

Carbon Nanofiber Modified Graphite Electrode Performance for Lithium Ion Secondary Battery

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Introduction

Carbonaceous materials have received considerable interest as anode material for lithium ion secondary battery. The graphitic carbon anode has the theoretical specific capacity of 372 mAh/g [1]. However, the specific capacity of carbon anode decreases significantly after several charge/discharge cycles, so many researchers have tried to control the physical property of carbonaceous materials for reducing the capacity decrease. In this study, carbon nanofibers were incorporated into natural graphite particles by mixing and ball milling [2–5]. The effect of carbon nanofibers content and ball milling on the electrical property, cycle performance, and charge/discharge capacity of the carbon nanofiber/graphite electrode was investigated.

Experimental

The active materials for anode electrode were prepared with carbon nanofibers and natural graphite particles by mixing and ball milling. The carbon nanofibers were synthesized by CCVD (catalytic chemical vapor deposition) method [6]. The active materials were mixed with 13 wt.% PVdF dissolved in N-methyl-2-pyrrolidone as a binder. The obtained mixture was coated on Cu mesh and dried at 80 °C for 12 hr. The dried electrode was rolled at 120 °C in a roll press and shaped 2×2 cm² size. The molded electrodes were dried at 80 °C under vacuum for 24 hr before use. The charge and discharge characteristics of carbon nanofiber/graphite electrodes were tested in two-electrode cells. Lithium foils were used as the counter (reference) electrode and carbon nanofiber/graphite electrodes were used as the working electrode. The mixture of 1M LiPF₆ in ethylene carbonate (EC), ethyl methyl carbonate (EMC), and dimethyl

carbonate (DMC) in 1:1:1 volume ratio was used as the electrolyte. The cells were discharged at a constant current density of 20 mA. The surface layer impedance of carbon nanofiber/graphite electrodes was measured at 10^{-2} – 10^5 Hz frequency and 10 mV amplitude. The Raman spectra were obtained to analyze the structure of active materials using a Jobin Yvon T6400 micro raman spectrometer over the range 800~2000 cm^{-1} . Thermogravimetric analysis (TGA) was performed using an auto TGA 2950HR V5.4A at a heating rate of 10 $^{\circ}$ /min.

Results and Discussion

The properties of active materials used for carbon anode are shown in Table 1. The natural graphite was basic material and the carbon nanofibers were incorporated into the natural graphite particles by mixing and ball milling in the range of 4~14 wt.%. The BET Surface areas and electric conductivities were increased as the carbon nanofiber content was increased, but the average particle size and the d_{002} were not changed significantly.

Table 1. The properties of natural graphite powder and carbon nanofibers /graphite mixtures with various carbon nanofiber content.

Carbon nanofiber Content (wt.%)	Average Particle size (μm)	D_{002}	Electric Conductivity (S/cm)	BET Surface area (m^2/g)
0	24.5	0.3358	10.6	1.7-2.5
0*	33.1	0.3378	12.1	7.7
4*	30.8	0.3358	26.4	15.7
6*	29.9	0.3361	32.8	16.6
10*	31.1	0.3376	36.7	25.4
14*	29.4	0.3368	39.5	26.8

* after 24 hr ball milling

The Raman spectra of anode material are shown Figure 1. In general the peaks at 1360 cm^{-1} and 1580 cm^{-1} are the well known D-peaks and G-peaks which correspond to amorphous sp^3 -bonding and graphitic sp^2 -bonding. The intensity ratio of 1350 cm^{-1} and 1580 cm^{-1} bands ($R = I_{1360} / I_{1580}$) is proportional to the degree of structural disorder at the surface of graphite[7]. The natural graphite and ball milled graphite Raman spectra are presented in graph (a). The Raman peak position of D-peak shifted from 1350 cm^{-1} to 1355 cm^{-1} and the R-value increased from 0.70 to 0.99 after ball milling, which indicate that the natural graphite contains some degree of structural defects on the surface and the defects increased after ball milling. These results indicate that the degree of structural disorder increased after ball milling. The graph (b) of Figure 1 shows raman spectra as a function of carbon nanofiber content. The R-value increased from 0.70 to 1.07 and 0.96 respectively as 6 and 10 wt% of carbon nanofibers were incorporated into the natural graphite.

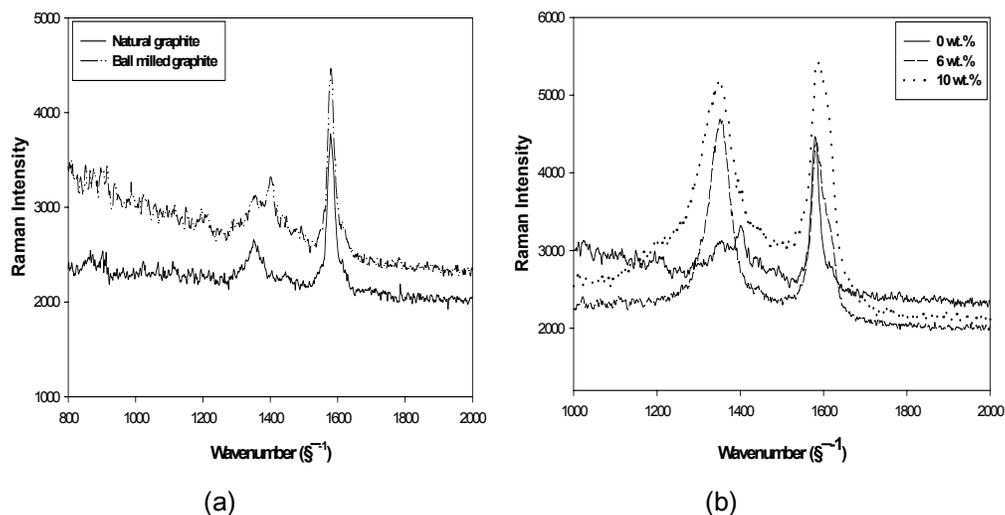


Figure 1. The Raman spectra of (a) graphite and ball milled graphite powder (b) ball milled graphite powder with various carbon nanofiber contents with 24 hr ball milling.

The TGA profiles of various active materials are shown in Figure 2. The rapid mass loss

of carbon nanofibers was occurred at 560 °C. The rapid mass loss of graphite was shifted from 755 °C to 780 °C by ball milling. In the case of 6 wt.% carbon nanofibers/graphite mixture, there were two points of mass losses at 610 and 755 °C, representing the characteristics of carbon nanofibers and natural graphite.

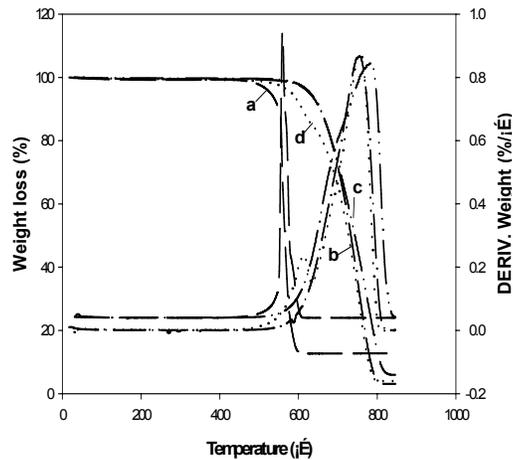


Figure 2. The TGA profiles of (a) carbon nanofiber, (b) natural graphite, (c) ball milled graphite, and (d) 6 wt.% carbon nanofibers/graphite mixture.

The graph (a) of Figure 3 shows the discharge capacity of graphite electrode and ball milled graphite electrode as a function of cycle number. The discharge capacity of ball milled graphite was increased by about 60 mAh/g with 24 hr ball milling. The graph (b) represents the discharge capacity of ball milled graphite electrode with various carbon nanofibers contents and 24 hr ball milling. As the carbon nanofibers were incorporated into the graphite particles in the range of 4–10 wt.%, the cycle performance was improved. However, the cycle performance was deteriorated, as the carbon nanofibers content was further raised to 14 wt.%.

The initial discharge/charge capacity is presented in Table 2. The 6 wt.% carbon nanofiber/graphite electrodes showed the highest capacities, in which the 2nd and 3rd cycle discharge/charge capacities were 330.5/330.6 and 329.8/330.0 mAh/g respectively.

Figure 3 also represents the cycle performance of 6 wt.% carbon nanofibers/graphite electrode is more stable that of other carbon nanofiber contents.

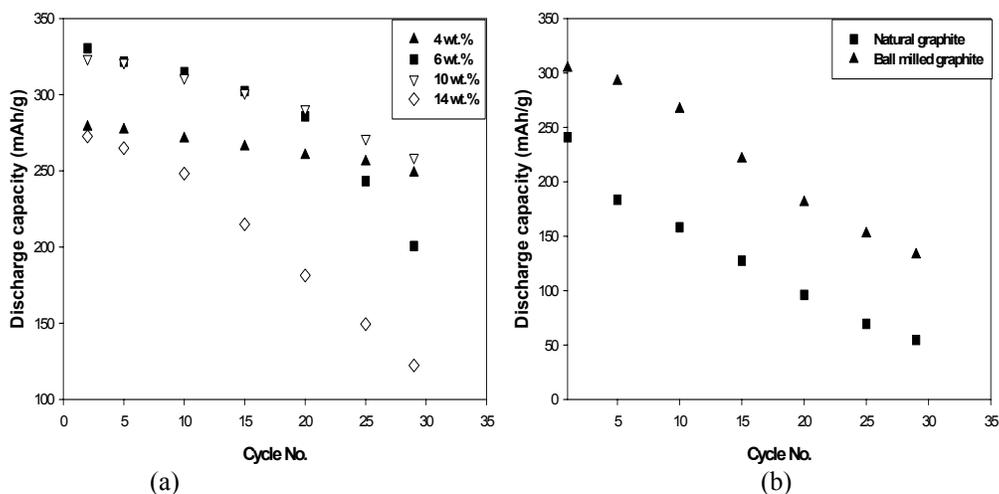


Figure 3. The cycle performance of (a) graphite electrode and ball milled graphite electrode with 24 hr ball milling, and (b) ball milled graphite electrode with various carbon nanofiber contents and 24 hr ball milling.

Table 2. 2nd and 3rd cycle discharge/charge capacity of ball milled graphite electrodes as a function of carbon nanofiber with 24 hr ball milling.

Preparation method	Carbon nanofibers content (wt.%)	2nd cycle	3rd cycle
		discharge/charge capacity (mAh/g)	discharge/charge capacity (mAh/g)
Mixing and ball milling	0	311.4 / 309.5	308.2 / 306.1
	4	279.1 / 278.9	278.9 / 279
	6	330.5 / 330.6	329.8 / 330.0
	10	323.6 / 319.5	321.7 / 317.7
	14	272.6 / 274.4	275.3 / 273.8

Figure 4 presents the AC impedance of various carbon nanofiber/graphite electrodes at the interface between electrode surface and electrolyte. The surface impedance of natural graphite electrode was decreased by both the ball milling treatment and the incorporation of carbon nanofibers. The surface impedance was decreased, as the carbon nanofiber content was increased up to 6 wt.%, However, the surface impedance was increased again with the further raise of carbon nanofiber content. As the carbon nanofibers were over critical content, the surface layer impedance increased, and the

cycle performance and initial charge/discharge capacity were decreased as shown Figure 3, Figure 4, and Table 2.

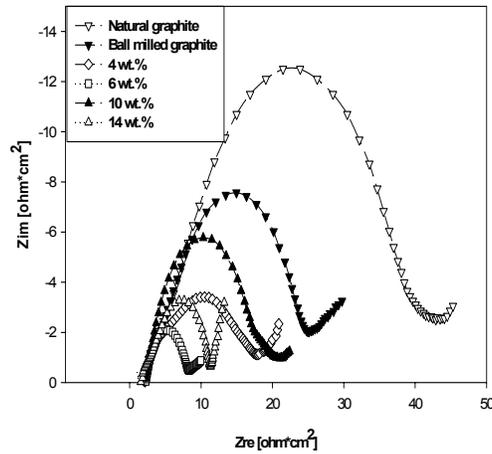


Figure 4. The Nyquist plots of various carbon nanofiber/graphite electrodes at 10^{-2} – 10^5 Hz frequency and 10 mV amplitude (electrolyte; 1M LiPF_6 /EC:EMC:DMC)

Conclusion

In order to improve the performance of lithium ion secondary battery, the ball milling treatment of active materials and the incorporation of carbon nanofibers into natural graphite particles before fabrication as the anode electrodes were carried out. The ball milling treatment increased the discharge capacity by about 60 mAh/g and the incorporation of carbon nanofibers in the range of 4–10 wt.% improved the cycle performance as well as the initial charge/discharge capacity. The surface layer impedance also decreased significantly at 6 wt.% of carbon nanofiber content and ball milling treatment for 24 hr.

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Acknowledgments

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