

# A study on the irreversible capacity of initial doping/undoping of lithium into carbon

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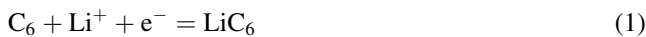
## Abstract

The initial irreversible capacity,  $Q_i$ , is one of the parameters to express the material balancing of the cathode to anode in lithium-ion cells. In this work, a new terms are introduced, namely, 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. The terms depend on the active-materials and composition of the electrode, but do not change with charging state. Mesophase carbon microbeads (MPCF) have the highest value of IIE and the lowest value of  $Q_{is}$  in 1 M LipF<sub>6</sub>/ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1 volume ratio) electrolyte. The IIE value of a LiCoO<sub>2</sub> electrode is 97–98%, although the preparation conditions of the material and the electrolyte are different. The  $Q_{is}$  value of LiCoO<sub>2</sub> is 0–1 mAh g<sup>-1</sup>. The MPCF-LiCoO<sub>2</sub> cell system has the lowest latent capacity. The  $Q_{is}$  value increases slightly on adding conductive material. The IIE and  $Q_{is}$  values vary with the electrolyte. By introducing propylene carbonate to the EC + DEC mixed solvent, the IIE values are retained, but  $Q_{is}$  is increased. With the addition of methyl propionate, the IIE value is increased, and the  $Q_{is}$  value is also increased slightly. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Carbon; Initial irreversible capacity; Initial intercalation Ah efficiency; Initial irreversible; Specific capacity; Latent capacity

## 1. Introduction

Lithium-ion cells [1–3] have excellent performance in terms of high voltage, high specific energy and long cycle life. An organic medium [4–7] results in a high voltage for the cell, compared with aqueous systems. An organic medium, however, leads to not only a decrease in ion conductivity but also to the irreversible decomposition of organic molecules at the surface of the anode during cell operation. The products of decomposition [8–11] are insoluble salts, which are deposited on the surface of the electrode, and gaseous products. Carbon [12] has an excellent properties as an anode in lithium-ion cells and has a structure which differs with the method of preparation. In the lithium-ion cell, a honeycomb-like layered structure of carbon serves as a host for the intercalation of lithium ions. Carbon anodes are reversibly intercalated by lithium ions via an electrochemical redox process, i.e.



while carbon has a good performance as an anode, it reacts irreversibly with an organic electrolyte. The irreversible

reaction effects the material balancing of the cathode to anode, i.e.

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

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

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

where  $Q_{Cc}$ ,  $Q_{Cd}$ , and  $Q_{Ci}$  represent the charge capacity, the discharge capacity, and the irreversible capacity in the cathode, respectively, and  $Q_{Ac}$ ,  $Q_{Ad}$ , and  $Q_{Ai}$  the charge capacity, the discharge capacity, and the irreversible capacity in the anode [13,14], respectively. If the irreversible capacity in the anode,  $Q_{Ai}$ , is higher than the irreversible capacity in cathode,  $Q_{Ci}$ , and the charge capacity is same in both electrodes, the discharge capacity of the cathode,  $Q_{Cd}$ , will be higher than that of the anode,  $Q_{Ad}$ . Therefore, the discharge capacity of the cell is just  $Q_{Ad}$ . The difference in discharge capacity between the cathode and the anode,  $Q_{Cd} - Q_{Ad}$ , cannot be discharged and lowers the specific energy of the cell. We define this lost capacity as the ‘latent capacity,  $Q_L$ ’.

It is well known that the irreversible capacity of the carbon anode usually originates from: (i) decomposition of solvent at the surface of the carbon; (ii) irreversible reaction of lithium with surface functional groups such as

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carboxyl, hydroxyl and carbon hydride [15,16]; (iii) irreversible insertions of lithium into the carbon. Xing and Dahn [17] analyzed the reaction of surface functional groups of carbon, both qualitatively and quantitatively. When the surface of the carbon is 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 the irreversible capacity loss of carbon materials using a stepwise method, which controlled the limit of charge potential. When ribbon-like carbon was heat-treated at 1500°C, the irreversible capacity in the total irreversible capacity was 66% over the potential range 0.25–0.01 V versus Li/Li<sup>+</sup>, and 66% of lithium remained in the carbon after being decomposed in HCl solution. The authors concluded that lithium remained on the surface and also in the bulk of the discharged carbon electrode.

The extent of the irreversible reaction varies with the charging state of the electrode. Therefore, new terms which do not vary with charging state are required to express the irreversible capacity of the electrode–electrolyte system. In this study, we introduce two new parameters, namely, the initial intercalation efficiency, IIE, and the initial irreversible capacity at the surface,  $Q_{is}$ . Electrode/electrolyte/Li cells are prepared and their electrochemical properties are investigated by controlling the initial specific capacity to evaluate the initial irreversible capacity.

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 PCG	SEC Osaka gas Co.	
Cathode	LiCoO <sub>2</sub>	Nippon chem. Co.	$D_{50} = 7 \mu\text{m}$
	LiCoO <sub>2</sub>	Sumitomo Co.	$D_{50} = 5 \mu\text{m}$
	LiNi <sub>0.81</sub> Co <sub>0.16</sub> Al <sub>0.03</sub> O <sub>2</sub>	Sumitomo Co.	$D_{50} = 9 \mu\text{m}$

## 2. Experiment

### 2.1. Materials

Mesophase carbon microbeads (MCMB), mesophase carbon fibres (MPCF), natural graphite (SNO) and pitch-coated graphite (PCG) were used as the anode. The 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 are summarized in Table 1. Metallic lithium foil was used for both the counter and the reference electrodes, and a porous polyethylene film with thickness of 25 μm was used as the separator. Copper foil was used as a current collector for the anode and the counter electrode, and aluminum foil for the cathode.

Table 2  
IIE and  $Q_{is}$  values in various electrode–electrolyte systems

No.	Electrode	Electrolyte	IIE (%)	$Q_{is}$ (mAh g <sup>-1</sup> )
1	MCMB-6-28s	1 M LiPF <sub>6</sub> /EC + DEC (50:50 vol.%) <sup>c</sup>	84.0	56
2	MPCF3000	1 M LiPF <sub>6</sub> /EC + DEC (50:50 vol.%)	96.0	8
3	PCG100	1 M LiPF <sub>6</sub> /EC + DEC (50:50 vol.%)	95.2	19
4	SNO15	1 M LiPF <sub>6</sub> /EC + DEC (50:50 vol.%)	95.1	23
5	LiCoO <sub>2</sub> <sup>a</sup>	1 M LiPF <sub>6</sub> /EC + DEC (50:50 vol.%)	98.1	1
6	LiCoO <sub>2</sub> <sup>b</sup>	1 M 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>	1 M LiPF <sub>6</sub> /EC + DMC (50:50 vol.%)	94.9	17
8	MPCF3000 + SSB	1 M LiPF <sub>6</sub> /EC + DEC (50:50 vol.%)	96.3	12
9	MPCF3000 + SSB	1 M LiPF <sub>6</sub> /PC + EC + DEC (4:48:48 vol.%) <sup>e</sup>	96.4	23
10	MPCF3000 + SSB	1 M LiPF <sub>6</sub> /PC + EC + DEC (8:46:46 vol.%) <sup>f</sup>	96.3	26
11	MPCF3000 + SSB	1 M LiPF <sub>6</sub> /EC + DEC + MP (48:48:4 vol.%) <sup>g</sup>	96.1	14
12	MPCF3000 + SSB	1 M LiPF <sub>6</sub> /EC + DEC + MP (46:46:8 vol.%) <sup>h</sup>	97.8	13
13	MPCF3000 + SSB	1 M LiPF <sub>6</sub> /EC + DEC + MP (44:44:12 vol.%) <sup>i</sup>	97.1	17
14	MPCF3000 + SSB	1 M 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> 1PEDECMP44412.

<sup>j</sup> 1PEDECMP424216.

## 2.2. Preparation of electrode and cell

The *N*-methylpyrrolidone (NMP) was used as a dispersing solvent. Carbon (90 wt.%) and PVDF polyvinylidene fluoride (PVDF, 10 wt.%) were mixed with zirconia balls at room temperature for 2 h. Super s black (SSB) was used as a conductive material and the mixing proportions of carbon, SSB and PVDF were 88, 4 and 8 wt.%, respectively. For the cathode, a binary conductive material of SSB and Lonza KS6 was used. The slurry was coated on the copper and the aluminum by a doctor blade technique with a 200  $\mu$ m slit. The electrodes were dried at 120°C in a ventilated drying oven. The composite electrode coated on one-side was pressed by a roll calender. The composite electrode had an area of 20 mm  $\times$  40 mm. The lithium electrode was wider than the

composite electrode and was connected with nickel ribbon tab. The composite and the counter electrodes were wound into a 'jelly roll' with the separator.

## 2.3. Electrochemical characterization

The electrolyte was 1 M LiPF<sub>6</sub> (Mitsubishi Chem. Co.)/EC + DEC (1:1 volume ratio), where EC and DEC are ethylene carbonate and diethyl carbonate, respectively. The electrolyte was manipulated in a glove box filled argon gas of high purity. Other electrolytes in (Table 2) were also prepared to investigate the effect of the electrolyte. The electrode–electrolyte systems are listed in Table 2. Galvanostatic charge–discharge behavior was investigated by means of a Maccor series 2000 charge–discharge tester.

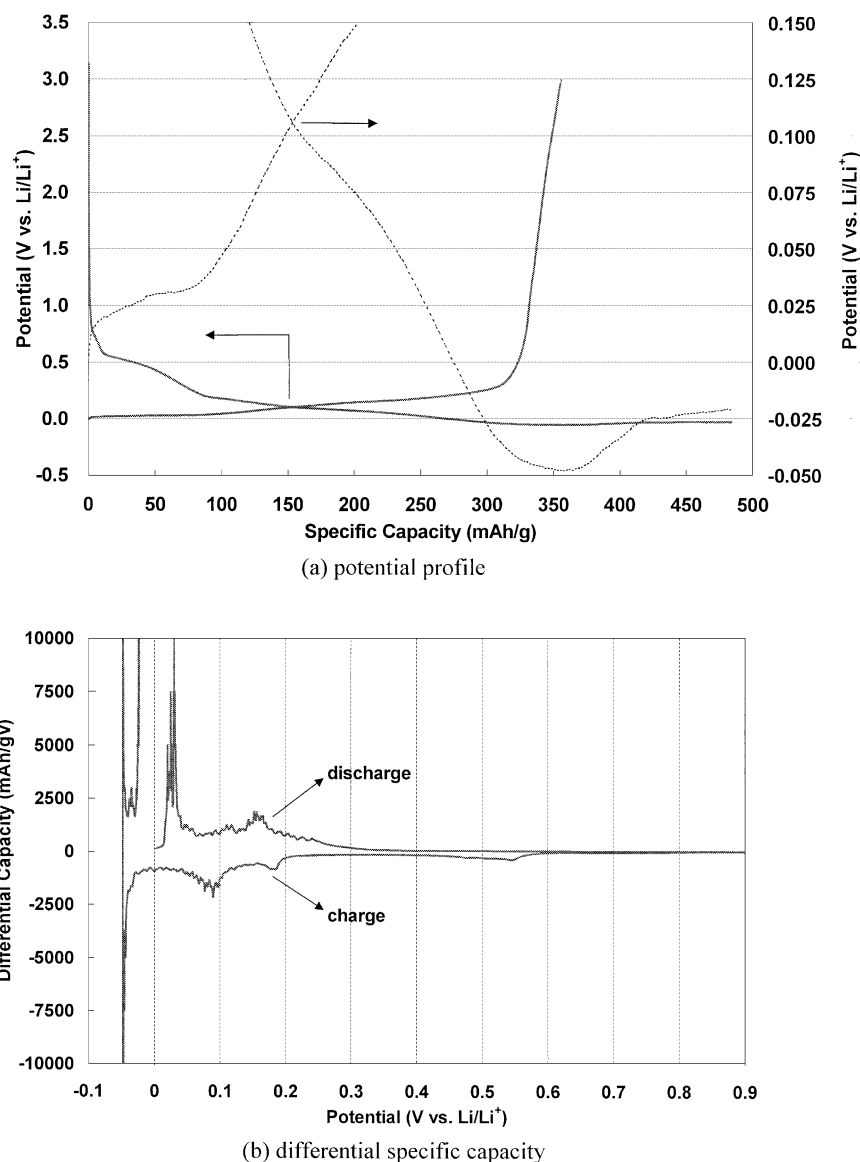


Fig. 1. (a) Charge and discharge potential profile and (b) differential specific capacity of MCMB/1 M LiPF<sub>6</sub>/EC + DEC (1:1 vol.)/Li cell at a specific current of 27.35 mA g<sup>-1</sup>.

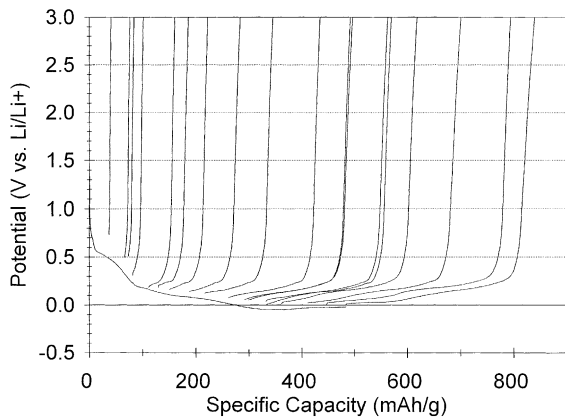


Fig. 2. Charge and discharge potential profiles as a function of specific capacity for a MCMB/1 M LiPF<sub>6</sub>/EC + DEC (1:1 vol.%) / Li cell.

The cut-off limit in charging was controlled by adjusting the specific capacity of a fresh cell. The cut-off limit in discharging was 3 V versus Li/Li<sup>+</sup> for the anode and 2 V versus Li/Li<sup>+</sup> for the cathode. In this work, the potential was expressed with respect to the V<sub>Li/Li<sup>+</sup></sub> electrode standard. Charge and discharge was conducted at the 10 h rate.

### 3. Result and discussion

The charge–discharge potential profiles of MCMB on the first cycle are presented in Fig. 1a. During charge, the potential of the carbon decreases rapidly until the specific capacity becomes about 360 mAh g<sup>-1</sup>. It then increases until the specific capacity reaches 420 mAh g<sup>-1</sup>. It is thought that the increase is due to the lithium plating, so it could not exceed 0 V. The potential of the carbon anode increases slightly at the beginning of lithium plating and remained constant at about -20 mV during charge. The minimum

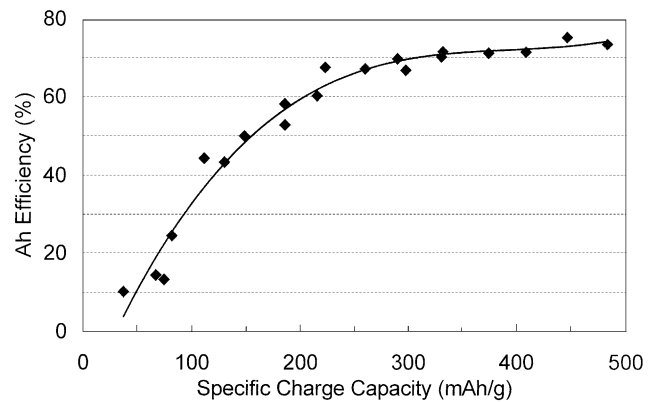


Fig. 3. Ah efficiency of a MCMB/1 M LiPF<sub>6</sub>/EC + DEC (1:1 vol.%) / Li cell as a function of specific charge capacity.

potential of the anode is -48 mV. Dahn and coworkers [17,20,21] have reported that nucleation of metallic lithium proceeds at a potential of <0 V, when the discharge cut-off potential of carbon anode was set -30 mV at a specific current of 18.6 mA g<sup>-1</sup>. Some studies [20–22] have also reported that the potential of the anode varies with intercalation of lithium into MCMB. The relationship between the differential specific capacity and the potential of MCMB is shown in Fig. 1b. The value of the differential specific, 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 about -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 took place over the potential range between about 15 and 40 mV in discharge process.

Typical potential-specific capacity profiles for MCMB are presented in Fig. 2. The potential at which the discharge

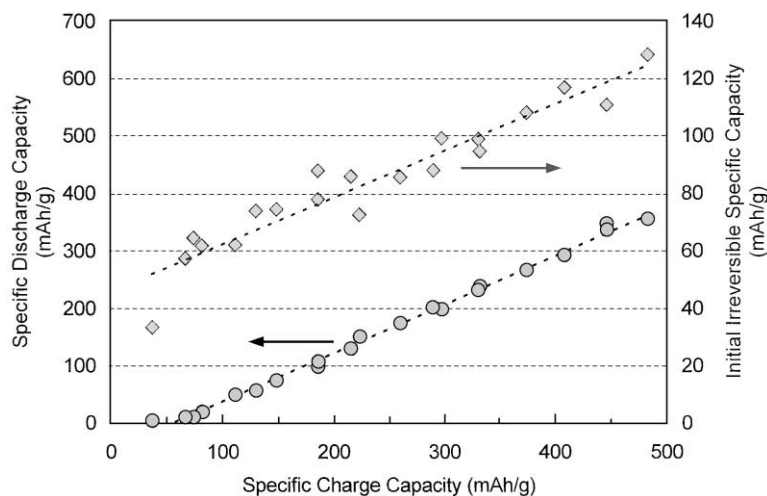


Fig. 4. Specific discharge capacity and initial irreversible specific capacity of a MCMB/1 M LiPF<sub>6</sub>/EC + DEC (1:1 vol.%) / Li cell as a function of specific charge capacity.

starts is the open-circuit potential. Therefore, the difference in potential between the open-circuit potential and the potential at discharge profile is due to  $iR$  drop.

The Ah efficiencies, the specific discharge capacities and the initial irreversible specific capacities of MCMB are shown in Figs. 3 and 4. The Ah efficiencies increase with increasing specific charge capacities and remain constant at a specific charge capacity of about  $300 \text{ mAh g}^{-1}$ . The specific discharge capacity,  $Q_c$ , and the irreversible specific capacity,  $Q_i$ , show a linear relationship with the specific charge capacity,  $Q_c$ , i.e.

$$Q_c = 0.84^{-1}Q_d + 55.5 \quad (5)$$

$$Q_i = 0.16Q_c + 46.6 = 0.19Q_d + 55.5 \quad (6)$$

where  $Q_c$ ,  $Q_d$  and  $Q_i$  are the specific charge capacity ( $\text{mAh g}^{-1}$ ), the specific discharge capacity ( $\text{mAh g}^{-1}$ ) and the initial irreversible specific capacity ( $\text{mAh g}^{-1}$ ), respectively. The initial irreversible capacity,  $Q_i$ , originates from the decomposition of solvent at the surface of the carbon and also the irreversible insertion of lithium into the carbon host. The former occurs predominantly in the low capacity region and is independent of the charge capacity. Insertion of Lithium occurs predominantly at a high specific capacity region and is dependent of the charge capacity. These two features show the surface and the bulk characteristics of carbon, respectively. Therefore, a capacity of  $55.5 \text{ mAh g}^{-1}$  in Eqs. (5) and (6) corresponds to the initial irreversible specific capacity that originates from solvent decomposition at the carbon surface. A slope of  $dQ_d/dQ_c = 0.84$  is found from Eq. (5): the Ah efficiency of the lithium intercalation into carbon at the first charge–discharge.

The initial irreversible specific capacity can be classified by two terms, namely, the initial irreversible specific capacity at the surface and the initial irreversible specific capacity in the bulk. In MCMB, the initial irreversible specific capacity at the surface is  $55.5 \text{ mAh g}^{-1}$  and the initial irreversible specific capacity in the bulk is 0.19 times lower than the specific discharge capacity as shown in Eq. (6). The initial irreversible specific capacity at the surface of  $55.5 \text{ mAh g}^{-1}$  corresponded to  $19.5 \text{ mAh m}^{-2}$ , if a specific area of  $2.85 \text{ m}^2 \text{ g}^{-1}$  is considered at the surface. Dahn and coworkers [23] and Koshina [24] have reported that the irreversible specific capacity is  $7 \text{ mAh m}^{-2}$  in  $1 \text{ M LiAsF}_6/\text{PC} + \text{EC}$  (1:1 volume ratio) and  $5 \text{ mAh m}^{-2}$  in  $1 \text{ M LiPF}_6/\text{EC} + \text{DEC}$  (1:1 volume ratio) electrolyte, respectively.

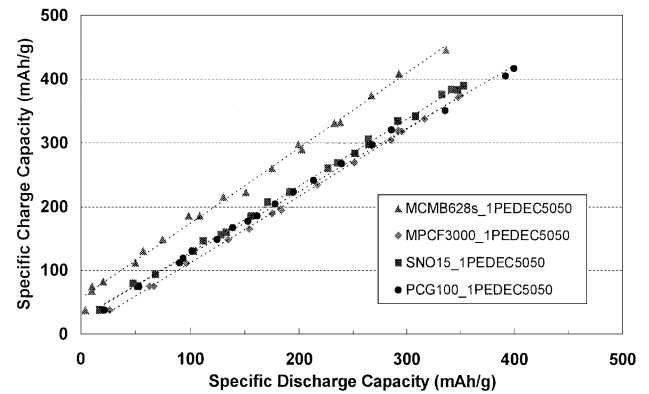
The Ah efficiency is insufficient to express precisely the reversibility of an electrode–electrolyte system because it varies with the charging state of the electrode. By contrast, the initial intercalation efficiency, IIE, and the initial irreversible specific capacity at the surface,  $Q_{is}$ , do not vary with charging state. The initial irreversible specific capacity of the anode can be expressed by Eq. (7). We consider that this relationship can be used to evaluate exactly the reversibility

of the electrode–electrolyte system, i.e.

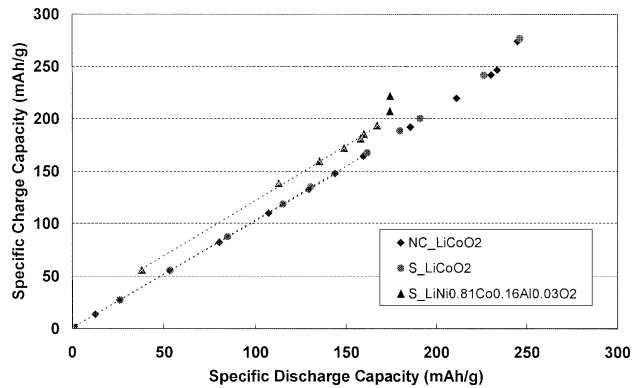
$$Q_i = Q_{ib} + Q_{is} = (\text{IIE}^{-1} - 1)Q_d + Q_{is} \quad (7)$$

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

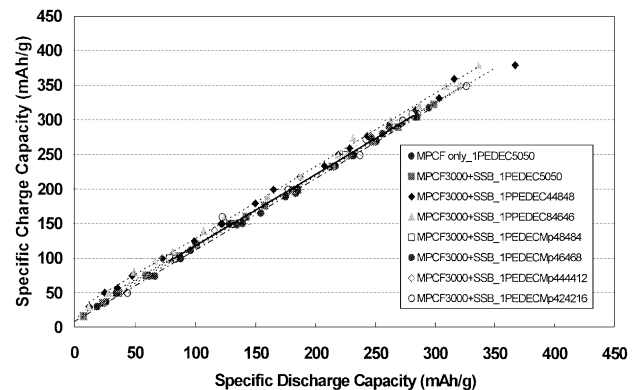
Eq. (7) was verified in another cathode and electrode–electrolyte system. The specific charge capacity patterns in various carbons, cathodes, and electrolytes are presented in Fig. 5. There is a linear relationship between the specific



(a) specific charge capacity of carbon materials



(b) specific charge capacity of cathode materials



(c) specific charge capacity of MPCF in various electrolytes

Fig. 5. Specific charge capacity as a function of specific discharge capacity for various composite electrode/electrolyte/Li cells.

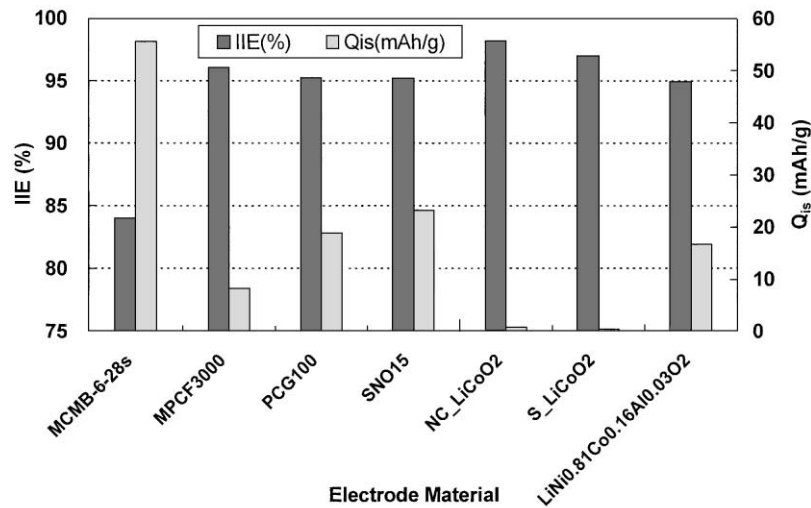
charge capacity and the specific discharge capacity in all cases. Therefore, the values of IIE and  $Q_{is}$  can be obtained by a first-order function and are summarized in Table 2.

The values of IIE and  $Q_{is}$  for various electrodes in 1 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$  (1:1 volume ratio) are given in Fig. 6a. The value of IIE in MCMB, MPCF, SNO and PCG is 84, 96, 95.1 and 95.2%, respectively. The value of  $Q_{is}$  in MCMB, MPCF, SNO and PCG is 56, 8, 19 and 23  $\text{mAh g}^{-1}$ , respectively. Therefore, MPCF may be better electrode than MCMB, because IIE is high and  $Q_{is}$  is low; MPCF has a high reversibility and a low irreversible capacity.

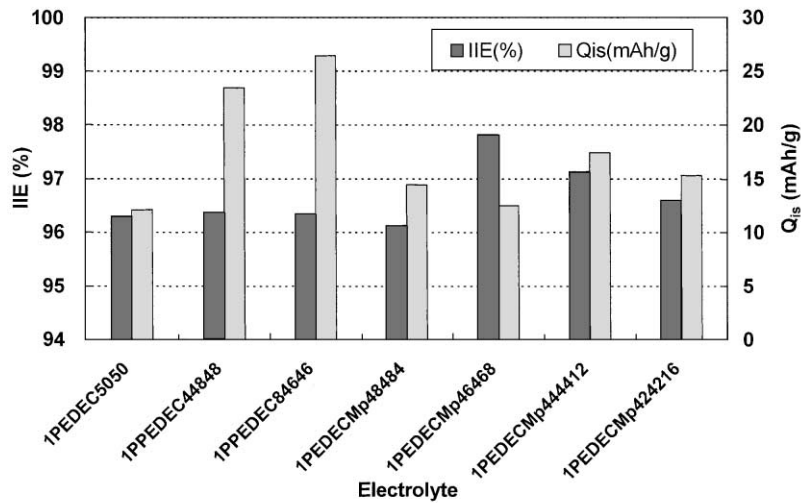
The value of IIE in  $\text{LiCoO}_2$  electrode is 97–98%, although the preparation conditions of the material are different. The

value of IIE in  $\text{LiNi}_{0.81}\text{Co}_{0.16}\text{Al}_{0.04}\text{O}_2$ , however, is 95%. The value of  $Q_{is}$  in  $\text{LiCoO}_2$  and  $\text{LiNi}_{0.81}\text{Co}_{0.16}\text{Al}_{0.04}\text{O}_2$  is 0–1 and 17  $\text{mAh g}^{-1}$ , respectively. It is concluded that  $\text{LiCoO}_2$  has a better battery performance than  $\text{LiNi}_{0.81}\text{Co}_{0.16}\text{Al}_{0.04}\text{O}_2$  when the reversibility of the intercalation and the irreversible capacity at the surface are compared.

For a MPCF/ $\text{LiCoO}_2$  cell, the value of IIE in MPCF is lower than that of  $\text{LiCoO}_2$ , and the value of  $Q_{is}$  in MPCF is higher than that of  $\text{LiCoO}_2$ . Therefore, the latent capacity  $Q_L$  is low for the MPCF- $\text{LiCoO}_2$  system. The value of  $Q_{is}$  in MPCF-1 M  $\text{LiPF}_6/\text{EC} + \text{DEC}$  (1:1 volume ratio) system increases when a conductive material is added. It is considered that the increase in  $Q_{is}$  is due to the high specific surface area of the conductive material. Nevertheless, the



(a) IIE and  $Q_{is}$  of active-materials



(b) IIE and  $Q_{is}$  of MPCF in various electrolytes

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

value of IIE is slightly changed to 96.3%. This might be due to the blending of super s black as the conductive material.

The value of IIE and  $Q_{is}$  varies with the type of electrolyte, as shown in Fig. 6b. By introducing propylene carbonate (PC) to a EC + DEC mixed solvent, the value of IIE is retained at 96.3–96.4%, but the value of  $Q_{is}$  increases from 12 mAh g<sup>-1</sup> (0 wt.%-PC) to 26 mAh g<sup>-1</sup> (8 wt.%-PC), as shown by systems No. 8–10 in Table 2. By adding methyl propionate (MP), the value of IIE increases from 96.3% (0 wt.% MP) to 97.8% (8 wt.% MP). The value of  $Q_{is}$  increased slightly to 13–17 mAh g<sup>-1</sup> (4–16 wt.% MP), as shown by systems No. 11–14 in Table 1.

#### 4. Conclusion

There is a good linear relationship between the specific charge capacity and the specific discharge capacity in all the electrode–electrolyte systems that have been studied. The MPCF has the best battery performance among the carbon materials, because it has the highest reversibility and the lowest irreversibility of lithium intercalation.

The IIE value of a LiCoO<sub>2</sub> electrode is 97–98%, although the preparation conditions of the material and the electrolyte are different, but that of a LiNi<sub>0.81</sub>Co<sub>0.16</sub>Al<sub>0.04</sub>O<sub>2</sub> electrode is 95%. The  $Q_{is}$  value 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> is 0–1 and 17 mAh g<sup>-1</sup>, respectively.

For a MPCF/LiCoO<sub>2</sub> cell, the IIE value of MPCF is lower than that of LiCoO<sub>2</sub>, and  $Q_{is}$  value of MPCF is higher than that of LiCoO<sub>2</sub>. Therefore, the MPCF-LiCoO<sub>2</sub> cell system has the lowest latent capacity. The  $Q_{is}$  value increases slightly on adding conductive material.

The IIE and  $Q_{is}$  values vary with change of electrolyte. By introducing PC to a EC + DEC mixed solvent, the IIE values are retained, but  $Q_{is}$  increases with addition of MP, the IIE value increases while the  $Q_{is}$  value increases only slightly.

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