



Short communication

Comparison of multiwalled carbon nanotubes and carbon black as percolative paths in aqueous-based natural graphite negative electrodes with high-rate capability for lithium-ion batteries

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ABSTRACT

The effects of multiwalled carbon nanotubes (MWNTs) and carbon black (CB) as conducting additives on the rate capability of natural graphite negative electrodes in lithium-ion (Li-ion) batteries is investigated within concentration ranges where no degradation of anode capacity is observed. MWNT or CB solutions prepared with Nafion in an 80:20 volume mixture of water:1-propanol are incorporated into graphite precursor suspensions consisting of graphite particulates, carboxymethyl cellulose, and styrene butadiene rubber prepared in an aqueous medium. While negative electrodes with MWNTs demonstrate much better rate behaviour than those without MWNTs at a high C-rate, the rate capability of negative electrodes with MWNTs is not much different from that with CB. The reason for this similar behaviour is investigated with respect to the structural changes and aspect ratio of MWNTs, as well as the density difference between MWNTs and carbon black. Scanning electron microscopy images and Raman spectra for the dispersed MWNTs indicate that MWNTs are significantly damaged and shortened during dispersion, which reduces their electrical conductivity and increases their percolation threshold. This damage negatively affects the rate capability of graphite-nanotube composite electrodes.

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1. Introduction

Since the development of the first rechargeable lithium-ion battery in 1991, lithium-ion (Li-ion) batteries have become the state-of-the-art, rechargeable, compact energy-storage system not only for portable consumer electronics, but also for hybrid electric vehicles (HEVs) and plug-in HEVs (PHEVs) [1–3]. Among a variety of possible negative electrode (anode) materials, graphite is now commonly used for the fabrication of Li-ion secondary batteries, and provides a theoretical specific capacity of 372 mAh g⁻¹ [4–6]. However, Li-ion batteries with graphite negative electrodes are usually less powerful in terms of specific power or rate capability than those with other carbon materials as negative electrodes [7,8]. Thus, to improve the rate capability of negative electrodes for Li-ion batteries, various conducting agents such as vapour-grown carbon fibres (VGCFs), carbon nanofilaments (CNFs) and metals have been used as additives to anode materials due to their excellent

electrical conductivity [9–11]. Complete percolation of particles, however, requires significant quantities of material, which results in an increased irreversible loss of anode capacity [12]. Therefore, it is desirable to investigate the effects of conducting additives on the rate capability of lithium-ion battery negative electrodes within the concentration range where anode capacity suffers no degradation.

A carbon nanotube (CNT) is a new functional material that can be thought of as a graphitic sheet with a hexagonal lattice wrapped up into a cylinder [13]. It has a high aspect ratio, typically 10 000 or greater, as well as high electrical conductivity (1000 times greater than copper wire) [14]. Therefore, CNTs are very promising conducting additives for the negative electrodes of lithium-ion batteries.

In this study, the effect of CNTs as percolative additives for negative electrodes of lithium-ion batteries is investigated within a concentration range where anode capacity suffers no degradation. Carbon black (CB) is also evaluated as an additive for comparative purposes. Since the electrical conductivity of CNTs is reported to be higher than that of CB, the rate capability of negative electrodes with CNTs should be much better than that with CB. However, in this study, it is found that the anode rate capability of electrodes with CNTs is not much different from that of electrodes with CB. Thus, to understand the behaviour of graphite electrodes with CNTs,

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Table 1
Specifications of nanoparticles used in this study

	Diameter (nm)	Length (μm)	Bulk density (g cm^{-3})
Carbon black	50	–	0.125 ^a
MWCNT	$D_{\text{inner}} \sim 4.0 \text{ nm}$ $D_{\text{outer}} \sim 15 \text{ nm}$	Up to $50 \mu\text{m}$	2.09 ^b

^a Average value for carbon black provided by manufacturer.

^b Ref. [22].

their structural changes and aspect ratios have been investigated. The influence of the density difference between CNTs and CB on the rate capability of lithium-ion battery negative electrodes is also examined.

2. Experimental

2.1. Graphite suspension preparation

Natural graphite powder was obtained from commercial sources (90%, SL-20, Superior Graphite Company, Japan) and had a mean particle diameter of 5–20 μm . Carboxymethyl cellulose (CMC) from Daicel Co. Ltd., Japan with an average molecular mass of 330 000 and a degree of substitution of $DS = 1.28$, and styrene-butadiene rubber (SBR) (SB131, Zeon Corporation, Japan) with a solids loading of 40 wt.% were used as organic additives. Suspensions containing a graphite mass fraction of 35% were prepared with 2.5 wt.% of CMC and SBR based on the solid phase, respectively, by ball milling at room temperature for 12 h.

2.2. MWNT/CB suspension preparation

Multiwalled carbon nanotubes (MWNTs) were purchased from Nanocyl and used after heat treatment for 24 h at 200 °C. Carbon black (Denka, hereinafter denoted CB) was used for comparison. Table 1 provides information on the density and size of the MWNTs and CB used in this investigation. A Nafion dispersant (Dupont de Nemours & Co.) was used and had an average molecular weight of 70 000–120 000 in the form of a solution containing 5 wt.% Nafion, 50 wt.% 1-propanol, and 45 wt.% water. For the preparation of the MWNT or CB solution, 20 mL of bisolvent with a volume mixture of water:1-propanol of 80:20 in a 25 mm \times 95 mm vial was formulated. Then, 0.4 g of commercial 5 wt.% Nafion solution was added to 20 mL of prepared bisolvent. Finally, 2 mg of either MWNTs or CB were added to the bisolvent. The resulting weight ratio of solid phase to dispersant was 1:10. The prepared solutions were then treated in a bath-type sonicator (RK 106, Bandelin Electronic, Berlin, Germany) for 24 h at a power level of 240 W. No centrifugation was performed after sonication.

2.3. Natural graphite/MWNT or CB composite preparation

MWNT or CB solutions were incorporated into the prepared graphite suspension to make the two types of composites. The prepared composite solutions were homogeneously mixed by magnetic stirring for 12 h. The mass fraction of MWNT or CB was 0.0088 wt.% based on the graphite phase.

2.4. Measurements

Negative electrodes were fabricated by tape-casting the precursor suspension on to a 10- μm thick copper substrate (Furukawa, Japan). After forming, the sheet was first air-dried and then vacuum-dried at 150 °C to remove residual water. The density of the negative electrodes was 1.5 g cm^{-3} , irrespective of the type of electrode materials used. The rate capability of a 2032-type coin half-cell employing a natural graphite negative electrode prepared with MWNT or CB was evaluated based on its discharge characteristics at various current densities. In addition, the microstructure of the prepared negative electrodes was observed by means of scanning electron microscopy (S-4700, Hitachi, Japan). Finally, the prepared MWNT solutions were characterized by Raman spectroscopy (Renishaw RM1000-Invia) with a laser excitation energy of 633 nm.

3. Results and discussion

The rate behaviour of the prepared natural graphite negative electrodes is shown in Table 2. The 2032-type half coin cells were fully charged (0 V) using a constant current (CC)–constant voltage (CV) protocol. They were then discharged at different rates to a voltage of 1.5 V. Graphite electrodes with CB were evaluated for comparison. We found that the addition of CB or MWNTs did not affect the voltage profiles of the commercial graphite electrodes at various rates, which was observed in our previous investigation [4]. However, the graphite anodes prepared with MWNTs showed much improved rate behaviour at high-C rates, i.e., 5 C and 6 C, when compared with those without MWNTs. This is attributed to the fact that the high electron conductivity of MWNTs helps to provide conducting paths between anode graphite particles. Previous work has shown that the electrical conductivity of MWNT thin films was around $(1\text{--}4) \times 10^2 \text{ S cm}^{-1}$ along the nanotube axis and $5\text{--}25 \text{ S cm}^{-1}$ perpendicular to the axis [15]. It has also been reported that since nanotubes have a high aspect ratio of about 10 000 [14], the electrical contact between graphite particulates can be improved, which contributes to enhanced rate behaviour. This is consistent with a previous study that found that when VGCFs were used as an anode material, they showed good cycleability and high discharge capacity [11].

Table 2
Rate capability of prepared graphite negative electrode

Charge rate	Discharge rate	Graphite		Graphite + CNT		Graphite + Carbon black	
		Coulombic efficiency (%)	Rate capability (%) ^a	Coulombic efficiency (%)	Rate capability (%) ^a	Coulombic efficiency (%)	Rate capability (%) ^a
0.1 C	0.1 C	93.99		92.48		92.06	
0.2 C	0.2 C	99.97		99.79		99.74	
0.5 C	0.5 C	100.00	100.00	99.81	100.00	99.79	100.00
0.5 C	1.0 C	99.71	99.80	99.64	99.84	99.70	99.91
0.5 C	2.0 C	98.95	98.95	98.56	98.63	98.73	98.86
0.5 C	5.0 C	92.07	91.32	94.43	93.34	94.41	93.57
0.5 C	6.0 C	92.00	84.81	96.49	90.73	96.15	90.67

^a Discharge capacity at various rates/discharge capacity at 0.5 C.

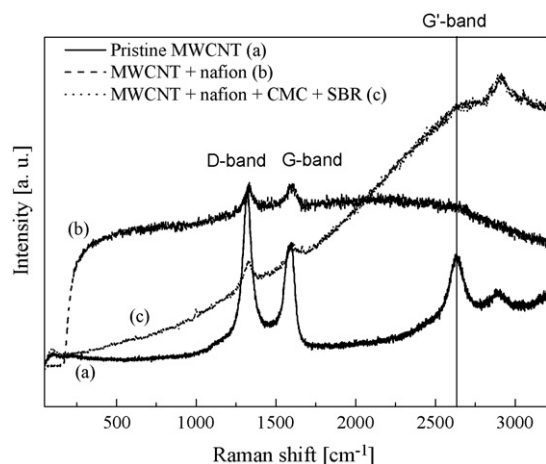


Fig. 1. Raman spectra for MWNTs with laser excitation energies of 633 nm.

The rate behaviours of graphite electrodes with CB are not much different from those with MWNTs. Since the electrical conductivity of CB is much lower than that of MWNTs, these results are in contrast to expectation, which would hold that the rate capability of graphite electrodes with MWNTs would be enhanced compared with those with CB. Therefore, the reason for the similarity in performance was examined from the standpoint of electrical conductivity by studying the structural changes and aspect ratio of MWNTs, as well as the density difference between MWNTs and CB.

Structural changes in MWNTs were investigated using Raman spectroscopy, as shown in Fig. 1. The structural changes from sp²- to sp³-carbon interrupt the conjugation and induce distortion of the graphitic layer, which reduces the electrical conductivity of the individual nanotubes, since sp³-carbon is regarded as a defect [16]. The values of $I_{D/G}$ appears to be almost identical to those of pristine MWNTs. Nevertheless, the G' peak is significantly reduced compared with that of pristine MWNTs, which implies that the MWNTs experienced significant damage during the dispersion process. Any processing of CNTs that directly affects their surface results in significant changes in their electrical transport properties [16]. Therefore, a significant reduction of the G' band can indicate a degradation of the electrical conductivity of MWNTs.

Fig. 2 presents SEM images of MWNTs as both dispersed MWNTs prepared with Nafion (Fig. 2A) and graphite-MWNT composites (Fig. 2B). For MWNTs prepared with Nafion, it is found that they are highly dispersed with a diameter of about 15 nm. In a previous investigation, we reported that 1-propanol provides a steric effect among nanotubes by changing the conformation of Nafion, which resulted in improvement of the dispersion properties of the nanotubes [17]. Another item of note is that the MWNTs are significantly shortened. According to the information provided by the manufacturer, the length of the MWNTs is up to 50 μm . In the present investigation, however, the length of a single MWNT is less than 1 μm .

Generally, the cutting of a CNT requires the exploitation of damaged sidewall sites progressing from the outer to inner layers. These sites can be formed by acidic oxidation, sonication, or a combination of the two [18]. Nafion plays the role of an oxidant, which results in MWNT cutting during a longer sonication treatment. For single walled carbon nanotubes dispersed for 8 h using sonication, individual nanotubes were not attacked during treatment and long nanotubes were maintained [17]. In this investigation, however, since the as-received MWNTs were significantly damaged as can

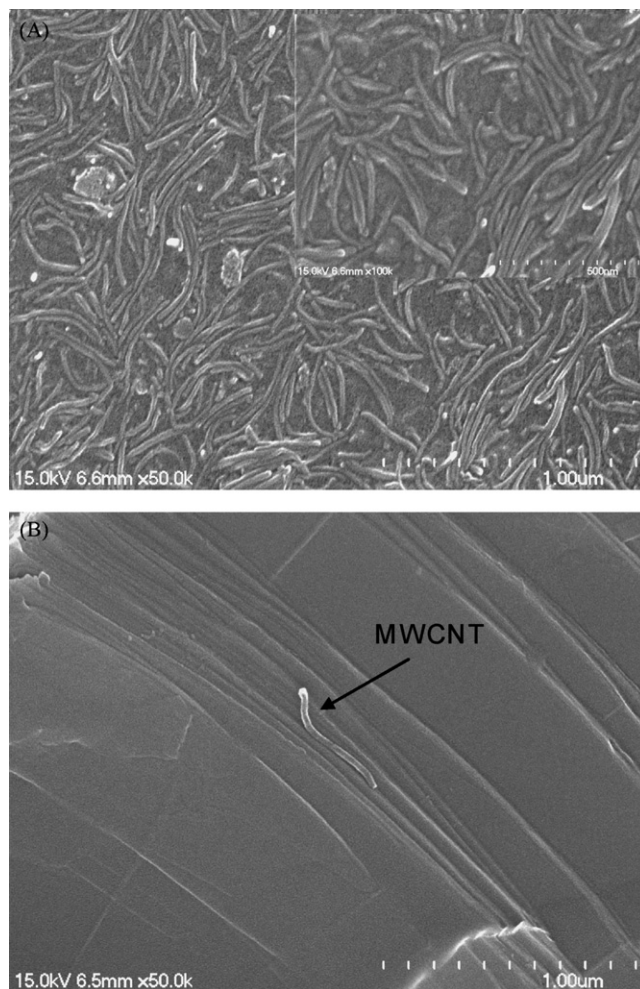


Fig. 2. Scanning electron microscopy images: (A) for dispersed MWNTs prepared with Nafion and (B) for graphite-MWNT composites. Very low concentration of MWNTs (0.0088 wt.% based on graphite) prevents investigation of a large number of MWNTs in negative electrodes.

be seen in Fig. 1, the combination of Nafion and longer sonication treatment resulted in MWNTs shortened to about 1 μm .

Cutting of MWNTs increases the percolative concentration of nanotubes. According to advanced percolation theory [19,20], the aspect ratio of particles affects the critical volume fraction required to achieve a conducting, percolated network. It has been reported that the percolation threshold for rod-like particles with aspect ratios of >100 was 0.24–1.35 vol.% [20]. In particular, MWNTs were reported to have a percolation threshold of 0.4 vol.% [21]. In this investigation, assuming that the aspect ratio of the dispersed MWNTs is less than 100 (from the SEM image, the length and diameter of CNT is assumed to be about 1 μm and 15 nm, respectively), the percolation threshold is calculated to be 0.9 vol.% [21]. Thus, the reduced aspect ratio significantly increases the percolation threshold of the MWNTs, which decreases the rate-capability of the graphite-MWNT composites.

A third effect to be considered is the density difference between MWNTs and CB. The volume fractions for CB and MWNTs are calculated as 0.074 and 0.004 vol.%, respectively. It is well known that electrical conductivity is directly proportional to the volume fraction of conducting particles up to the percolation threshold. In this investigation, the volume fraction of CB is nearly fifteen times higher than that of MWNTs. Even though the electrical conductivity of MWNTs is much higher than that of CB, the large volume differ-

ence between CB and MWNTs may compensate for the relatively poor electrical conductivity of CB.

4. Conclusions

The effect of MWNTs and CB as conducting additives on the rate capability of natural graphite negative electrodes for lithium-ion batteries have been investigated in concentrations where the anode capacity experiences no degradation. It is found that while negative electrodes with MWNTs show much better rate behaviour than those without MWNT, especially at a high C-rate, the rate capability of negative electrodes with MWNTs is not much different from that of negative electrodes with CB. Studies indicate that the MWNTs are significantly damaged and shortened during the dispersion process and this reduces their electrical conductivity and increases their percolation threshold. Furthermore, the large volume difference between CB and MWNTs may compensate for the relatively poor electrical conductivity of CB. The rate capability of negative electrodes will be investigated as a function of the length of MWNTs in a future study.

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