

A Study on the Electrochemical Properties of Carbon Nanotube Anodes Using a Gradual Increasing State of Charge Method

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

Abstract - From the gradual increasing state of charge (GISOC) observations, electrochemical behavior of multi-walled carbon nanotube (1M LiPF₆, EC, DEC, DME 3:5:5 volume ratio) lithium cells was evaluated using the galvanostatic charge-discharge process. A MWCNT delivers a specific charge capacity of 1,300 mAh/g in a Li cell when cycled up to an end voltage of 0 V (vs. Li/Li⁺) at a constant current rate every 10 hours. However, in the present study, the specific discharge capacity obtained is 338 mAh/g, thus amounting to a coulombic efficiency of only 26%. Further, when the MWCNT/Li cells were tested using the GISOC method, two distinguishable linear-fit ranges were observed due to the intercalation/deintercalation of lithium, which were found to have IIE₁, IIC_{S1} and IIE₂ of 27.3%, 372 mAh/g, and 25.5%, respectively. Q_{C1} could be calculated from the data of IIE and IICs of each range by the modified equation "IIC_{Sum} = Σ(Q_C - Q_D) = (IIE₁⁻¹ - 1)Q_{D1} + (IIE₂⁻¹ - 1)(Q_{D2} - Q_{D1}) + IIC_{S1} = Q_{C1} - Q_{D1}". Results of the GISOC method could be converted to the results of galvanostatic charge-discharge process, irrespective of the state of charge of the cell or battery.

Keywords: Lithium battery, anode, multi-walled carbon nanotube, IIC, IIE, IICs.

1. Introduction

The specific energy of a lithium secondary battery is about 180 Wh/kg, which is roughly 6 times higher than that of a lead-acid battery. Generally, the performance of any battery must be increased so as to meet the requirements of the growing concerns and demands of electronic devices. Also it is known that the energy density of a battery can be enhanced by improving the performance of electrodes, electrolytes and the optimization of packaging, etc. Initially, pitch coke has been used as the anode material in the production of the lithium ion battery, but now-a-days it is becoming replaced by graphite. Graphite synthesized using recent technology has a specific capacity of 340 mAh/g with an initial coulombic efficiency of 93%. In order to obtain higher capacity than the theoretical specific capacity of 372 mAh/g for graphite, some high capacity materials such as polyparaphenylene, polyacene, and metal oxide have been suggested.

Recently developed carbon nanotubes are reported to have various structures similar to tubular, rope, single-walled, multi-walled, etc. Following brief speculation, the electrochemical Li⁺ doping is believed to be achievable at inter-spacing between graphene layers, interstitial sites of tubes, interior sites of tubes, and exterior sites of tubes.

Thus, the electrochemical characteristics of Li⁺ doping are reported in the literature by many researchers [1-4].

In this communication, we present our results on the electrochemical characteristics of the carbon nanotube (CNT) as being yet another potential anode material for the lithium secondary battery using the galvanostatic charge-discharge method as well as observation of the gradual increasing state of charge (GISOC) [5].

2. Experimental

2.1 Materials

Multi-walled carbon nanotube (MWCNT) material was obtained from the Guangzhou Yorkpoint New Energy Sci. & Tech. Development Co. Ltd. It has the diameter of 10~40 nm. It contains 6.4% ash, 0.003% chloride, 0.08% sulfide, 0.38% iron, and 0.0001% zinc as impurities. This MWCNT was used as the active anode material while metallic lithium foil was used as the counter and the reference electrode was separated by a porous polyethylene film with a thickness of 25 μm. Copper foil was used as the current collector and electrolyte was used without further purification as received from Cheil Industries Co.

2.2 Preparation of electrode and cell

Three electrode test cells were constructed with an

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electrode of $4 \times 4 \text{ cm}^2$ for the lithium ion battery. The working electrode was made from a mixture of MWCNT (90 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) and the electrolyte consisted of 1M LiPF_6 in EC (ethylene carbonate): DEC (diethyl carbonate) : DMC (dimethyl carbonate) in a 3:5:5 volume ratio [5, 7]. Lithium metal was used as counter and reference electrodes. The electrolyte was in a glove box with high purity argon gas.

2.3 Electrochemical characterization

Test cells, containing the anode half cell of MWCNT/Li^0 for the lithium secondary battery, were tested by the galvanostatic charge-discharge using Toscat 3100K cycler at room temperature using a current rate of ca. $C/10$ rate based on the cell capacities. The potential cut-off limits of the normal galvanostatic test were controlled by potential of 0~3 V versus Li/Li^+ . GISOC test [5] was performed using a constant current of about $C/10$ rate. Charge (cathodic reaction, potential decreasing, Li^+ insertion) and discharge (anodic reaction, potential increasing, Li^+ desertion) limits were controlled as follows: the cells were charged up to a capacity of ca. $C/10$ for the 1st charge and then twice the $C/10$ capacity at the 2nd charge. It meant that the charge end potential decreased with cycle numbers. Following each charge, the cell for the anode was discharged until 3 V versus Li/Li^+ . A rest time of 1 hour was used between every charge and discharge.

3. Results and Discussion

The XRD pattern of a multi-walled carbon nanotube (MWCNT) electrode is shown in Fig. 1 with the average layer spacing of 3.415 Å seeming like d_{002} of the layer structure in MWCNT.

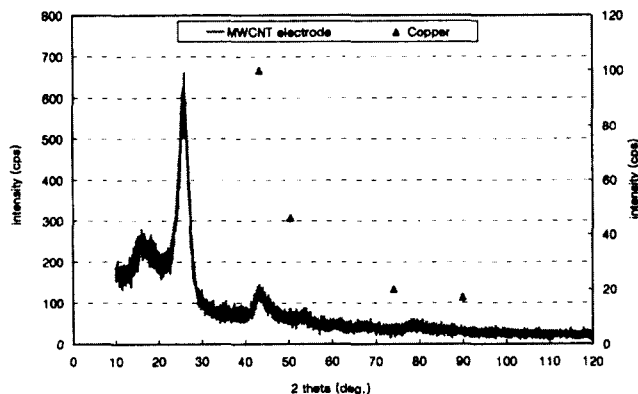
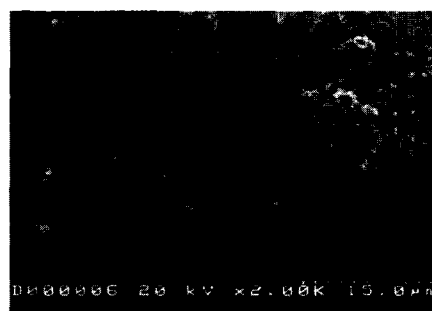


Fig. 1 X-ray diffraction pattern of a MWCNT electrode.

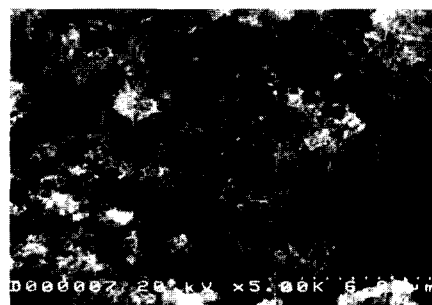
The full width end half maximum (FWHM) was found to be 2.86° in the 2 theta scale. The average layer spacing

of 5.34 Å, 4.66 Å as a shoulder, 2.264 Å, and 1.21 Å were also observed as broad bands.

The SEM image indicated that the MWCNT is a foamy material as shown in Fig. 2. The average particle size (D_{50}), D_{10} and D_{90} of granulates were ca. 120 μm , 48 μm and 191 μm , respectively as shown in Fig. 3. On the other hand, the shape of the material was found to have a fibrous morphology upon magnification, which had not been considered.



(a) magnification: x 2,000



(b) magnification: x 5,000

Fig. 2 Scanning electron microscope image of a MWCNT electrode.

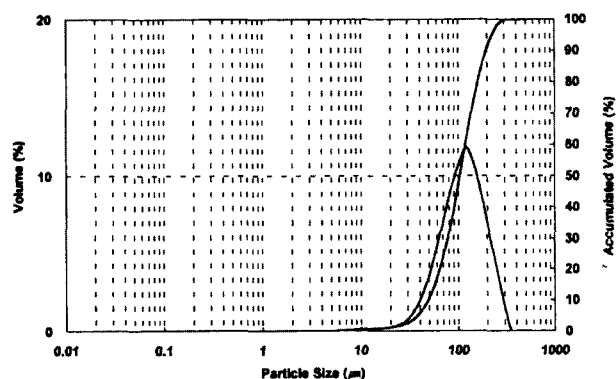


Fig. 3 Particle size distribution of MWCNT material.

Electrochemical behavior of MWCNT/Li cell using galvanostatic charge-discharge test is depicted in Fig. 4. A large amount of irreversible capacity was observed during the 1st cycle including the irreversible potential plateau at 0.8 V versus Li/Li^+ . The 1st charge and discharge capacities were 1,300 and 338 mAh/g respectively and an average

discharge capacity of 312 mAh/g was observed until the 24th cycle. The potential decreasing pattern near 0V vs. Li/Li⁺ at the end of the charge was similar to that of hard carbon and low temperature heat treated carbon such as the single walled carbon nanotube [1], and vapor grown carbon fibers [8], but slightly different from that of graphite [9]. The potential decreasing pattern at the end of the charge showed the possibility for imperfectness of the charge even if the potential was 0 V versus Li/Li⁺. It could be caused by the kinetic non-equilibrium of lithium concentration into the bulk of the material. Therefore, it is understood that the reversibility of an electrode to intercalate the lithium ion process could be determined by the slower charge-discharge than 10 hours rate of specific current in the case of normal galvanostatic charge-discharge. Similarly, the reversibility of an electrode to intercalate the lithium ion could also be evaluated through GISOC.

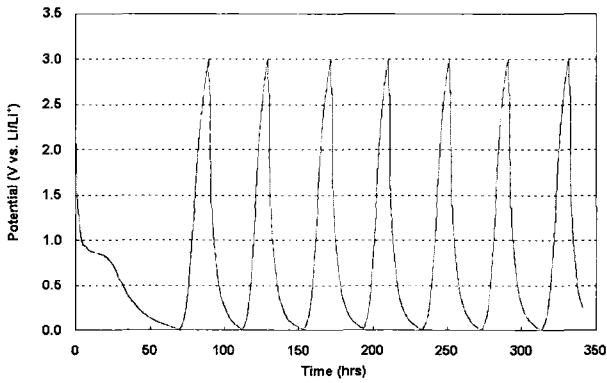


Fig. 4 A potential profile of a MWCNT|(1M LiPF₆, EC,DEC,DMC 3:5:5 volume ratio)|Li cell by the galvanostatic charge-discharge.

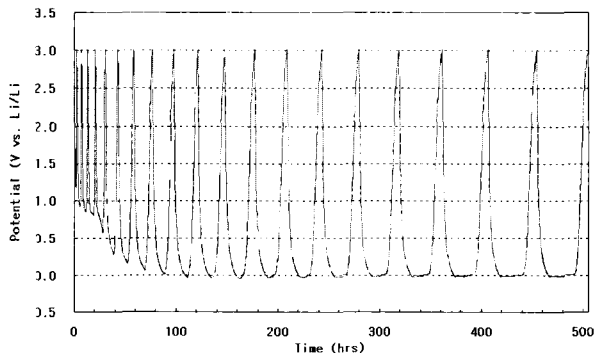


Fig. 5 A potential profile of a MWCNT|(1M LiPF₆, EC,DEC,DMC 3:5:5 volume ratio)|Li cell by GISOC charge-discharge.

A MWCNT|Li cell was cycled by the GISOC method to evaluate the initial intercalation coulombic efficiency (IIE) and the initial irreversible capacity at the surface (IICs) [5] and the results are presented in Fig. 5 as a potential profile. Fig. 6 illustrates the linear relationship of the accumulation

of the irreversible capacity of each step (IIC_{SUM}) against Q_d, and the results are summarized in Table 1. For GISOC, IIC_{SUM} can be represented by the following relationships of Eq. (1) [5-7]:

$$IIC_{SUM} = \Sigma(Q_C - Q_D) = (IIE^{-1}-1)Q_D + IIC_S \quad (1)$$

Where, Q_D and Q_C were the specific discharge and charge capacities.

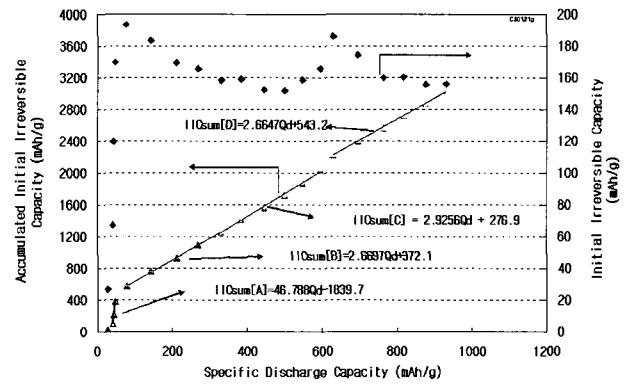


Fig. 6 Relationship between initial irreversible capacities and specific capacities of a MWCNT|(1M LiPF₆, EC,DEC,DMC 3:5:5 volume ratio)|Li cell.

Four different slopes were obtained for Q_c and IIC_{sum} against Q_d. The 1st stage, which ranged to the maximum charge and discharge capacities of 217 and 48 mAh/g, respectively, is found to have a good linear correspondence. However, IIE and IICs were only 2.1% and -1,840 mAh/g due to the absolute irreversibility. Similarly, the 2nd stage, which ranged in the charge capacity from 218 mAh/g to 489 mAh/g and in the discharge capacity from 48 mAh/g to 331 mAh/g, is also found to have a solid linear relationship. Corresponding IIE and IICs were 27.3% and 372 mAh/g, respectively. For 489 mAh/g of Q_c, Q_d and the potential at the end of the charge were respectively of 331 mAh/g and 19 mV versus Li/Li⁺. The 3rd stage, which ranged from 331 mAh/g to 629 mAh/g based on Q_d, also seems to pertain a good linear correspondence with IIE and IICs as 25.5% and 277 mAh/g, respectively. For 815 mAh/g of Q_c, Q_d was 629 mAh/g and the potential of the end of the charge was -21 mV versus Li/Li⁺. It is quite interesting to note that the IIE of the 2nd and the 3rd stages are not much different. Also, it is known that IICs of 372 mAh/g at the 2nd stage could be acceptable for the lithium doping/undoping. IICs of 277 mAh/g at the 3rd stage need not be considered because the 3rd stage is an extension from the end of the 2nd stage only. The 4th stage, which ranged from 629 mAh/g of Q_d, also showed good linear relationship with IIE and IICs as 27.3 % and 543 mAh/g, respectively. IIE of the 4th stage was similar to that of the 2nd stage. But the potential plateau around -10 mV for

charge and +10 mV for discharge seemed to be a region of reversible lithium plating/dissolution.

Table 1 The Initial Irreversible Capacities of the Surface (IICs) and the Initial Coulombic Efficiency of the Intercalation (IIE) of MWCNT/Li Cell for the Different Range of Capacities

Linear-fit range (mAh/g)		IIE (%)	IICs (mAh/g)
Qc (max)	Qd (max)		
217	48	2.1	-1,840
489	331	27.3	372
815	629	25.5	277
1,087	931	27.3	543

There were two different lithium doping/undoping mechanisms in MWCNT. At the 1st stage, lithium is intercalated into the graphene interlayer of MWCNT and in the 2nd stage, lithium is doped/undoped into the cavity or pore of MWCNT.

When a composition is made on the two distinguishable linear-fit ranges of lithium doping/undoping, the first linear-fit range had a maximum Qd of 331 mAh/g with IIE₁ and IIC_{S1} of 27.3% and 372 mAh/g, respectively. The second linear-fit range had a maximum Qd of 629 mAh/g with IIE₂ of 25.5%. Q_{C1} could be delivered from the data of IIE and IICs of each range by the modified equation (2), which originates from equation (1).

$$IIC_{Sum} = \Sigma(Q_C - Q_D) = (IIE_1^{-1} - 1)Q_{D1} + (IIE_2^{-1} - 1)(Q_{D2} - Q_{D1}) + IIC_{S1} = Q_{C1} - Q_{D1} \quad (2)$$

Examples of calculation are as follows: For Qd of 331 mAh/g, IIC_{SUM} and Qc can be calculated as 1,253 and 1,584 mAh/g, respectively, to account for a coulombic efficiency of 20.9% as shown in equation 3; For Qd of 629 mAh/g, IIC_{SUM} and Qc can be calculated as 2,124 and 2,753 mAh/g, respectively, leading to a coulombic efficiency of 22.8% as shown in equation 4; And for Qd of 338 mAh/g, IIC_{SUM} and Qc can be calculated as 1,277 and 1,611 mAh/g, respectively, against a coulombic efficiency of 21.0% as shown in equation 5. Calculated Qc were found to be higher than these of results observed from the galvanostatic charge-discharge process. This is the reason why the irreversible capacity can be almost visible during GISOC.

$$IIC_{Sum} = (0.273^{-1} - 1) \times 331 + (0.255^{-1} - 1) \times (331 - 331) + 372 = 1,253 \quad (3)$$

$$IIC_{Sum} = (0.273^{-1} - 1) \times 331 + (0.255^{-1} - 1) \times (629 - 331) + 372 = 2,124 \quad (4)$$

$$IIC_{Sum} = (0.273^{-1} - 1) \times 331 + (0.255^{-1} - 1) \times (338 - 331) + 372 = 1,277 \quad (5)$$

Characteristics of a MWCNT electrode-electrolyte can be analyzed using the GISOC method in terms of IIE and IICs from the linear-fit range of the lithium insertion-desertion. Results of the GISOC method could thus be converted to the results of galvanostatic charge-discharge process irrespective of the state of charge of the system.

4. Conclusion

Characteristics of multi-walled carbon nanotube (MWCNT) in lithium cells using 1M LiPF₆ in EC:DEC:DMC (3:5:5) volume ratio as electrolyte were evaluated using the galvanostatic charge-discharge and the gradual increasing state of charge (GISOC) test method. A MWCNT electrode was charged at a specific current rate every 10 hours exhibiting a large amount of specific charge capacity of 1,300 mAh/g until 0 V versus Li/Li⁺. However, the observed specific discharge capacity of 338 mAh/g accounts to a coulombic efficiency of only 26%. Therefore, it is believed that at a specific current rate every 10 hours, the anode was not fully charged even if the potential was 0 V versus Li/Li⁺, presumably due to the kinetic non-equilibrium of lithium concentration into the bulk of the material. When a MWCNT/Li cell was tested using the GISOC method, two distinguishable linear-fit ranges were obtained due to lithium doping/undoping. Q_{C1} could be delivered from the data of IIE and IICs of each ranges by the modified equation of "IIC_{Sum} = Σ(Q_C - Q_D) = (IIE₁⁻¹ - 1)Q_{D1} + (IIE₂⁻¹ - 1)(Q_{D2} - Q_{D1}) + IIC_{S1} = Q_{C1} - Q_{D1}". The calculated Qc value was found to be higher than that obtained from the galvanostatic charge-discharge process. Characteristics of the MWCNT electrode-electrolyte can be analyzed using the GISOC method in terms of IIE and IICs with the linear-fit range of the lithium insertion-desertion. Results of the GISOC method could be correlated to the results of the galvanostatic charge-discharge irrespective of the state of charge of the battery system.

Acknowledgements

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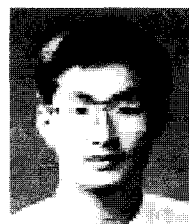
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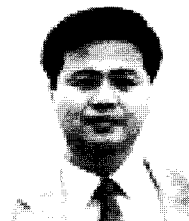
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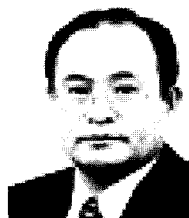
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