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ELECTROCHEMICAL PROPERTIES OF THE MULTI-WALLED CARBON NANOTUBE ELECTRODE FOR SECONDARY LITHIUM-ION BATTERY

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Abstract. In this study, multi-walled carbon nanotubes (MWNTs) were synthesized by the thermal chemical vapor deposition (CVD) process. Various chemical compounds such as benzene, xylene, cyclohexane, and n-hexane were used as carbon precursor, and ferrocene and thiophene were adopted as catalyst and promoter, respectively. Microstructure of the as-grown MWNTs was examined by XRD and FESEM. The MWNTs were adopted for fabricating the electrode of the secondary lithium ion batteries, and the electrochemical properties of the coin half-cells were measured. The influences of the MWNTs synthesized by different precursors on the electrochemical properties will be investigated.

1. INTRODUCTION

During the past decade, the rapid development of 3C devices drives the researches in high performance battery. Due to the excellent properties such as good cycleability, high working voltage, and fast charge-discharge rate, secondary lithium ion battery is one of the promising candidates of power supply in high technology applications.

One of the drawbacks in secondary Li ion battery applications is insufficient electric capacity. Carbon materials such as mesophase carbon microbeads (MCMB) and graphite were used for the anode instead of Li metal foil mainly because of safety consideration although the theoretical capacity (372 mAh/g) of carbon-based secondary Li ion battery is much lower than Li metal. Many researches were proceeded to enhance the capacity by adopting hard carbon, modified graphite carbon, and metal oxide compounds as the anode electrode [1]. Although the electric capacity indeed increased to a certain extent, some obstacles such as irreversibility and constant discharge voltage still need to be overcome.

The unique properties in MWNTs include nanoscale, one-dimensional, and well-graphitized structure with a central hollow core. Thus, it is expected that the discovery of MWNTs provides an opportunity to improve the electrochemical properties of the secondary Li ion battery.

To get enough MWNTs used as electrode material, this work adopted the floating catalyst method [2] to produce batch scale MWNTs. In this study, the characterizations such as specific surface area and X-ray diffraction on the raw materials were made, and the charge-voltage tests were performed. The correlation between microstructure and electrochemical properties is discussed.

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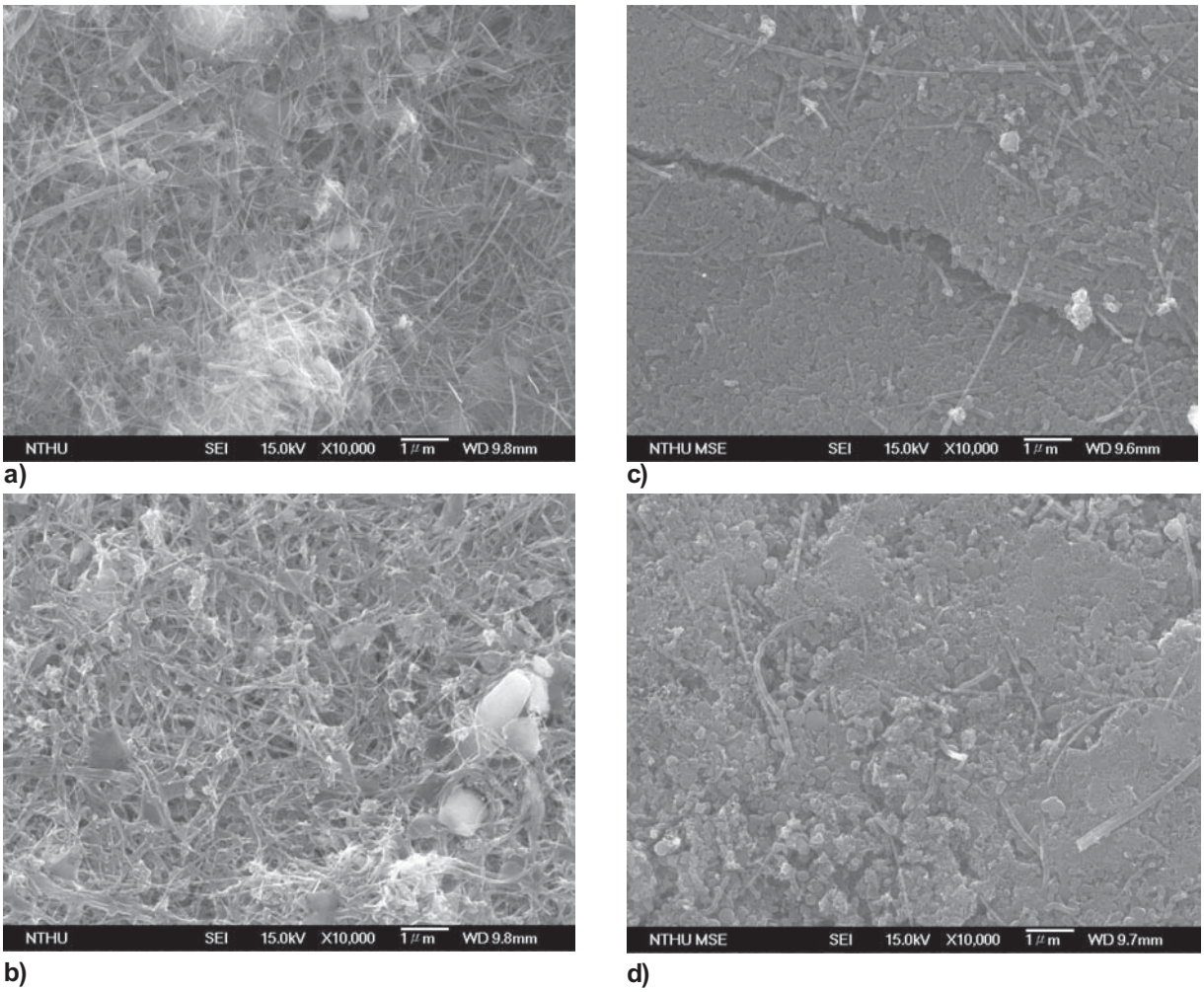

Fig. 1. (a) SEM image of as-prepared benzene-based MWNT electrode before the first charge-discharge cycle (10K); (b) SEM image of as-prepared xylene-based MWNT electrode before the first charge-discharge cycle (10K); (c) SEM image of as-prepared cyclohexane-based MWNT electrode before the first charge-discharge cycle (10K); (d) SEM image of as-prepared n-hexane-based MWNT electrode before the first charge-discharge cycle (10K).

2. EXPERIMENTAL

The scheme of CVD apparatus and floating catalyst method procedure were shown elsewhere [3]. Benzene, xylene, cyclohexane, and n-hexane were adopted as precursors to fabricate MWNTs, and the synthesis processes were performed in the temperature from 1100 °C to 1250 °C under hydrogen atmosphere.

The synthesized MWNTs were collected from the furnace wall, and the synthesized MWNTs were mixed with PVDF (Polyvinylidene Pluoride) in a ratio of 9:1 (in wt%) in NMP (N-methyl-2-pyrrolidine) solution. The slurry was poured on Cu foil and then the drying process was performed. The as-fabricated plates were pressed and punched for forming electrodes. After re-drying in vacuum, each plate was wetted in $LiPF_6$ in a solution containing ethylene carbonate (EC), diethyl carbonate (DEC), and propylene carbonate (PC) in a ratio of 3:5:2 (in volume). The wetted electrode was assembled with separator and a counter/reference Li foil electrode inside a ϕ2032 coin-cell module. After checking the open circuit voltage (OCV) value, the electrochemical test was proceeded with a rate of 15 Am/g.

3. RESULTS AND DISCUSSION

The morphologies of these four electrode plates made from four as-synthesized MWNTs are shown in Fig. 1. The microstructures of the benzene-based

Table 1. Capacities and efficiency of the fist five charge-discharge tests.

Types of MWNTs		*Capacity* (mAh/g)		*Columbic Efficiency*
		Discharge	*Charge*	
Benzene-based MWNTs	1	602.45769	171.37046	28.44
	2	211.86917	176.82007	83.46
	3	202.34943	174.22253	86.10
	4	200.46585	168.96344	84.30
	5	199.72152	167.07746	83.60
Xylene-based MWNTs	1	910.35145	160.32853	17.61
	2	240.80969	155.25283	64.47
	3	207.35959	153.10766	73.83
	4	187.72495	150.52951	80.18
	5	180.87817	149.95427	82.90
Cyclohexane-based	1	362.44461	213.61478	58.93
MWNTs	2	228.26890	211.84498	92.80
	3	221.19533	211.46351	95.60
	4	220.37593	212.60970	96.47
	5	219.28769	212.86905	97.07
N-hexane-based	1	466.13106	208.26338	44.68
MWNTs	2	227.86904	201.46410	88.41
	3	217.04134	200.61120	92.43
	4	212.56794	199.83738	94.01
	5	209.38149	199.06132	95.07

and xylene-based electrodes are different from those made from cyclohexane-based and n-hexane-based MWNTs. The compact structures of the cyclohexane-based and the n-hexane-based electrodes indicated higher impurity such as nanoparticles in these two materials. The voltage-capacity data of the electrodes made from these four MWNTs and MCMB are plotted in Fig. 2. The discharge capacity of the first cycle is in the following order: xylene-based MWNTs > benzene-based MWNTs > n-hexane-based MWNTs > cyclo-hexane-based MWNTs > MCMB. It is interesting to notice that the order of the first charge capacity is contrary to the one of discharge (Table 1).

One of the parameters affecting significantly the electrochemical properties of the carbon electrode is specific surface area. In this work, the specific surface area of the as-synthesis MWNTs was measured. Benzene-based and xylene-based MWNTs, as shown in Fig. 3, show higher specific surface area than that of the n-hexane-based and cyclo-hexane-based MWNTs. In the first discharge process, an obvious plateau observed at ~0.9 V, which is attributed to electrolyte decomposition and formation of solid electrolyte interface (SEI). Higher surface area induces more SEI layer formation, which results in higher irreversibility. The difference in discharge capacity between the high specific surface area (benzene-based MWNTs and xylene-based MWNTs) and low specific surface area (cyclohexene-based MWNTs and n-hexane-based MWNTs) is near 100 mAh/g in the first discharge test. It is probably due to the formation of SEI layer on the different micropore surface area. All these four MWNTs show no well-defined intercalation voltage plateau below 0.75 V, which implies there is no staging transition in MWNTs. The results are similar to those previously reported [4].

Graphitization of the synthesized MWNTs is another important parameter for Li intercalation. It is reported that due to the formation of SEI layer, both degree of graphitization and specific surface area affect the irreversibility; well graphitization results in high irreversibility [5] and larger specific surface area provides higher opportunity of interplay of carbon material and electrolyte. Carbon material such as MCMB has highly graphitized structure, but it has low specific surface area; therefore, it is

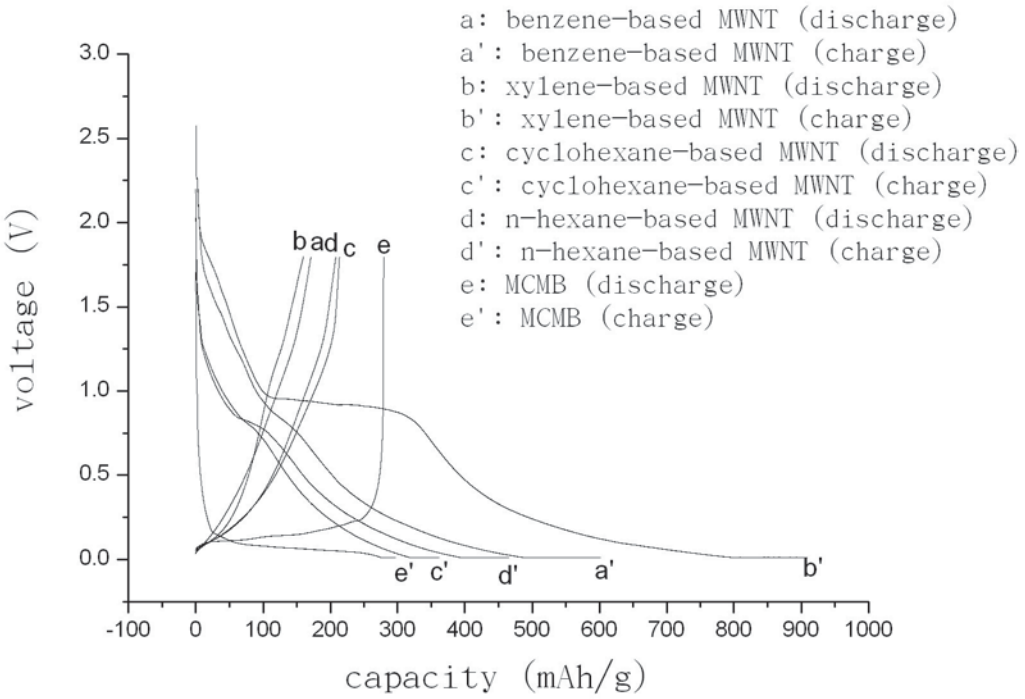

Fig. 2. First cycle charge-discharge plots for different precursor-based MWNTs.

still used commercially. Unfortunately, the as-synthesized xylene-based MWNTs show both well-graphitized structure (d_{002} = 0.3376 nm, close to d_{002} = 0.3354 nm for graphite) (Table 2) and high specific surface area; thus, high irreversibility is expected. In the plot of first discharge test, xylene-based MWNTs shown more significant plateau than the other three MWNTs. It believes that the obvious plateau corresponds to the formation of SEI layer, which is matching the characteristics of well graphitization structure and high specific surface area of the xylene-based MWNTs.

The monotonic increasing in charge capacity indicates no obvious staging transition for Li ion de-intercalation. Moreover, the charge-discharge curves almost coincide in the successive tests from the

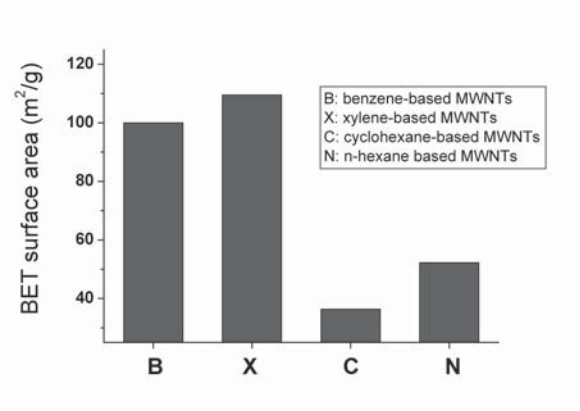

Fig. 3. BET surface area of the four as-synthesized MWNTs.

Table 2. XRD parameters of the synthesized MWNTs.

	2θ(°)	B_{002}(rad)	d_{002}(Å)	L_c(Å)	L_c/d_{002}
Benzene-based MWNTs	25.330	$4.84 \cdot 10^{-2}$	3.513	29.36	8.36
Xylene-based MWNTs	26.382	$2.46 \cdot 10^{-2}$	3.376	57.89	17.15
Cyclohexane-based MWNTs	24.707	$5.58 \cdot 10^{-2}$	3.600	25.44	7.09
N-hexane-based MWNTs	25.844	$3.37 \cdot 10^{-2}$	3.445	42.21	12.25

Table 3. Li intercalation comparison (< 0.25V) of xylene-based MWNTs / MCMB.

Sample	*1st discharge capacity* < 0.25 V	*2nd discharge capacity* < 0.25 V	*Maintainability*
Xylene-based MWNT	416.28 (mAh/g)	182.24 (mAh/g)	43.8 (%)
MCMB	315.31 (mAh/g)	265.18 (mAh/g)	84.1 (%)

second cycle, which reveals in-significant formation of the new SEI layer.

As shown in Table 3, the discharge capacity of xylene-based MWNTs decayed obviously under 0.25 V, on the other hand, MCMB shows higher maintainability. The discharge capacity under 0.25 V represented the capability for Li ion intercalation between graphene layers. The irreversibility in capacity of the MWNTs probably results from the following aspects: (1) Li intercalation into the inner core of the tubes; (2) Li ions forming a chain macromolecular Li_n; (3) electrostatic attracting of charged species preventing deintercalation of lithium ions from the inner core [5]; and (4) capillary force. To enhance the reversible capacity, enlarging the core size may be one of the methods to overcome the drawbacks and to improve the irreversible capacity.

4. CONCLUSIONS

MWNTs prepared by the thermal chemical vapor deposition process using different precursors were performed. Electrochemical properties of the coin half-cells fabricated by the synthesized MWNTs were tested. The results show that MWNTs with high BET area and high degree of graphitization behaves high irreversibility. All these four as-grown MWNTs show no well-defined intercalation and deintercalation voltage plateau below 0.75 V, which implies there is no staging transition in MWNTs.

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