest value of  $Q_{is}$  in 1M LiPF<sub>6</sub>/EC + DEC (1 : 1 volume ratio) electrolyte. IIE value of LiCoO<sub>2</sub> electrode was 97-98%, although the preparation condition of the material and the electrolyte were different.  $Q_{is}$  value of LiCoO<sub>2</sub> was 0~1 mAh/g. MPCF-LiCoO<sub>2</sub> cell system had the lowest of the latent capacity.  $Q_{is}$  value increased slightly by adding conductive material. IIE and  $Q_{is}$  value varied with the electrolyte. By introducing PC to EC+DEC mixed solvent, IIE values were retained, but  $Q_{is}$  increased. In case of addition of MP, IIE value increased and  $Q_{is}$  value also increased a little.

**Keywords :** Carbon, Initial Irreversible Capacity, Initial Intercalation Ah Efficiency, Initial Irreversible Specific Capacity at the Surface, Latent Capacity.

## 1. Introduction

Lithium ion cell [1-3] has the excellent performance such as high voltage, high energy density and long cycle life. An organic medium [4-7] results in high voltage of the cell, comparing to an aqueous one. However, organic medium leads to not only the decrease of ion conductivity but also the irreversible decomposition of organic molecules at the surface of the anode during cathodic reaction. The decomposed materials [8-11] are insoluble salts, which are deposited on the surface of the electrode, and gaseous products. Carbon [12] has an excellent property as the anode in the lithium ion cell and the structures of carbon are different with its preparation. In the lithium ion cell, honeycomb-like layered structure serves as a host for intercalation of lithium ions. Carbon anode is reversibly intercalated by lithium ion under electrochemical redox process as shown in eq. (1) [1]



While carbon has a good performance as an anode, carbon reacted irreversibly with an organic electrolyte. The irreversible reaction gives an effect on the material balancing of the cathode to anode as shown in eqs. (2)~(4).

$$Q_{CC} - Q_{Cd} = Q_{Ci} \quad (2)$$

$$Q_{Ac} - Q_{Ad} = Q_{Ai} \quad (3)$$

$$Q_L = Q_{Cd} - Q_{Ad} \quad (4)$$

Where,  $Q_{CC}$ ,  $Q_{Cd}$ , and  $Q_{Ci}$  represent the charge capacity, the

discharge capacity, the irreversible capacity in cathode, respectively. And,  $Q_{Ac}$ ,  $Q_{Ad}$ , and  $Q_{Ai}$  mean the charge capacity, the discharge capacity, the irreversible capacity in anode [13, 14], respectively. If the irreversible capacity in anode,  $Q_{Ai}$ , is higher than the irreversible capacity in cathode,  $Q_{Ci}$ , and the charge capacity is same in the cathode and the anode, the discharge capacity of cathode,  $Q_{Cd}$ , will be higher than that of anode,  $Q_{Ad}$ . Therefore, the discharge capacity of the cell comes to just  $Q_{Ad}$ . In the viewpoint of cathode, the difference of the discharge capacity between the cathode and the anode,  $Q_{Cd} - Q_{Ad}$ , could not be discharged and it made the energy density of the cell low. We would like to define it as the latent capacity,  $Q_L$ .

It is well known that the irreversible capacity of carbon anode is usually originated from follows; (1) decomposition of solvent at the surface of the carbon, (2) irreversible reaction of lithium with surface functional groups such as carboxyl, hydroxyl and carbon hydride [15, 16], and (3) irreversible insertions of lithium into the carbon. Dahn *et al.* [17] analyzed on the reaction of surface functional groups of carbon qualitatively and quantitatively. When the surface of the carbon was exposed and reacted with gases such as steam, air and oxygen, the initial irreversible capacity increased. Jean *et al.* [18] reported that the initial irreversible capacity of petroleum coke varied linearly with the initial charge capacity. Matsumura *et al.* [19] also studied on the irreversible capacity loss of carbon materials using by stepwise method, which controlled the charge limit potential. When the ribbon-like carbon was heat-treated at 1500°C, the irreversible capacity in the total irreversible capacity was

66% at the potential range between 0.25 V and 0.01 V vs. Li/Li<sup>+</sup>, and 66 % of lithium remained in the carbon after being decomposed in HCl solution. They concluded that lithium remained on the surface and also in the bulk of discharged carbon electrode.

However, the quantity of irreversible reaction varied with charging state of the electrode. Therefore the new terms that do not vary with charging state are required to express the irreversible capacity of an electrode-electrolyte system. In this study, we introduced new two parameters; the initial intercalation efficiency, IIE, and the initial irreversible capacity at the surface, Q<sub>is</sub>. Electrode/electrolyte/Li cells were prepared and their electrochemical properties were investigated by controlling the initial specific capacity to evaluate the initial irreversible capacity.

## 2. Experimental

### 2.1. Materials

MCMB (mesophase carbon microbead), MPCF (meso-phase carbon fiber), natural graphite (SNO), and PCG (pitch-coated graphite) were used as the anode. Two kinds of LiCoO<sub>2</sub> and LiNi<sub>0.81</sub>Co<sub>0.16</sub>Al<sub>0.03</sub>O<sub>2</sub> were used as the cathode.

The materials used in this study were summarized in Table 1. Metallic lithium foil was used as the counter and the reference electrode, and a porous polyethylene film with thickness of 25 μm was used as the separator. Current collector was copper foil for the anode and the counter, and aluminum foil for the cathode.

### 2.2. Preparation of electrode and cell

NMP (N-methylpyrrolidone) was used as dispersing solvent. Carbon (90 wt%) and PVDF (polyvinylidene fluoride, 10 wt%) were mixed with zirconia ball at room temperature for 2 hours. Super s black (SSB) was used as a conductive material and a mixing ratio of carbon, SSB and PVDF was 88, 4 and 8 wt%, respectively. For the cathode, a binary conductive material of SSB and Lonza KS6 was used. Obtained slurry was coated on the copper and the aluminum by the doctor blade technique with 200 μm slit. And then those were dried at 120°C in ventilated drying oven. Composite electrode coated on one-side was pressed by the roll calender. The composite electrode has an area of 20 × 40 mm<sup>2</sup>. Lithium electrode was wider than the composite electrode and connected with nickel ribbon tab. The composite and the counter electrode were wound, so-called jelly roll, with separator.

Table 1. Materials used in anode and cathode

	Material	Maker	Remarks
Anode	MCMB	Osaka Gas Co.	heat-treated at 2800°C
	MPCF	Petoca Co.	heat-treated at 3000°C
	Refined Natural Graphite	SEC	
	PCG	Osaka Gas Co.	
Cathode	LiCoO <sub>2</sub>	Nippon Chem.	D <sub>50</sub> =7 μm
	LiCoO <sub>2</sub>	Sumitomo Co.	D <sub>50</sub> =5 μm
	LiNi <sub>0.81</sub> Co <sub>0.16</sub> Al <sub>0.03</sub> O <sub>2</sub>	Sumitomo Co.	D <sub>50</sub> =9 μm

Table 2. IIE and Q<sub>is</sub> values in various electrode-electrolyte systems

No.	Electrode	Electrolyte	IIE (%)	Q <sub>is</sub> (mAh/g)
1	MCMB-6-28s	1M LiPF <sub>6</sub> /EC+DEC (50:50 vol%) <sup>c)</sup>	84.0	56
2	MPCF3000	1M LiPF <sub>6</sub> /EC+DEC (50:50 vol%)	96.0	8
3	PCG100	1M LiPF <sub>6</sub> /EC+DEC (50:50 vol%)	95.2	19
4	SNO15	1M LiPF <sub>6</sub> /EC+DEC (50:50 vol%)	95.1	23
5	LiCoO <sub>2</sub> <sup>a)</sup>	1M LiPF <sub>6</sub> /EC+DEC (50:50 vol%)	98.1	1
6	LiCoO <sub>2</sub> <sup>b)</sup>	1M LiPF <sub>6</sub> /EC+DMC (50:50 vol%) <sup>d)</sup>	96.9	0
7	LiNi <sub>0.81</sub> Co <sub>0.16</sub> Al <sub>0.03</sub> O <sub>2</sub> <sup>b)</sup>	1M LiPF <sub>6</sub> /EC+DMC (50:50 vol%)	94.9	17
8	MPCF3000+SSB	1M LiPF <sub>6</sub> /EC+DEC (50:50 vol%)	96.3	12
9	MPCF3000+SSB	1M LiPF <sub>6</sub> /PC+EC+DEC (4:48:48 vol%) <sup>e)</sup>	96.4	23
10	MPCF3000+SSB	1M LiPF <sub>6</sub> /PC+EC+DEC (8:46:46 vol%) <sup>f)</sup>	96.3	26
11	MPCF3000+SSB	1M LiPF <sub>6</sub> /EC+DEC+MP (48:48:4 vol%) <sup>g)</sup>	96.1	14
12	MPCF3000+SSB	1M LiPF <sub>6</sub> /EC+DEC+MP (46:46:8 vol%) <sup>h)</sup>	97.8	13
13	MPCF3000+SSB	1M LiPF <sub>6</sub> /EC+DEC+MP (44:44:12 vol%) <sup>i)</sup>	97.1	17
14	MPCF3000+SSB	1M LiPF <sub>6</sub> /EC+DEC+MP (42:42:16 vol%) <sup>j)</sup>	96.6	15

<sup>a)</sup>Nippon Chem. Co., <sup>b)</sup>Sumitomo Co., <sup>c)</sup>1PEDEC5050, <sup>d)</sup>1PEDMC5050, <sup>e)</sup>1PPEDEC44848, <sup>f)</sup>1PPEDEC84646, <sup>g)</sup>1PEDECMP48484, <sup>h)</sup>1PEDECMP46468, <sup>i)</sup>1PEDECMP444412, <sup>j)</sup>1PEDECMP424216

### 2.3. Electrochemical characterization

The used electrolyte was 1 M LiPF<sub>6</sub> (Mitsubishi Chem. Co.)/EC + DEC (1 : 1 volume ratio), where EC and DEC were ethylene carbonate and diethyl carbonate, respectively. The electrolyte was manipulated in the glove box with high purity argon gas. Other electrolytes shown in Table 2 were also prepared to investigate an effect of the electrolyte. The electrode-electrolyte system used in this study was mentioned as the abbreviation shown in annotation of Table 2. The galvanostatic charge-discharge behavior was analyzed using by the Maccor series 2000 charge-discharge tester. The cut-off limit in charging was controlled by controlling the specific capacity of a fresh cell. But, the cut-off limit in discharging was 3 V vs. Li/Li<sup>+</sup> for the anode and 2 V vs. Li/Li<sup>+</sup> for the cathode. In this paper, potential was expressed by the V<sub>Li/Li<sup>+</sup></sub> electrode standard. Current used in charge and discharge was 10 hours rate.

### 3. Results and Discussion

Fig. 1a shows charge-discharge potential profiles of MCMB at first cycle. During charge, the potential of the carbon decreased rapidly until the specific capacity became to about 360 mAh/g, and then increased until the specific capacity became to 420 mAh/g. It was thought that the increase was due to the lithium plating, so it could not be

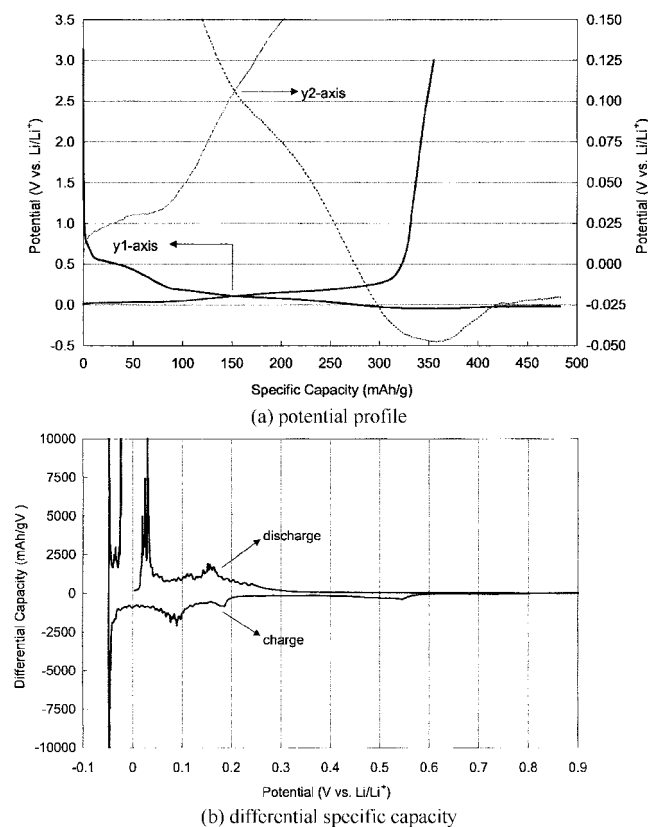


Fig. 1. Charge and discharge potential profile and differential specific capacity of MCMB/1M LiPF<sub>6</sub>/EC+DEC(1 : 1 vol%)/Li cell at specific current of 27.35 mA/g.

exceeded 0 V. The potential of carbon anode increased slightly at the beginning of lithium plating and remained constant at about -20 mV during the charge. The minimum potential of anode was -48 mV. Dahn *et al.* [17, 20, 21] have reported that nucleation of metallic lithium was proceeded at potential less than 0 V, when discharge cut-off potential of carbon anode set -30 mV at specific current of 18.6 mA/g. Some papers [20-22] have been also reported that the potential of anode varied with intercalation of lithium into MCMB. Fig. 1(b) shows the relationship between the differential specific capacity and the potential of MCMB. The value of the differential specific capacity, dQ/dV, was calculated from dividing the differential specific capacity by the differential potential. When the potential increased with plating of lithium, a few small peaks in dQ/dV were observed. It was thought that the peak at potential of ca. -10 mV in dQ/dV was due to the potential plateau with the plating of lithium on the surface of the carbon anode. Lithium stripping was progressed at the potential range between about 15 mV and 40 mV in discharge process.

Fig. 2 shows the typical potential-specific capacity profiles of MCMB. The potential at which the discharge started was the open circuit potential. Therefore, the difference of potential between the open circuit potential and the potential

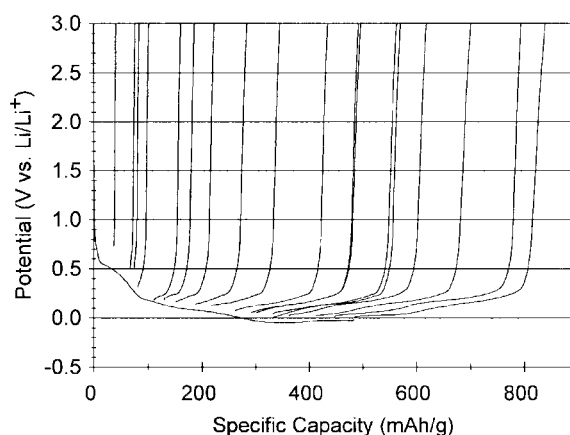


Fig. 2. Charge and discharge potential profiles as a function of specific capacity of MCMB/1M LiPF<sub>6</sub>/EC+DEC(1 : 1 vol%)/Li cell.

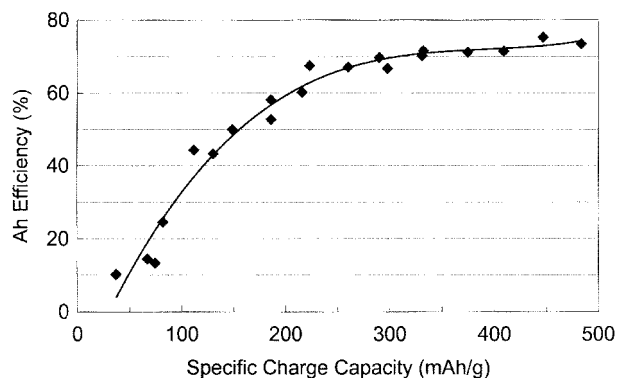


Fig. 3. Ah efficiency of MCMB/1M LiPF<sub>6</sub>/EC+DEC(1 : 1 vol%)/Li cell as a function of specific charge capacity.

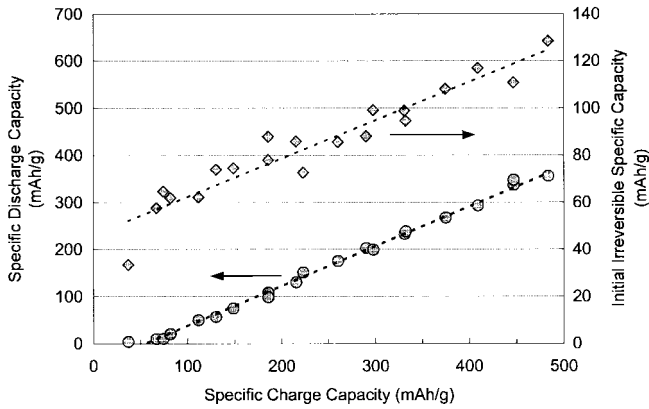


Fig. 4. Specific discharge capacity and initial irreversible specific capacity of MCMB/1M LiPF<sub>6</sub>/EC+DEC(1 : 1 vol%)/Li cell as a function of specific charge capacity.

at discharge profile is due to iR drop.

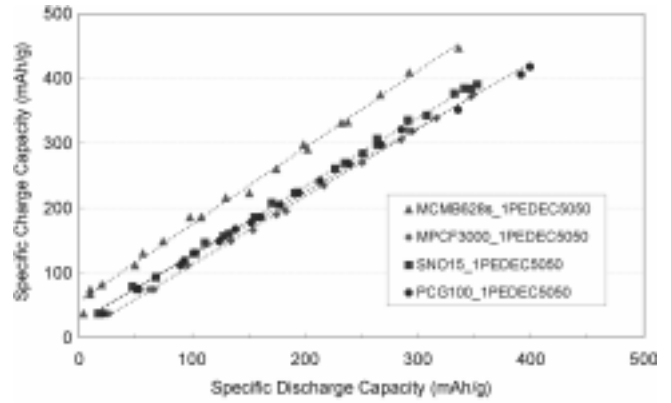
The Ah efficiencies, the specific discharge capacities and the initial irreversible specific capacities of MCMB were shown in Fig. 3 and 4. The Ah efficiencies increased with increasing the specific charge capacities and remained constant at the specific charge capacity of ca. 300 mAh/g. The specific discharge capacity, Q<sub>c</sub>, and the irreversible specific capacity, Q<sub>i</sub>, had linear relationship with the specific charge capacity, Q<sub>d</sub>, as shown in eqs. (5) and (6), respectively.

$$Q_c = 0.84Q_d + 55.5 \quad (5)$$

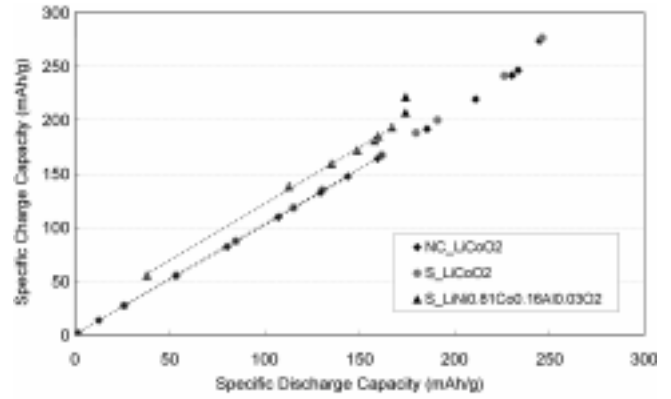
$$Q_i = 0.16Q_c + 45.9 = 0.19Q_d + 55.5 \quad (6)$$

Where, Q<sub>c</sub>, Q<sub>d</sub> and Q<sub>i</sub> were the specific charge capacity (mAh/g), the specific discharge capacity (mAh/g) and the initial irreversible specific capacity (mAh/g). The initial irreversible capacity, Q<sub>i</sub>, was originated from the decomposition of solvent at the surface of the carbon and also the irreversible insertion of lithium to carbon host. The former occurred predominantly at a low capacity region and was independent of the charge capacity. The latter occurred predominantly at a high specific capacity region and was dependent of the charge capacity. Those showed the surface and the bulk characteristics of the carbon, respectively. Therefore, a constant of 55.5 mAh/g at eqs. (5) and (6) corresponded to the initial irreversible specific capacity that originated from the solvent decomposition at the carbon surface. A slope of dQ<sub>i</sub>/dQ<sub>c</sub> achieved from eq. (5) was 0.84; the Ah efficiency of the lithium intercalation into carbon at the first charge-discharge.

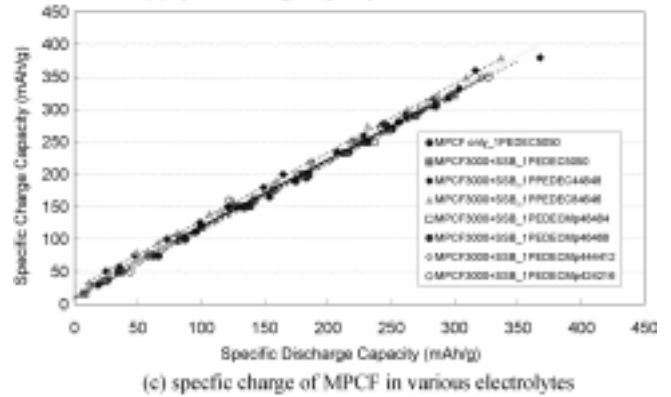
The initial irreversible specific capacity could be classified by two terms; the initial irreversible specific capacity at the surface and the initial irreversible specific capacity at the bulk. In MCMB, the initial irreversible specific capacity at the surface was 55.5 mAh/g and the initial irreversible specific capacity at the bulk was 0.19 times lower than the specific discharge capacity as shown in eq. (6). The initial irreversible specific capacity at the surface of 55.5 mAh/g corresponded to 19.5 mAh/m<sup>2</sup>, if the specific area of 2.85 m<sup>2</sup>/g was considered at the surface. Dahn *et al.* [23] and



(a) specific charge capacity of carbon materials



(b) specific charge capacity of cathode materials



(c) specific charge of MPCF in various electrolytes

Fig. 5. Specific charge capacity plots against specific discharge capacity in various composite electrode/electrolyte/Li cells.

Matsushita co. [24] have reported that the value was 7 mAh/m<sup>2</sup> in 1 M LiAsF<sub>6</sub>/PC+EC (1 : 1 volume ratio) and 5 mAh/m<sup>2</sup> in 1 M LiPF<sub>6</sub>/EC+DEC (1 : 1 volume ratio) electrolyte, respectively.

The Ah efficiency was insufficient to express precisely the reversibility of an electrode-electrolyte system because it varied with the charging state of the electrode. However, the initial intercalation efficiency, IIE, and the initial irreversible specific capacity at the surface, Q<sub>is</sub>, do not varied with the charging state. The initial irreversible specific capacity of the anode could be expressed as eq. (7). It is thought that this relationship may be used to evaluate exactly the reversibility of an electrode-electrolyte system.

$$Q_i = Q_{ib} + Q_{is} = (IIE^{-1}-1)Q_d + Q_{is} \quad (7)$$

Where,  $Q_{ib}$  and  $Q_{is}$  are the initial irreversible specific capacity due to the surface and the bulk of the electrode, respectively.

Eq. (7) was verified in another cathode and electrode-electrolyte system. Fig. 5 shows the specific charge capacity patterns in various carbon, cathode, and electrolyte. There were linear relationship between the specific charge capacity and the specific discharge capacity at all cases. Therefore, the value of IIE and  $Q_{is}$  could be obtained by the first order function and were summarized in Table 2.

Fig. 6(a) represents the value of IIE and  $Q_{is}$  for the various electrodes in 1M LiPF<sub>6</sub>/EC+DEC (1 : 1 volume ratio). The value of IIE in MCMB, MPCF, SNO and PCG was 84, 96, 95.1 and 95.2 %, respectively. And, the value of  $Q_{is}$  in MCMB, MPCF, SNO and PCG was 56, 8, 19 and 23 mAh/g, respectively. Therefore, MPCF might be better electrode than MCMB, because IIE was high and  $Q_{is}$  was low; MPCF had a high reversibility and a low irreversible capacity.

The value of IIE in LiCoO<sub>2</sub> electrode was 97~98 %, although the preparation condition of the material was different. But, the value of IIE in LiNi<sub>0.81</sub>Co<sub>0.16</sub>Al<sub>0.04</sub>O<sub>2</sub> was 95 %. The value of  $Q_{is}$  in LiCoO<sub>2</sub> and LiNi<sub>0.81</sub>Co<sub>0.16</sub>Al<sub>0.04</sub>O<sub>2</sub> were 0~1 and 17 mAh/g, respectively. It was thought that LiCoO<sub>2</sub> had better battery performance than LiNi<sub>0.81</sub>Co<sub>0.16</sub>

Al<sub>0.04</sub>O<sub>2</sub> when the reversibility of the intercalation and the irreversible capacity at the surface were compared.

For MPCF/LiCoO<sub>2</sub> cell, the value of IIE in MPCF was lower than that of LiCoO<sub>2</sub>, and the value of  $Q_{is}$  in MPCF was higher than that of LiCoO<sub>2</sub>. Therefore, the latent capacity,  $Q_L$ , was low in MPCF-LiCoO<sub>2</sub> system. The value of  $Q_{is}$  in MPCF-1M LiPF<sub>6</sub>/EC+DEC (1 : 1 volume ratio) system increased, when the conductive material was added. It is thought that the increase of  $Q_{is}$  is due to the high specific surface area of the conductive material. Nevertheless, the value of IIE was slightly changed to 96.3 %. It might be due to the blending of super s black as the conductive material.

The value of IIE and  $Q_{is}$  varied with the kinds of the electrolyte as shown in Fig. 6(b). By introducing propylene carbonate (PC) to EC+DEC mixed solvent, the value of IIE was retained to be 96.3~96.4 %, but the value of  $Q_{is}$  increased from 12 mAh/g (0 %-PC) to 26 mAh/g (8 %-PC) as shown in Nos. 8~10 in Table 2. By adding methyl propionate (MP), the value of IIE increased from 96.3 % (0 %-MP) to 97.8 % (8 %-MP), and the value of  $Q_{is}$  also increased a little to be 13~17 mAh/g (4~16 %-MP) as shown in Nos. 11~14 in Table 1.

#### 4. Conclusions

There was good linear relationship between the specific charge capacity and the specific discharge capacity in all electrode-electrolyte systems. MPCF had the best battery performance among carbon materials, because it had the highest reversibility and the lowest irreversibility of lithium intercalation.

IIE value of LiCoO<sub>2</sub> electrode was 97~98 %, although the preparation condition of the material and the electrolyte were different, but that of LiNi<sub>0.81</sub>Co<sub>0.16</sub>Al<sub>0.04</sub>O<sub>2</sub> electrode was 95 %.  $Q_{is}$  of LiCoO<sub>2</sub> and LiNi<sub>0.81</sub>Co<sub>0.16</sub>Al<sub>0.04</sub>O<sub>2</sub> were 0~1 and 17 mAh/g, respectively.

For MPCF/LiCoO<sub>2</sub> cell, IIE value of MPCF was lower than that of LiCoO<sub>2</sub>, and  $Q_{is}$  value of MPCF was higher than that of LiCoO<sub>2</sub>. Therefore, MPCF-LiCoO<sub>2</sub> cell system had the lowest of the latent capacity.  $Q_{is}$  value increased slightly by adding conductive material.

IIE and  $Q_{is}$  value varied with the electrolyte. By introducing PC to EC+DEC mixed solvent, IIE values were retained, but  $Q_{is}$  increased. In case of addition of MP, IIE value increased, and,  $Q_{is}$  value also increased a little.

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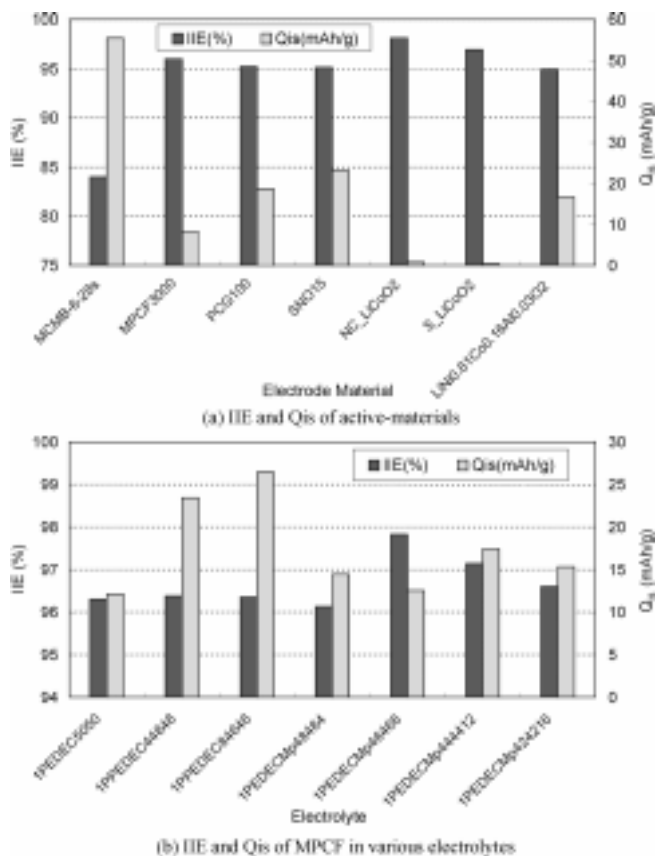


Fig. 6. IIE and  $Q_{is}$  values in various composite electrode-electrolyte systems.

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