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The Initial Irreversible Capacity of the Lithium Ion Battery System Using by the Gradual Control of State of Charge

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Abstract. Electrochemical characteristics of a graphite/lithium and a $LiCoO_2$/lithium half cell and a graphite/$LiCoO_2$ full cell were analyzed using a GCSOC (gradual control test of the state of charge) technique. The IIE (initial intercalation coulombic efficiency), which represents lithium intercalation property of the electrode material, and the IIC_s (initial irreversible capacity by the surface), which represents irreversible reaction between the electrode surface and the electrolyte were obtained from the GCSOC analysis. Linear-fittable capacity ranges of IIE of graphite and $LiCoO_2$ electrodes were 370 and 150 mAh/g, respectively, based on material weight. The value of IIE for graphite and $LiCoO_2$ electrodes were 93~94% and 94~95%, respectively. The value of IIC_s for graphite and $LiCoO_2$ electrodes were 15~17 mAh/g and 0.3~1.7 mAh/g, respectively. The value of IIE for graphite/$LiCoO_2$ full cell, used GX25 and DJG311 as a graphite, was 89~90% that lower than that for the half cells. Parameters of IIE and IIC_s can also be used to represent not only half cell but also full cell.

Key words : Lithium battery, Initial irreversible capacity, Initial intercalation coulombic efficiency, Initial irreversible specific capacity at the surface, Latent capacity.

1. Introduction

The initial irreversible capacity (IIC) is one of the parameters to represent material balancing of a cathode to an anode. Usually, IIC has been analyzed without considering the irreversible reaction due to the surface and the bulk of material. So, when IIC was used in the property of the cell, it is required to be specified the test condition such as a charge cut-off potential. To represent precisely the irreversibilityof an electrode/electrolyte system, two invariable parameters of the initial intercalation coulombic efficiency (IIE) and the initial irreversible capacity at the surface (IIC_s) have to be separated in IIC. IIE and IIC_s can be obtained by the following equations.

$$IIE = \frac{dQ_d}{dQ_c} \tag{1}$$

$$IIC = (IIE^{-1} - 1)Q_d + IIC_s \tag{2}$$

Where Q_c and Q_d is the charge capacity and the discharge capacity, respectively. Two terms, IIE and IIC_s, depended on kinds of active-materials and compositions of the electrode, but did not change with charging state. The correlation between IIC and the discharge capacity can be evaluated using the control test of the state of charge (CSOC)[1,2] and the gradual control test of the state of charge (GCSOC)[3,4].

Electrochemical properties of a full cell can be expressed using by IIE and IIC_s that represents the electrochemical characteristics of the electrode/electrolyte in the cell. Initial irreversible capacity of half cell can be determined from Eq. 3 and Eq. 4.

$$IIC^A = Q_c^A - Q_d^A \tag{3}$$

$$IIC^C = Q_c^C - Q_d^C \tag{4}$$

Charge capacity(Q_c) of full cell, cathode and anode is just same. Inherent discharge capacity of each electrode depends on IIC^C and IIC^A and is $Q_d{}^C$ and $Q_d{}^A$, respectively. Electrochemical potential of an electrode in full cell is related each other. Therefore, more strict consideration must be paid to solve potential relation, because potential of full cell is difference between cathode and anode. An effective discharge capacity in the full cell is determined from the discharge capacity of the electrode having larger IIC. The electrode having a smaller IIC can not be discharged fully, because its potential reached up to the cut-off potential in the full cell. This residual capacity was described as latent capacity(Q_L) and Q_L could be obtained from Eq. 5 and it was shown in Fig. 1.

$$Q_L = \left|Q_d^A - Q_d^C\right| \tag{5}$$

$$\frac{Q_d^e - Q_L}{Q_d^e} = \frac{Q_d^l}{Q_d^e} = B_Q \tag{6}$$

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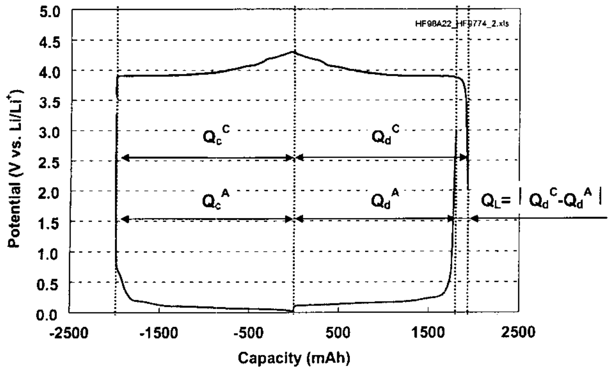

Fig. 1. The relationship of Q_L against capacities.

Q_L is an extensive property to be varied with size of full cell. Q_L can be transformed to an intensive property as shown at Eq. 6. Where Q_d^e and Q_d^l are the discharge capacity of capacitively excessive electrode and the discharge capacity of capacitively limited electrode, respectively. Therefore, B_Q (coefficient of capacity balance) would be not only an intensive property that is independent to the size of the full cell, but also inherent ratio in a given electrode/electrolyte system. Eq. 9 can be obtained from Eq. 7 and Eq. 8.

$$Q_d^e = q_d^e \times w^e \tag{7}$$

$$Q_d^e = q_d^e \times w^l \tag{8}$$

$$B_Q = \frac{Q_d^l}{Q_d^l} = \frac{Q_d^l \times w^l}{Q_d^e \times w^e} = B_M \times \frac{Q_d^l}{Q_d^e} \tag{9}$$

Where q_d^e and q_d^l are the specific discharge capacity of capacitively excessive electrode and the specific discharge capacity of capacitively limited electrode, respectively. B_M is the coefficient of material weight balance. B_Q can be expressed as the ratio of the specific charge capacity and the specific IIC_s, as shown at Eq. 10, Eq. 11 and Eq. 12 can be obtained, because the charge capacity of each electrode is just same to that of full cell.

$$B_Q = \frac{Q_d^l}{Q_d^e} = \frac{IIE^l(Q_c^l - IIC_s^l)}{IIE^e(Q_c^e - IIC_s^e)} = \frac{IIE^l(q_c^l - IIc_s^l) \times w^l}{IIE^e(q_c^e - IIc_s^e) \times w^e} \tag{10}$$

$$Q_c^e = Q_c^l = q_c^l \times w_c^l = q_c^e \times w_c^e \tag{11}$$

$$\frac{w^l}{w^e} = \frac{q_c^e}{q_c^l} \tag{12}$$

To get optimum material balancing in a chemical system, potential behaviors as the function of capacity in the cathode and the anode must be measured. And then we can calculate the charge cut-off potential of each electrode in the full cell. (q_c^e/q_c^l) can also be obtained, because w^l and w^e is known in full cell. Potential, shown at Eq. 15, in the full cell during charge can be calculated as the difference between the anodic potential (Eq. 13) and the cathodic potential (Eq. 14). Potential behavior of full cell can also be expressed as the function of the specific capacity and the weight of the active materials.

$$V^A = f(Q^A) = f(q^A \cdot w^A) \tag{13}$$

$$V^C = f(Q^C) = f(q^C \cdot w^C) \tag{14}$$

$$V^{Cell} = f(Q^{Cell}) = V^C - V^A = f(Q^C) - f(Q^A)$$

$$= f(q^C \cdot w^C) - f(q^A \cdot w^A) \tag{15}$$

When the charge cut-off potential of full cell was determined, q^C and q^A can be calculated because B_M is also known. Therefore, the charge cut-off potential of the electrode is obtained from Eq. 13 and Eq. 14.

In this study, IIE and IIC_s were evaluated in the half cells, and were compared with the value obtained in the full cells.

2. Experimental

Three electrode type a half cell and a full cell were prepared using the described method[1)]. A lithium foil was used as a counter and a reference electrode. 1 M $LiPF_6$/EC:DEC:DMC(3:5:5 volume ratio) was used as an electrolyte. Three types of graphite, i.e. GX25, MP1 and DJG311, and a $LiCoO_2$ (FMC) were used as an active material.

A cathode of 4x4 cm^2 and a anode of 4.1x4.1 cm^2 were used in the full cell. The cells were tested at C/10 rate by the galvanostatic charge-discharge cycler (Toscat 3100K) at room temperature. Charge and discharge limits were controlled as follows: the cells were charged up to ca. C/10 at the 1st charge and up to ca. (C/10)×2 at the 2nd charge. It means that the charge potential increases with cycle numbers. However, the half cell was discharged until 3 and 2 V (vs. Li/Li^+) in the anode and the cathode, respectively. The cells was stored for 1 hour between every charge and discharge. The full cells was charged up to 5 V and discharged to 2 V at every cycles.

3. Results and Discussion

The values of IIE and IIC_s for the half cells in various materials were obtained using GCSOC test and summarized at Table 1. There was a linear relationship between Q_c and/or IIC and Q_d up to 150 mAh/g in the $LiCoO_2$ electrode. IIE(dQ_d/dQ_c), which represents a property of the bulk in material, and IIC_s, which represents a property of the interface between material and electrolyte, were 94% and 1 mAh/g, respectively. A linear relationship between the two was observed up to 370 mAh/g in the three types of graphite electrodes. The value of IIE for GX25, MP1 and DJG311 were 93.7, 93.9 and 92.5%, respectively. The value of their IIC_s were 17, 16 and 15 mAh/g, respectively. Potential profiles of $LiCoO_2$/Li and graphite(MP1)/Li in

GCSOC test were shown in Fig. 2, 3 showed the relationship between the specific capacity and the initial irreversible specific capacity.

Results of GCSOC test on graphite/$LiCoO_2$ cells was summarized in Table 2. Material ratio of electrodes (B_M) was not optimized for the full cells. The value of B_M in GX25/$LiCoO_2$ cell was 1.23(287.1 mg/233.6 mg). GX25/$LiCoO_2$ cell had a linear-fitting range till 46 mAh based on Q_d. It corresponded to 160 mAh/g for a cathode and 197 mAh/g for an anode. The cathode was overcharged higher than 4.2 V (vs. Li/Li^+). It means that the capacity of cathode was 17% higher than the conventional reversible range of 137 mAh/g. Q_d of the anode was 197 mAh/g. Therefore, the utilization of anode was ca. 56% based on the 350 mAh/g of available specific capacity. The value of IIE and IIC_s in GX25/$LiCoO_2$ cell was 89.4% and 3 mAh in linear-fitting range. The value of IIE in full cell was lower than that of half cell: 94% in the cathode and 93.7% in the anode, respectively. IIC_s of each electrode, can be simply calculated from IIC_s of full cell (3 mAh) with material weight of each electrode and its value of the cathode and the anode was 10.8 and 13.3 mAh/g, respectively. The value of IIC_s for the cathode in full cell, i.e. 10.8 mAh/g, was higher than that of $LiCoO_2$ electrode half cell, i.e. 1 mAh/g, and the value of IIC_s for the anode in full cell, i.e. 13.3 mAh/g, was lower than that of graphite(GX25) electrode half cell, i.e. 17 mAh/g.

Battery performance would be improved with increasing IIE and decreasing IIC_s[1]. The value of IIE in full cell was small compared to that of half cells. Full cell was controlled by the voltage of full cell. Therefore, potential of cathode and anode was controlled other as shown in Fig. 4, which is only an example for the explanation. Here, IIC of anode was higher than that of cathode generally. At the end of discharge of full cell, potential of anode increased but potential of cathode retained because of the excessive latent capacity compared to that of anode. As the result, IIC_s of cathode in full cell was higher than that in half cell. IIE of full cell was also low compared to IIE of half cell due to the mismatching of electrode performance. Detailed relationship between full cell and half cell will be discussed in near future.

For GX25/$LiCoO_2$ cell having B_M of 1.08, a linear-fitting range of the cathode and the anode was 186 mAh/g and 200 mAh/g, respectively. MP1/$LiCoO_2$ and DJG311/$LiCoO_2$ cell showed similar relationship as in GX25/$LiCoO_2$ cell. MP1/$LiCoO_2$ cell having B_M of 1.79 has a linear-fitting range of 186 mAh/g for the cathode and 332 mAh/g for the anode. Available specific capacity of the anode in full cell closely depended on the B_M, but that of the cathode was kept nearly constant. Product of available specific capacity of the anode and B_M was same to available specific capacity of the cathode. The optimum B_M of GX25/$LiCoO_2$ cell, MP1/$LiCoO_2$ cell and DJG311/$LiCoO_2$ cell might be 2.47 based on the liner-fit range, 370 mAh/g for the anode and 150 mAh/g for the cathode.

A typical potential profiles of GX25/$LiCoO_2$ obtained by GCSOC were presented at Fig. 5. Relationship of Q_c, Q_d, and IIC for each full cells were also showed at Fig. 6.

4. Conclusion

Characteristics of graphite(GX25, MP1 and DJG311)/1 M

Table 1. IIE and IIC_s of electrode/1 M $LiPF_6$ EC:DEC:DMC(3:5:5)/Li half cell evaluated from GCSOC.

Electrode material	Class	Linear-fit range (mAh/g)	IIE (%)	IIC_s (mAh/g)
Graphite(GX25)	Anode	370	93.7	16.9
Graphite(MP1)	Anode	370	93.9	16.0
Graphite(DJG311)	Anode	370	92.5	15.0
$LiCoO_2$(FMC)	Cathode	150	94.8	0.3
$LiCoO_2$(FMC)	Cathode	150	93.9	1.7

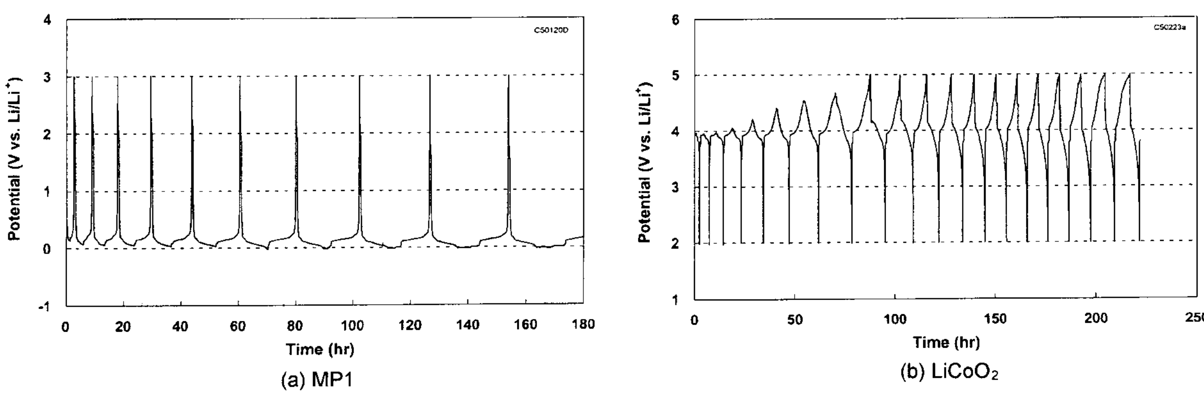

Fig. 2. Potential variation during GCSOC.

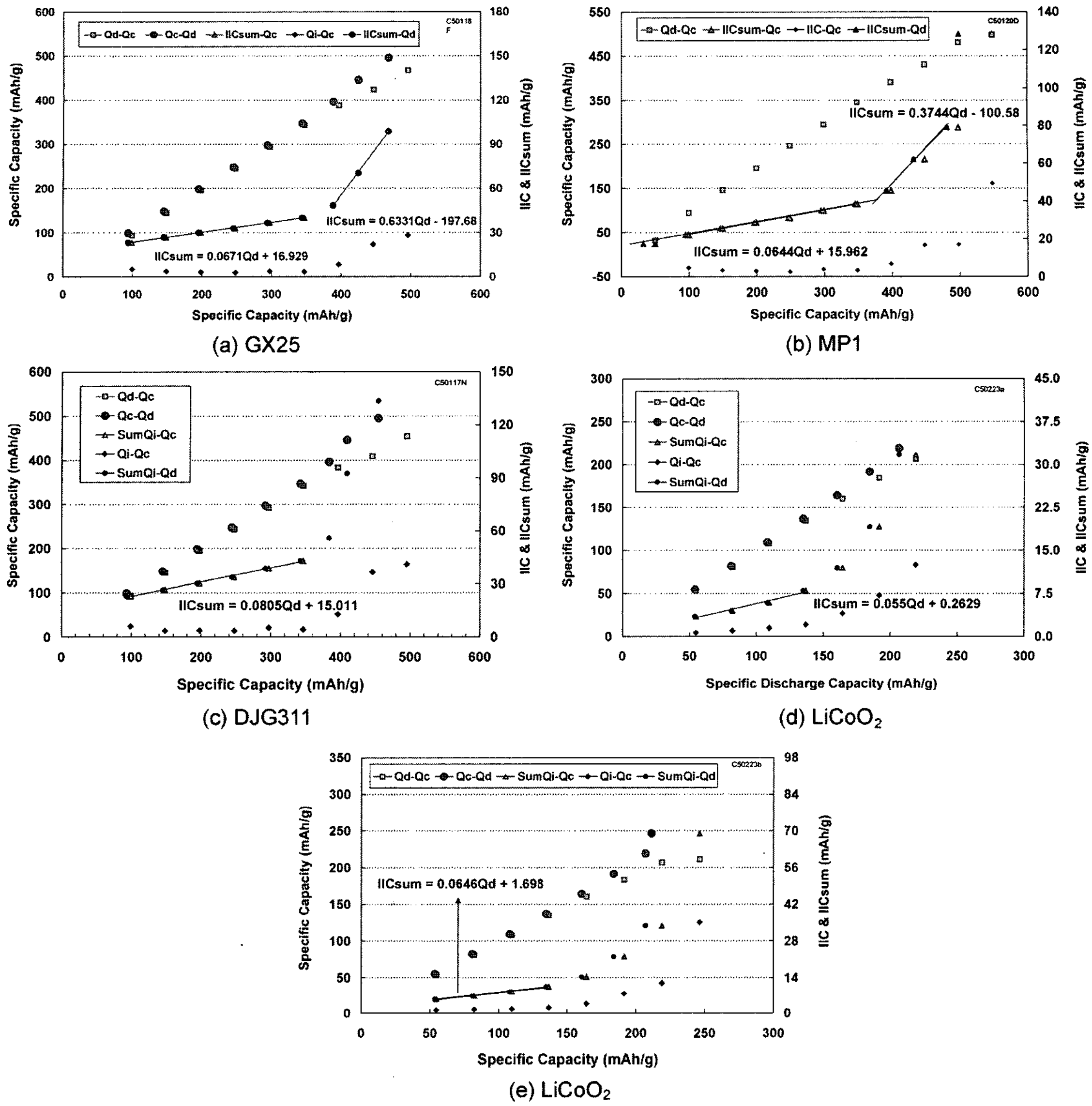

Fig. 3. Relationship of specific capacities and initial irreversible specific capacities by results of GCSOC.

Table 2. IIE and IIC_s of graphite/1M $LiPF_6$ EC:DEC:DMC(3:5:5)/$LiCoO_2$ full cell evaluated from GCSOC.

Cell configuration		Linear-fit range[cell (+, -), mAh (mAh/g)	IIE (%)	IIC_s (mAh)
(+)/(-)	material weight(+ / - = +/-)			
$LiCoO_2$/GX25	287.1/233.6 = 1.23	46.1 (161, 197)	89.4	3
$LiCoO_2$/GX25	254.1/236.2 = 1.08	47.2 (186, 200)	86.9	3
$LiCoO_2$/MP1	261.4/146.4 = 1.79	48.6 (186, 332)	85.8	1
$LiCoO_2$/DJG311	265.6/236.4 = 1.12	49.5 (186, 209)	89.4	3
$LiCoO_2$/DJG311	268.9/218.4 = 1.23	50 .0 (186, 229)	89.9	3

$LiPF_6$ EC:DEC:DMC/Li half cell were evaluated using GCSOC. Linear-fit range of initial irreversible capacity was 370 mAh/g against specific discharge capacity. The values of IIE for GX25, MP1 and DJG311 graphite were 93.7, 93.9 and 92.5%, respectively. Their values of IIC_s were 17, 16 and 15 mAh/g, respectively. Linear-fitting range for $LiCoO_2$/ 1 M $LiPF_6$ EC:DEC:DMC(3:5:5)/Li cell was 150 mAh/g. IIE and IIC_s were 94~95% and 0.31.7 mAh/g, respectively. Specific capacity of the anode in full cell closely depended on B_M but that of the cathode was kept constant. Liner-fitting range for the cathode in full cell was up to 186 mAh/g, but that for the anode depended to B_M. The optimum B_M for graphite (GX25, MP1 and DJG311)/1 M $LiPF_6$ EC:DEC:DMC(3:5:5) /$LiCoO_2$ cell was 2.47.

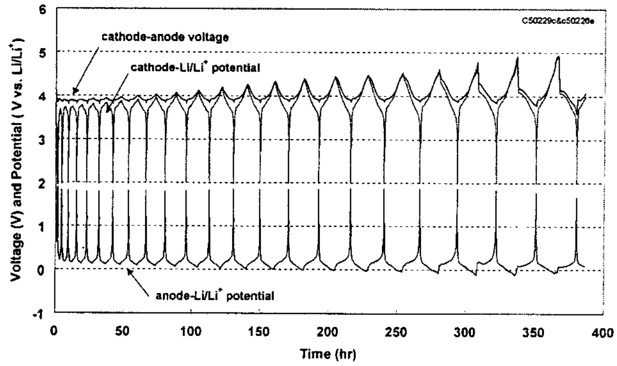

Fig. 4. Potential variation of GX25/1 M $LiPF_6$ EC:DEC:DMC(3:5:5) /$LiCoO_2$ during GCSOC.

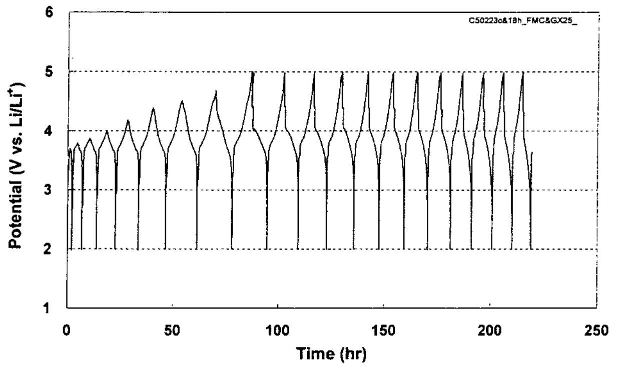

Fig. 5. Potential variation of GX25/1 M $LiPF_6$ EC:DEC:DMC(3:5:5) /$LiCoO_2$ during GCSOC.

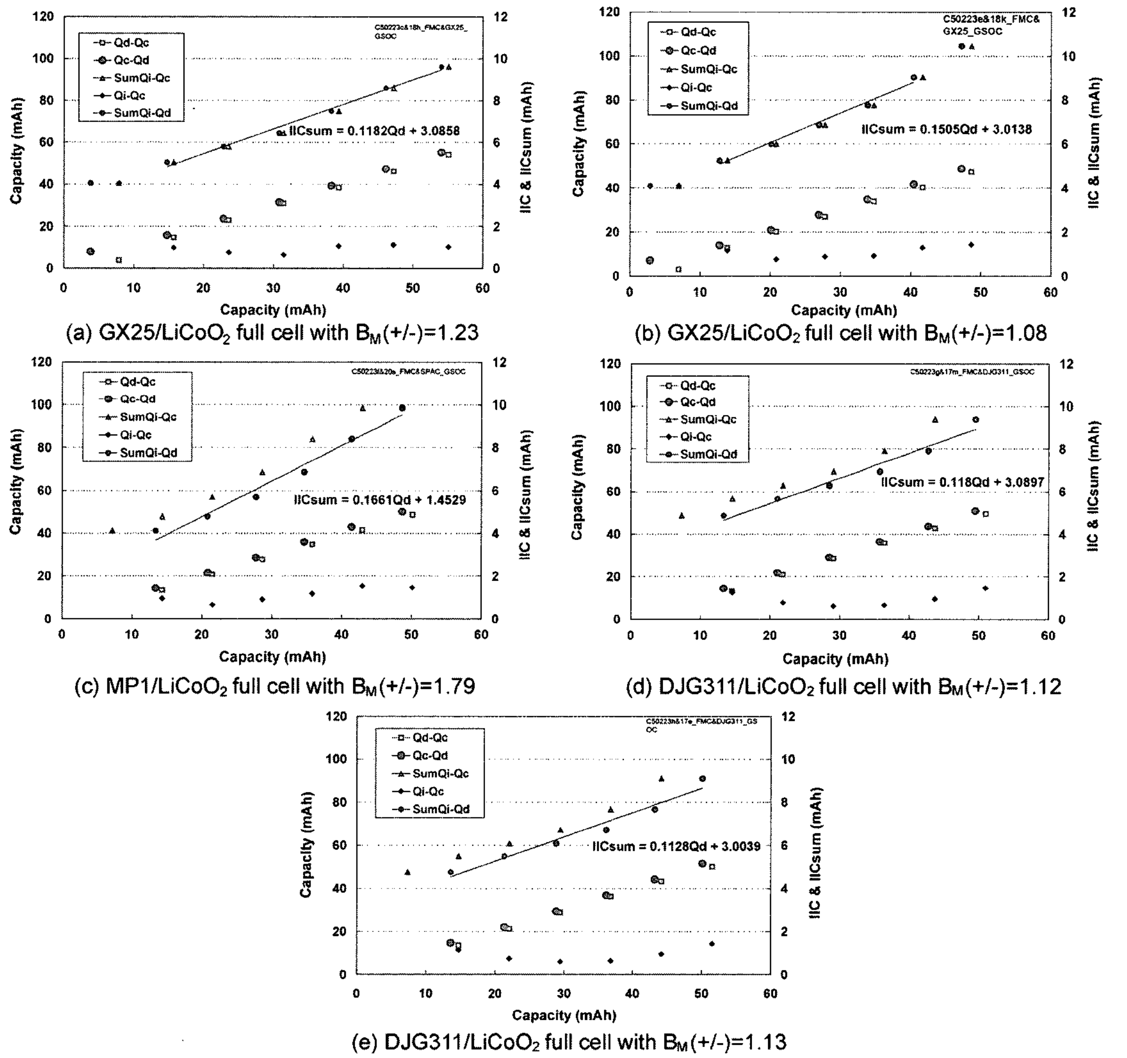

Fig. 6. Relationship of capacities and IIC of graphite/$LiCoO_2$ full cell by results of GCSOC.

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