

A Study on the Initial Irreversible Capacity of Lithium Intercalation Using Gradually Increasing State of Charge

Chil-Hoon Doh*, Bong-Soo Jin*, Chul-Wan Park*, Seong-In Moon* and Mun-Soo Yun*

Abstract - Initial irreversible capacity (IIC) can be defined by means of the initial intercalation Ah efficiency (IIE) and the initial irreversible specific capacity at the surface (IIC_s) with the linear-fit range of the intercalation so as to precisely express the irreversibility of an electrode-electrolyte system. Their relationship was $IIC = Q_C - Q_D = (IIE^{-1} - 1) Q_D + IIC_s$ in the linear-fit range of IIE. Here, Q_C and Q_D signify charge and discharge capacity, respectively, based on a complete lithium ion battery cell. Charge indicates lithium insertion to carbon anode. Two terms of IIE and IIC_s depended on the types of active materials and compositions of the electrode and electrolyte but did not change with charging state. In an ideal electrode-electrolyte system, IIE and IIC_s would be 100%, 0 mAh/g for the electrode and mAh for the cell, respectively. These properties can be easily obtained by the Gradual Increasing of State of Charge (GISOC).

Keywords: Lithium battery, initial irreversible capacity (IIC), initial intercalation Ah efficiency (IIE), initial irreversible specific capacity at the surface (IIC_s), latent capacity.

1. Introduction

The initial irreversible capacity (IIC) [1] is one of the parameters used to express the material balancing of cathode to anode. It is well-known that the irreversible capacity of carbon anode usually originates from the following: first, breakdown of solvent at the surface of the carbon; second, irreversible reaction of lithium with surface functional groups such as carboxyl, hydroxyl and carbon hydride [3, 4], and; third, irreversible insertions of lithium into the carbon as the quantity of irreversible reaction varies with the charging state of the electrode.

IIC has typically been analyzed based on the control of the charge limit potential, and considered without the separate reflection of the irreversible reaction due to the surface and the bulk of materials [3-6]. Therefore, the description of IIC requires test conditions such as charge cut-off potential. Further, the IIC out-range of the described condition cannot be obtained. Therefore, we can say that the expression of IIC is uncertain. Matsumura et al. [6] studied the irreversible capacity loss of carbon materials using the stepwise method, which controlled the charge limit potential. They concluded that lithium remained on the surface and also in the bulk of discharged carbon electrodes. Jean et al. [7] also reported that the initial irreversible capacity of petroleum coke varied linearly with the initial charge

capacity. These results show that the quantity of irreversible reaction varied in conjunction with the charging state of the electrode. Therefore, new terms that do not vary with charging state are required to express the irreversible capacity of an electrode-electrolyte system.

To precisely express the irreversibility of an electrode-electrolyte system, IIC was distinguished in two invariable parameters of the initial intercalation Ah efficiency (IIE) and the initial irreversible capacity at the surface (IIC_s). IIC_s and IIE describe the IIC due to the surface and the bulk of materials, respectively. The initial irreversible capacity at the bulk (IIC_B) can be obtained via IIE. Two terms of IIE and IIC_s depended on the type of active-materials and compositions of the electrode but did not change with charging state. The correlation between IIC and the 1st discharge (Li⁺ desertion) capacity of materials (Q_{D1}) have been evaluated using the state of charge control test (S.O.C.) (CSOC) with each fresh cell [1, 2] to obtain the parameters of IIC_s and IIE. The terminology of charge and discharge was based on the concept of the lithium ion battery. Accordingly, during the charging of carbon anodes, potential decreased and lithium ion was inserted. However, for the CSOC control test, a fresh batch of cells were needed to acquire reliable data and slight capacity to cause the irreversible reaction remained due to only one time charge-discharge. To avoid this problem in the CSOC method, another simple method was developed using the Gradual Increasing of S.O.C. (GISOC). The capacity to cause the irreversible reaction is intense during the GISOC test.

Electrode/electrolyte/Li cells were prepared and their electrochemical properties were investigated controlling

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the state of charge to evaluate the characteristics of the initial irreversible capacity.

2. Experimental

2.1 Materials

Graphites of GX25 (Carbonix Co.), MP1 (Micropowder Co.), DJG311 (Daibeck Advanced Materials Co.), MCMB-25-28 (Osaka Gas Co.), and MPCF3000 (Petoca Co.) were used as the active materials. 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 a separator. The current collector was copper foil. Electrolyte was received from Cheil Industries Co. and used without further purification.

2.2 Preparation of cells and electrodes

Three electrode test cells were prepared with an electrode of $4 \times 4 \text{cm}^2$ for the lithium ion battery and a lithium salt based organic electrolyte as described elsewhere [1]. Lithium metal was used as counter and reference electrodes. The electrolyte was manipulated in the glove box using high purity argon gas.

2.3 Electrochemical characterization

The cells were tested at C/10 rates galvanostatically using a charge-discharge life cycle (Toscat 3100K) tester at room temperature. Charge and discharge limits were controlled as follows. The cells were charged (reduced by cathodic reaction, potential decreasing) up to capacity of ca. C/10 at the 1st charge and up to ca. twice the capacity of C/10 for the 2nd charge indicating that the charge end potential decreases with cycle numbers. After each charge, the cell for the anode was discharged (oxidized by anodic reaction, potential increasing) until 3 V versus Li/Li⁺. A rest time of 1 hour was used between every charge and discharge.

3. Results and Discussion

S.O.C. increased gradually with each increase in step number as the GISOC test proceeded. Charge-discharge results were analyzed to obtain IIE and IICs through the relationship between charge and discharge capacities. IIC can be expressed as Eq. 1, definition to follow. For the GISOC test, the accumulation of the irreversible capacity of each step (IIC_{SUM}) as shown in Eq. 2, corresponds to the IIC of the CSOC test. Assuming that IIC appears during the 1st cycle only, Q_D of the GISOC test corresponds for

Q_{D1} of the CSOC test as shown in Eq. 3. Eq. 4 is a concentrated relationship of the CSOC test [1, 2]. Eq. 5 can be produced by the combination of equations 1, 2, 3 and 4.

$$\text{IIC} = Q_{C1} - Q_{D1} = \text{IIC}_B + \text{IIC}_S \quad (1)$$

$$\text{IIC} = \text{IIC}_{\text{SUM}} = \Sigma(Q_C - Q_D) \quad (2)$$

$$Q_D = Q_{D1} \quad (3)$$

$$\text{IIC} = \text{IIC}_B + \text{IIC}_S = (\text{IIE}^{-1} - 1) Q_{D1} + \text{IIC}_S \quad (4)$$

$$\text{IIC}_{\text{SUM}} = \Sigma(Q_C - Q_D) = (\text{IIE}^{-1} - 1) Q_D + \text{IIC}_S \quad (5)$$

Where, Q_{D1} and Q_{C1} were the 1st specific discharge and charge capacities, and Q_D and Q_C were specific discharge and charge capacities. Fig. 1 shows a typical potential profile of GISOC test in a graphite (MP1) | 1M LiPF₆, EC (ethylene carbonate), DEC (diethyl carbonate), DMC (dimethyl carbonate) 3:5:5 volume ratio) (1P/EC, DEC, DMC 3:5:5) | lithium cell. The graphite (MP1) electrode was made from 90 wt.% of MP1 material and 10 wt.% of PVDF (polyvinylidene fluoride). Results were analyzed and are depicted in Fig. 2. Q_D had the 1st order relationship to IIC_{SUM} in the range of 100~370 mAh/g of Q_D due to the intercalation. Q_D also had the 1st order relationship to IIC_{SUM} in the range of 370~500 mAh/g of Q_D due to the lithium deposition. As such, a linear-fit range for the intercalation of this cell was about 370 mAh/g based on Q_D. For this range, IIC_{SUM} had a relation of equation 6 against Q_D to give IIE and IICs of 93.9% and 16 mAh/g, respectively. For the range of lithium deposition, IIE was 73% from equation 7.

$$\text{IIC}_{\text{sum}} = 0.0644Q_D + 15.962 \quad (6)$$

$$\text{IIC}_{\text{sum}} = 0.3744Q_D - 100.58 \quad (7)$$

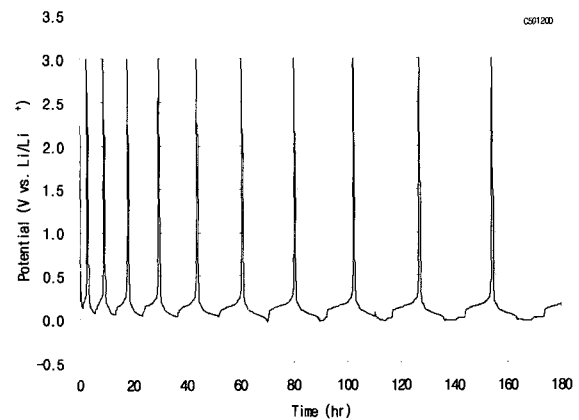


Fig. 1 Potential profile of graphite (MP1) | (1M LiPF₆, EC, DEC, DMC 3:5:5 volume ratio) | Li cell as a function of charge-discharge time.

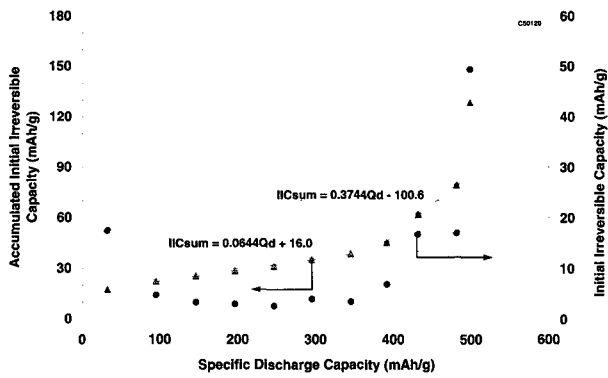


Fig. 2 Relationship between initial irreversible capacities and specific capacities of graphite (MP1)|(1M LiPF₆, EC, DEC, DMC 3:5:5 volume ratio)|Li cell.

Fig. 3 shows a typical result of the GISOC test in another cell of graphite (GX25)|(1P/EC, DEC, DMC 3:5:5)|lithium. Q_D had the 1st order relationship to IIC_{SUM} in the range of 370 mAh/g of Q_D due to the intercalation. For this range IIC_{SUM} had a relation of equation 8 against Q_D to give IIE and IICs of 93.7 % and 16.9 mAh/g, respectively.

$$IIC_{sum} = 0.0671Q_d + 16.9 \quad (8)$$

Graphite (GX25) had similar characteristics to graphite (MP1) in regards to IIE and IICs with linear-fit range.

Numerous tests were performed to evaluate the IIE and IICs. Their results are summarized in Table 1.

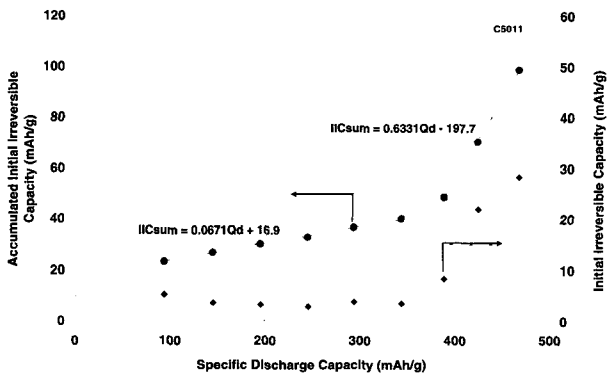


Fig. 3 Relationship between initial irreversible capacities and specific capacities of graphite (GX25)|(1M LiPF₆, EC, DEC, DMC 3:5:5 volume ratio)|Li cell.

Graphite (DJG311)|(1P/EC, DEC, DMC 3:5:5)|lithium had a linear-fit range of 370 mAh/g with IIE and IICs of 92.5% and 15.0 mAh/g, respectively. Therefore, MP1, GX25 and DJG311 had similar characteristics as each other.

The same graphite electrode showed different characteristics according to the change of electrolyte. Graphite (MP1)|(1M LiPF₆, EC, DEC 1:1 volume ratio)|(1P/EC, DEC 1:1)|lithium had a linear-fit range of 370 mAh/g with

Table 1 The Linear-fit Range, The Initial Surface Irreversible Capacities (IICs) and The Initial Coulombic Efficiency of The Intercalation (IIE)

Electrode	Electrolyte ¹⁾	Linear-fit range (mAh/g)	IIE (%)	IICs (mAh/g)
Graphite (MP1)	1P/EC,DEC, DMC 3:5:5	370	93.9	16.0
Graphite (GX25)	1P/EC,DEC, DMC 3:5:5	370	93.7	16.9
Graphite (DJG311)	1P/EC,DEC, DMC 3:5:5	370	92.5	15.0
Graphite (MP1)	1P/EC,DEC 1:1	370	94.1	12.0
Graphite (GX25)	1P/EC,DEC 1:1	370	94.9	19.5
Graphite (DJG311)	1P/EC,DEC 1:1	372	91.0	13.5
Graphite (Ceylon)	1P/EC,DEC 1:1	242	89.0	5.3
Graphite(MP1)+vgcf(90:3)	1P/EC,DEC 1:1	345	92.9	17.8
Graphite (Ceylon)+vgcf (90:3)	1P/EC,DEC 1:1	338	83.9	54.5
MCMB-25-28+vgcf	1P/MPC	-	95.0	4.7
MPCF3000+vgcf	1P/MPC	-	94.9	6.8
MPCF3000 +vgcf	1P/PC,EC,MPC 1:5:4	-	90.5	9.5
MPCF3000 +vgcf	1P/EC,MPC 8:2	-	83.4	24.2
MPCF3000 +vgcf	1P/PC,EC,MPC 1:7:2	-	86.3	22.5
MPCF3000 +vgcf	1P/PC,EC,MPC 2:6:2	300	83.8	82.0

¹⁾ electrolyte abbreviation: 1P/EC, DEC, DMC 3:5:5 - 1M LiPF₆, EC, DEC, DMC 3:5:5 volume ratio, 1P/EC, DEC 1:1 - 1M LiPF₆, EC, DEC 1:1 volume ratio, 1P/MPC - 1M LiPF₆, MPC, 1P/PC, EC, MPC 1:5:4 - 1M LiPF₆, PC, EC, MPC 1:5:4 volume ratio, 1P/EC, MPC 8:2 - 1M LiPF₆, EC, MPC 8:2 volume ratio, 1P/PC, EC, MPC 1:7:2 - 1M LiPF₆, PC, EC, MPC 1:7:2 volume ratio, 1P/PC, EC, MPC 2:6:2 - 1M LiPF₆, PC, EC, MPC 2:6:2 volume ratio.

IIE and IICs of 94.1% and 12.0 mAh/g, respectively. Another cell of graphite (MP1)|(1P/EC, DEC 1:1)|lithium, here, graphite (MP1) electrode was made from 90 wt.% of MP1 material, 3 wt.% of VGCF (vapor growth carbon fiber), and 7 wt.% of PVDF (polyvinylidene fluoride), and had a linear-fit range of 345 mAh/g with IIE and IICs of 92.9% and 17.8 mAh/g, respectively. By the introduction of VGCF as a conductive material, IIE decreased, and IICs increased. These results were originated by the intervention of VGCF as an active material to intercalate the lithium ion. IICs increased by the high surface area of VGCF material.

Graphite (Ceylon) was another natural graphitic material. Graphite (Ceylon)|(1P/EC, DEC 1:1)|Li cell has a linear-fit range of 242 mAh/g with IIE and IICs of 89.01% and 5.3 mAh/g, respectively. Another cell of graphite (Ceylon)|(1P/EC, DEC 1:1)|Li, here, graphite (Ceylon) elec-

trode was made from 90 wt.% of MP1 material, 3 wt.% of VGCF, and 7 wt.% of PVDF, and had a linear-fit range of 338 mAh/g with IIE and IICs of 83.9% and 53.5 mAh/g, respectively. Test results of graphite (Ceylon) were generally labile to results compared to MP1, GX25 and DJG311 materials.

Graphite (GX25)|(1P/EC, DEC 1:1)|Li and Graphite (DJG311)|(1P/EC, DEC 1:1)|Li cells had a linear-fit range of ca. 370 mAh/g with IIE and IICs of 94.9% and 19.5 mAh/g for GX25, and of 91.0% and 13.5 mAh/g for DJG311, respectively.

Graphite (MCMB-25-28)|1M LiPF₆, MPC(methyl propyl carbonate)|(1P/MPC)|Li cell, here, an artificial graphite (MCMB-25-28) electrode was made from 90 wt.% of MCMB-25-28, 3 wt.% of VGCF, and 7 wt.% of PVDF, and had IIE and IICs of 95.0% and 4.7 mAh/g, respectively. IICs showed very low due to low specific surface area of 0.5-1.5 m²/g.

Graphite (MPCF3000)|(1P/MPC)|Li cell, here, an artificial graphite fiber (MPCF3000) electrode was made from 90 wt.% of MPCF3000, 3 wt.% of VGCF, and 7 wt.% of PVDF, and had IIE and IICs of 94.9% and 6.8 mAh/g, respectively. IICs also showed very low due to low specific surface area of 1.8 m²/g. When electrolytes were changed to 1M LiPF₆, PC (propylene carbonate), EC, MPC 1:5:4 volume ratio (1P/PC, EC, MPC 1:5:4), 1M LiPF₆, EC, MPC 8:2 volume ratio (1P/EC, MPC 8:5:4), 1M LiPF₆, PC, EC, MPC 1:7:2 volume ratio (1P/PC, EC, MPC 1:7:2), and 1M LiPF₆, PC, EC, MPC 2:6:2 volume ratio (1P/PC, EC, MPC 2:6:2), IIE varied to 90.5, 83.4, 86.3, and 83.8%, respectively. An order of electrolytes was described without in-depth consideration of the properties. IIE were varied by the introduction of PC to electrolyte. In that case, IICs were also varied to 9.5, 24.2, 22.5, and 82 mAh/g, respectively. IICs was increased to add EC to (1P/MPC). Moreover IICs increased, increasing the content of PC to (1P/EC, MPC 8:2).

4. Conclusion

Characteristics of graphite (MP1, GX25, DJG311, Ceylon, MCMB-25-28, and MPCF3000)|Li salt based organic electrolyte|Li cells were evaluated using the Gradual Increasing of State of Charge (GISOC) method. Cells had the linear-fit relationship for the corresponding intercalation range. Linear-fit range of the initial irreversible capacity was approximately 370 mAh/g against specific discharge capacity for the graphite of MP1, GX25, and DJG311. IIE for MP1, GX25, and DJG311 graphite in an electrolyte of (1P/EC, DEC, DMC 3:5:5) were 93.9, 93.7 and 92.5%, respectively. Their IICs were 16, 17 and 15 mAh/g, respectively. Many other electrode-electrolytes were analyzed by GISOC. Test results can be summarized as follows: IICs

was labile to the surface of material and the composition of electrolyte and electrode including the conductive material. So, IICs could be used as a parameter to define the electrode-electrolyte property as its extent. The linear-fit range indicated the extent of reversible range of insertion/desertion of lithium to material, electrode or battery, so it is also a parameter used to describe the material. IIE showed the property of the bulk of material in the reversible range of insertion/desertion. For the ideal electrode-electrolyte, IIE and IICs are 100% and 0 mAh/g, respectively, with the largest linear-fit range. Characteristics of the electrode-electrolyte can be expressed as IIE and IICs with the linear-fit range of the intercalation. These properties were easily obtained by the Gradual Increasing of State of Charge (GISOC).

Acknowledgements

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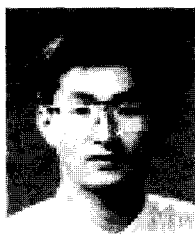
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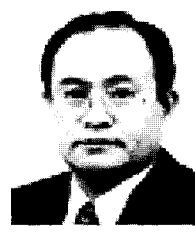
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