UTILIZING CARBON NANOTUBE (CNT)-BASED COMPOSITES AS ELECTRODE MATERIALS FOR RECHARGEABLE LITHIUM-ION BATTERIES REPRESENTS A TRANSFORMATIVE APPROACH IN ENERGY STORAGE TECHNOLOGY

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Abstract
The escalating need for enhanced energy density and increased power capacity in lithium-ion secondary batteries has spurred the exploration of electrode materials surpassing current standards. Carbon nanotubes (CNTs), owing to their distinctive one-dimensional tubular structure, elevated electrical and thermal conductivities, and remarkably vast surface area, emerge as ideal additives for augmenting the electrochemical properties of both anode and cathode in lithium-ion batteries. This augmentation is anticipated to result in significantly improved energy conversion and storage capabilities. The recent trajectory in electrode material advancement for LIBs predominantly revolves around hybrid nanostructures integrating Li storage compounds with CNTs. This paper undertakes a comprehensive review of recent strides in utilizing CNTs, encompassing methodologies for synthesizing CNT-based composites as electrode materials. The discourse delves into the physical, transport, and electrochemical dynamics of electrodes derived from CNT-containing composites. Furthermore, it accentuates the electrochemical performance of LIBs influenced by CNT presence, scrutinizing energy and power densities, rate capacity, cyclic life, and safety in contrast to configurations devoid of CNTs or containing alternative carbonaceous materials. The narrative concludes by addressing persisting challenges in deploying CNTs and CNT-based composites, alongside contemplation of prospects for their future exploitation.

I.   Introduction

The contemporary wireless and mobile society faces a formidable challenge: the provision of highly efficient, cost-effective, and environmentally friendly energy storage solutions to power an increasingly diverse array of applications. The efficacy of electronic devices hinges significantly on the performance of energy storage media, influenced by the properties of the materials used in their synthesis. Consequently, substantial efforts have been dedicated to developing novel and high-performance materials for battery components. Rechargeable lithium-ion batteries (LIBs), representing electrochemical energy storage and conversion technologies, stand out among various energy and power systems.

A typical LIB comprises a negative electrode (anode made of graphite), a positive electrode (cathode typically made of Li-CoO2), and a Li-ion-conducting electrolyte. During charging, Li ions move from the cathode through the electrolyte and are inserted into the anode. Upon discharge, the process reverses, with Li ions released by the anode and taken up again by the cathode. Electrons traverse external circuits in opposite directions, with the positive electrode half-reaction during charging represented by the equation:

$$LiCoO_2 \rightarrow Li_{1-x}CoO_2 + xLi^+ + xe^- \quad (1)$$

Rechargeable LIBs offer several advantages over traditional batteries such as lead-acid and Ni–Cd batteries, including high voltage, high energy-to-weight ratio (energy density), long cyclic life, absence of memory effect, and slow discharge when not in use. This makes LIBs the preferred choice for powering portable electronic devices and increasingly popular in defense, automotive, and aerospace applications. Despite their commercial success, intensive research continues on the electrodes and their constituent materials.

Various applications, including electric vehicles (EVs), hybrid electric vehicles (HEVs), power tools, uninterrupted power sources (UPS), stationary storage batteries (SSBs), microchips, and next-generation wireless communication devices like 3G mobile phones, are driving efforts to enhance

battery performance. Beyond energy/power density and cyclic performance, safety and cost are critical considerations limiting LIB applications in these areas. Recognizing that a single type of LIB cannot meet the diverse requirements of these applications, different types with specific properties must be considered. For instance, high-energy capacity batteries are essential for high-speed telecommunication devices, while high-power capacity batteries are desirable for EVs, HEVs, and power tools.
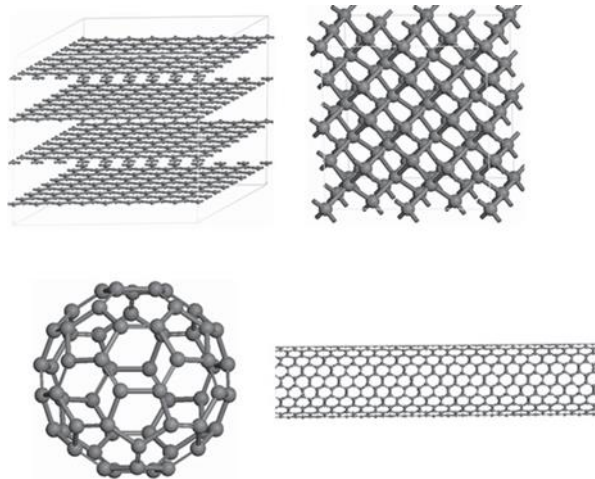

Fig. 2. Structures of different carbon materials. After Lin et al. [17], Moniruzzaman and Winey [18].

One of the notable drawbacks of lithium-ion batteries (LIBs) is their low power density, primarily attributed to high polarization, especially at elevated charge-discharge rates. Factors such as slow lithium ion diffusion rates, inadequate electrical and thermal conductivities in the electrode, and at the electrolyte-electrode interface contribute to this polarization. Addressing these challenges necessitates the development of novel electrode materials featuring a large surface area, short diffusion paths for ionic transport, and high electronic/thermal conductivities. Nanoscaled electrode materials offer several advantages, including reversible lithium intercalation/extraction without compromising the electrode material structure, increased Li ion insertion/removal rates due to shorter transport paths, enhanced electron transport properties, and increased contact area with the electrolyte, reducing volume changes associated with intercalation.

Carbon nanotubes (CNTs) have been explored, with varying success, as additives for both anode and cathode materials, or even as replacement materials for anodes, to meet the multifaceted requirements for LIBs. The unique properties of CNTs, such as their 1D structure, high aspect ratio, and large specific surface area, make them appealing for enhancing the performance of lithium-ion batteries.

Structure, Synthesis, and Properties of CNTs

Since the discovery of carbon nanotubes (CNTs), significant research efforts have been dedicated to understanding their fundamental properties and practical applications. Unlike other carbon allotropes such as graphite, diamond, and fullerene, CNTs exhibit a one-dimensional (1D) structure with a length-to-diameter ratio exceeding 1000. They are envisioned as cylinders composed of rolled-up graphene sheets around a central hollow core, with diameters on a nanometer scale and end caps exhibiting a hemisphere of fullerene structure. Two types of CNTs exist: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs).

CNTs can be synthesized through various methods, including arc-discharge, laser ablation, gas-phase catalytic growth from carbon monoxide, and chemical vapor deposition (CVD) from hydrocarbons. Among these, CVD is considered a more viable method for mass production of CNTs at a lower cost. The chirality of CNTs, determined by the rolling angle of the graphene sheet against the tube axis, influences their transport and electronic properties. CNTs exhibit exceptional mechanical properties, with a Young's modulus as high as 1.2 TPa and tensile strength ranging from 50 to 200 GPa, making them the strongest and stiffest materials on Earth.

In addition to their mechanical prowess, CNTs possess advantageous electrical and thermal properties, surpassing other carbon materials such as graphite, diamond, and fullerene. These properties make CNTs an ideal candidate for various applications, including field emission, thermal conductors, energy storage, conductive adhesives, thermal materials, structural materials, fibers, catalyst supports, biological applications, air and water filtration, ceramics, and more.

Recent Developments and Applications of CNTs in LIBs

Recent developments in lithium-ion batteries have focused on designing hybrid nanostructures by incorporating CNTs into Li-storage compounds as new electrode materials. CNTs offer attractive properties for LIBs, including their mechanical and transport properties, large specific surface area, and a structure highly accessible for Li interaction.

Notably, CNTs facilitate nearly 100% accessibility of the entire carbon structure to Li interaction, especially when tube ends are opened using techniques like ball milling. This high accessibility, even in the presence of agglomerated CNTs, provides superior mobility for ion exchange processes, a crucial requirement for dynamic response in batteries based on intercalation.

Cathode Materials and Layered LiMO2/MWCNT Nanocomposites

Cathode materials play a pivotal role in determining the functional performance of rechargeable LIBs. Popular cathode materials include layer-structured $LiCoO_2$, $LiMnO_2$, $LiNiO_2$, spinel $LiMn_2O_4$, $Li(Ni_{1/2}Mn_{1/2})O_2$, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, $Li(Ni_{1/2}Mn_{3/2})O_4$, and elemental sulfur. Li transition metal phosphates, such as $LiFePO_4$, have also gained attention due to their high theoretical specific capacity.

Despite the development of various cathode materials, $LiCoO_2$ remains widely used, but its high electrical resistance can lead to polarization and poor utilization of the active material. To address this, conductive additives like carbon black (CB), carbon fibers (CF), and MWCNTs are incorporated to form conductive networks within the material. Among these additives, MWCNTs have proven to be the most effective in reducing resistance and improving electrochemical performance.

MWCNTs, with their 1D geometry and high aspect ratio, efficiently establish continuous conductive networks at low percolation thresholds, allowing for effective electronic transport throughout the cathode material. The nanoscale structure of MWCNTs facilitates rapid electron transfer, outperforming traditional additives like carbon black.

Studies on $LiCoO_2$/MWCNT composite cathodes demonstrated enhanced capacity retention ratios compared to cathodes containing other conductive additives. The incorporation of MWCNTs offers advantages in terms of rate capability and cyclic efficiency, highlighting their potential in the development of high-performance LIBs.

Conclusion

In conclusion, the utilization of carbon nanotubes (CNTs) in lithium-ion batteries (LIBs) holds significant promise for overcoming challenges related to low power density and high polarization. The unique properties of CNTs, including their 1D tubular structure, high aspect ratio, and large specific surface area, make them ideal candidates for enhancing electrode materials in LIBs.

Recent developments focus on incorporating CNTs into Li-storage compounds, forming hybrid nanostructures that leverage the exceptional mechanical, transport, and electronic properties of CNTs. CNTs offer advantages such as reversible Li intercalation/extraction, increased Li ion insertion/removal rates, enhanced electron transport properties, and greater contact area with the electrolyte.

Notably, CNTs have been explored as additives for cathode materials, especially in layered LiMO2/MWCNT nanocomposites. These composites exhibit improved electrochemical performance, with MWCNTs proving to be more effective than traditional additives like carbon black. The development of high-performance LIBs involves careful consideration of cathode materials, and the incorporation of CNTs holds promise for addressing critical challenges and advancing the efficiency and capabilities of lithium-ion batteries.

Among many layered metal oxides, LiNi1/3Co1/3Mn1/3O2 (NCM) is considered a very promising cathode material because of its excellent thermal safety characteristics compared to LiCoO2, good capacity in a wide potential range and small volume changes upon cycling [56,57]. NCM has been chosen as the active material for po- sitive electrodes using 1% MWCNTs as conductive agent [58]. MWCNTs were well mixed with the active materials and attached onto the surface of particles, as shown in Fig. 5a. The addition of MWCNTs significantly enhanced the rate performance of NCM-based cathodes at different C-rates between C/5 and 5C. As shown in Fig. 5b, the specific discharge capacities delivered by the cath- odes containing MWCNTs were higher than those of the electrodes containing only the ordinary conductive agents at all investigated rates. The effect was more significant at higher current rates –
i.e. about 50% higher specific capacity at 5C. After cycling at rela- tively high currents and returning to C/5, the capacity values re- mained much the same as the initial values. The incorporation of CNTs of low contents as a conductive additive presented an effec- tive strategy to establish an electrical percolation network in the electrode, resulting in much improved rate capabilities of NCM electrodes.

LiFePO4/MWCNT nanocomposites

LIBs work when electrons are exchanged simultaneously as a result of intercalation and extraction of Li ions. Both the ion and electron transport properties are critical to cathode materials, and LiFePO4 has a poor electrical conductivity of around 10—9 S cm—1. MWCNTs were successfully used to replace the conventional filler, carbon black, in LiFePO4 [59], showing that LiFePO4–C/Li battery with 5 wt.% MWCNTs displayed much better electrochemical prop- erties with a discharge capacity of 142 mA Hg—1 at 0.25 C at room temperature than those with carbon black or without any additives (Fig. 6).

A novel network composite cathode made from LiFePO4 parti- cles mixed with MWCNTs was studied for high rate capability [60]. Fig. 7 shows the 3D networks consisting of MWCNTs inter- connecting LiFePO4 particles, which effectively improved the elec- tron transfer between the active material and current collector (Al foil), as well as the electrochemical performance, see Table 3. In the high-frequency region, the intercepts with real impedance [Re(Z)] axis of LiFePO4/MWCNTs and LiFePO4/acetylene black composites were 105 X and 154 X, respectively. These values are known to be the total electric resistance of the electrode materials, electro- lyte resistance and electric leads. The substantial reduction in total electrical resistance was attributed to the replacement of acetylene black (AB) by MWCNTs. The slope of the impedance of the LiFePO4/ MWCNT composite was higher than that of LiFePO4/AB, indicating enhanced electrochemical activity of LiFePO4 due to MWCNT net- works. The initial discharge capacity was improved to 155 mA Hg—1 at C/10 rate. MWCNTs were also known very effec- tive in improving rate capability and cyclic efficiency, which is cru- cial to high-power LIBs particularly for electric vehicles.

In another study on hybrid LiFePO4/MWCNT composites, LiFe- PO4 was synthesized based on a room-temperature solid-state reaction, followed by microwave heating and addition of both citric acid and MWCNTs [61]. The as-prepared LiFePO4/MWCNT compos- ite cathodes exhibited an excellent electrochemical capacity of 145 mA Hg—1 at C/2 and maintained a stable cyclic ability. The cy- cling behavior of LiFePO4 with and without MWCNT additives are shown in Fig. 8. The initial capacity of LiFePO4 cathodes was re- duced from 90 to 70 mA Hg—1 after 50 charge–discharge cycles. The large reduction in residual capacity was attributed to the slow diffusion of Li ions in LiFePO4 and poor contact between the LiFe- PO4 nanoparticles and conductors. In contrast, the corresponding reduction in capacity was almost negligible along with a much higher initial discharge capacity of ~145 mA Hg—1 when MWCNTs were added into the cathode material. MWCNTs facilitated the for- mation of 3D networks that connected the LiFePO4 particles, improving the transport characteristics of Li ions and electrons at high rates. It was also claimed that the expansion of citric acid dur- ing the charge–discharge process reduced the particle size, thus reducing the diffusion path, which in turn improved the reversibil- ity of Li ion intercalation/extraction.

A high-rate capability is essential for future battery applications like electric vehicles that require a high power density during oper- ation. The hierarchical nanostructure with $FePO_4$ shell directly grown on the CNT core was used as a cathode material for LIBs, which exhibited excellent electrochemical properties [62]. Fig. 9a schematically illustrates the core–shell structure of amorphous $FePO_4$/CNT hybrid nanowires, through which Li ions and electrons could readily diffuse into and out because of its nanometer scale and large surface area. It is expected that the improved transport can enhance the rate capability of LIBs. The high resolution trans- mission electron microscopy (HRTEM) image in Fig. 9b clearly identifies the amorphous nature of the outer shell.

The charge–discharge curves of the initial five cycles of the core– shell electrode at a current rate of 20 mA g—1 are shown in Fig. 9c. The discharge capacity measured based on the total weight of the core–shell structured nanowire electrodes was about 149 mA Hg—1 at the first cycle and then it was reduced to 140 mA Hg—1 after sev- eral cycles with high reversibility. A clear potential plateau near 3.4 V was similar to the crystalline olivine $LiFePO_4$ cathode. This behavior has an advantage in monitoring the state of charge during battery operation. The specific capacities of the nanowires at differ- ent current rates are shown in Fig. 9d. The left and right Y-axes rep- resent the specific capacities calculated based on the total weight of nanowires and the weight of amorphous $FePO_4$ shell alone, respec- tively. The high specific capacity of the nanowires was retained after 50 cycles even at high current rates up to 1000 mA g—1. The reversible capacities were about 160, 133, 125 and 100 mA Hg—1 based on the weight of the amorphous $FePO_4$ shell at current rates of 100, 200, 500, and 1000 mA g—1, respectively.

LiMn2O4/MWCNT nanocomposites

A few studies have also been reported for improving the elec- trochemical performance of $LiMn_2O_4$ electrodes by incorporating oxidized MWCNTs [63]. Fig. 10 presents the results from the galva- nostatic charge–discharge tests of $LiMn_2O_4$/MWCNT cathodes. The initial discharge capacities were 119.4, 110.6, 105.5 and 91.4 mA Hg—1 at the rates of 0.1, 0.5, 1 and 2 C, respectively, which were much higher than the conventional $LiMn_2O_4$/AB with the same additive content. It was concluded that the improved con- ductive networks facilitated connection between the active mate- rials and electron transport, with associated enhancements in rate capability and cyclic performance. Fig. 11 shows the electro- chemical impedance spectra (EIS) of $LiMn_2O_4$ with MWCNTs or AB additives. The charge transfer resistance Rct, a measure of elec- trochemical reactions at the electrode– electrolyte interface and particle-to-particle contact, was 34.32 and 53.2 X, respectively, for $LiMn_2O_4$/ox-MWCNT and $LiMn_2O_4$/AB composites, indicating a much lower charge transfer resistance of the former cathode material containing MWCNTs. The 3D networks formed by oxi- dized MWCNTs increased the contact area of active materials, effectively reducing the charge resistance.

$LiMn_2O_4$/MWCNT nanocomposites were also prepared by a fac- ile sol–gel method [64]. The nanocomposites showed high cyclic performance with a remarkable capacity retention of 99% after 20 cycles, which is much better than the corresponding initial capacity loss of 9% after 20 cycles for the neat $LiMn_2O_4$ nanoparti- cles, as shown in Fig. 12a. Fig. 12b presents a significant reduction in charge transfer resistance from 120.4 X for the spinel $LiMn_2O_4$ to 98.3 X for the $LiMn_2O_4$/MWCNT nanocomposite, a direct reflec- tion of the improved electrical conductivity arising from the inti- mate networking by MWCNTs among the spinel $LiMn_2O_4$ particlescan enhance the rate capability of LIBs. The high resolution trans- mission electron microscopy (HRTEM) image in Fig. 9b clearly identifies the amorphous nature of the outer shell.

The charge–discharge curves of the initial five cycles of the core– shell electrode at a current rate of 20 mA g—1 are shown in Fig. 9c. The discharge capacity measured based on the total weight of the core–shell structured nanowire electrodes was about 149 mA Hg—1 at the first cycle and then it was reduced to 140 mA Hg—1 after sev- eral cycles with high reversibility. A clear potential plateau near 3.4 V was similar to the crystalline olivine $LiFePO_4$ cathode. This behavior has an advantage in monitoring the state of charge during battery operation. The specific capacities of the nanowires at

differ- ent current rates are shown in Fig. 9d. The left and right Y-axes rep- resent the specific capacities calculated based on the total weight of nanowires and the weight of amorphous FePO4 shell alone, respec- tively. The high specific capacity of the nanowires was retained after 50 cycles even at high current rates up to 1000 mA g—1. The reversible capacities were about 160, 133, 125 and 100 mA Hg—1 based on the weight of the amorphous FePO4 shell at current rates of 100, 200, 500, and 1000 mA g—1, respectively.

Intrinsically conducting polymer (ICP)/MWCNT nanocomposites

LIBs with cathode materials made from intrinsically conducting polymers (ICP), such as polyaniline (PANI), polyacetylene, polythi- ophene, polypyrrole and polymethylthiophene, have several important advantages over conventional LIBs with metal oxide cathodes, such as a longer cyclic life, a lower self-discharge rate, higher endurance to overdischarge, a lower manufacturing cost, more flexible shapes to form and easiness to make thin films. Among many conducting polymers, PANI is a promising candidate for the electrode material because it has good redox reversibility, high stability in air and aqueous solutions, and can be easily pre- pared using a chemical or electrochemical method at low produc- tion costs. However, the electrodes synthesized from conducting polymers also have problems related to stability, adherence and conductivity that may affect the reversibility of the electrode and thus limit their applications in energy storage devices. Recent stud- ies have shown that the introduction of MWCNTs into PANI can en-hance the electrical properties by facilitating charge transfer pro- cesses between the two components [65–67]. An extremely high efficiency close to 100% with a discharge capacity of 120 mA Hg—1 was achieved using these composite electrodes along with Li metal and an ionic liquid electrolyte [65].

PANI/MWCNT composites prepared by an in situ chemical oxi- dative polymerization method were also extensively studied [68]. The charge transfer resistance of the electrode was reduced due to the incorporation of MWCNTs. Coulombic efficiency is an impor- tant index in assessing the performance of LIBs. An increase in Cou- lombic efficiency is often reflected by an increase in reversibility of charge–discharge cycle as the cycle number increases. As shown in Fig. 13a, the Coulombic efficiency approached 99% for the PANI/ MWCNT composites and only about 95% for the neat PANI. The variations of discharge capacity with the cycle number for these materials are shown in Fig. 13b. The discharge capacity of the PANI/MWCNT composites (122.8 mA Hg—1) was much higher than that (98.9 mA Hg—1) of the neat PANI. The result remained much the same even after the neat PANI was applied in the form of nanofibers [69].

To summarize the above discussions, the relative electrochem- ical performances of the cathode materials containing different types of carbon materials, such as MWCNTs, CB, AB and CF, are tab- ulated in Table 4. It is clearly seen that both the initial and residual discharge capacities of the composite cathodes containing MWCNTs are significantly higher than those with other types of additives, CB, AB or CFs, regardless of the types of metal oxide materials. In addition, the corresponding charge transfer resistance was generally lower for the former than the latter cathode materi- als. The CNTs facilitated the formation of electric/thermal conduc- tive networks that reduced the inner resistance and enhanced the thermal dissipation, ultimately resulting in higher specific capaci- ties even at high charge–discharge current rates as well as en- hanced safety for LIBs.

Other nanocomposites containing MWCNTs as conductive additive

Several other types of nanocomposite cathode materials have been synthesized using CNTs. For example, MWCNTs were coated with Co3O4 nanocomposites by a chemical precipitate method for use as cathode material [70]. The capacities of the MWCNT/Co3O4 nanocomposite cathodes measured during Li insertion and extrac- tion were 591.7 and 407.9 mA Hg—1, respectively. These values are almost twice those of the MWCNTs used (313.7 and 217.6 mA Hg—1, respectively), but were much lower than those of the Co3O4 cathodes (1100.5 and 682.7 mA Hg—1, respectively).

PVC/CNT nanocomposites were synthesized via electrochemical polymerization of N-vinyl carbazole (VC) on CNT films, whose charge–discharge characteristics were evaluated [71]. After 20 cy- cles, high specific discharge capacities of 45 and 115 mA Hg—1 were obtained for PVC-functionalized SWCNTs and MWCNTs, respec- tively. This study provided two important pieces of information: namely (i) the hybrid nanocomposites can perform much better than the neat PVC for use as cathode material and (ii) the PVC/ MWCNT nanocomposite presents a higher discharge capacity than the PVC/SWCNT nanocomposite.

The elemental materials to be used as positive electrode for LIBs should have an inherently high discharging capacity and an excel- lent cyclic life, along with long-term operation and a low cost. A Li/ S redox couple has a theoretical specific capacity of 1672 mA Hg—1, and a theoretical specific energy of 2600 W h kg—1, based on sulfur active material and assuming complete reactions between Li and S to form Li2S. Use of S is in general advantageous because it is envi- ronmentally benign and inexpensive. It also has disadvantages, such as a low conductivity and easy dissolution in the electrolyte to form polysulfide. MWCNTs were incorporated into sulfur to en- hance the electrical conductivity and thus to reduce the dissolution of sulfur [72]. The initial discharge capacity of the sulfur electrode containing MWCNTs was 485 mA Hg—1 at 2.0 V vs. Li/Li+. The cyclic life and rate capability of sulfur cathodes increased significantly as a result of adsorption of polysulfides by MWCNTs. In addition, the structural modification of the carbon matrix resulted in increases in both sulfur utilization and cyclic life of the Li/S batteries.

Anode materials

Considerable attention has recently been attracted to Li alloy materials containing elements such as Si, Al and Sn for application as negative electrodes of LIBs because these elements possess a higher theoretical specific capacity than that of the traditional an- ode material, graphite [73–76]. Among these, Si has the highest va- lue. The practical use of Si particles, however, is significantly hindered because of two major problems. One is the low electrical conductivity and the other is the severe volume expansion/con- traction during the alloying and de-alloying reactions with Li ions [77–80]. Several failure modes of Si particle electrodes have been identified [81,82]: Si particles expanded upon charging as a result of the alloying reaction, leading to swelling of the electrode layer, where carbon powder was also added to compensate for the poor conductivity of Si particles. In the following discharging period, the Si particles contracted as a result of the de-alloying reaction, but the electrode layer remained swollen because of its inelastic nat- ure. The net result after the charge–discharge cycles was break- down of the conductive networks that existed between Si, carbon particles and the current collector.

Several approaches have been proposed to address the above problems: for instance, breakdown of the conductive network can be minimized either by (i) applying a pressure on cells [83] using an elastomeric binder [84] or (ii) forming a composite with conductive materials, such as CNTs [85,86]. Different carbon addi- tives show different degrees of crystallinity, morphology and par- ticle sizes, which in turn influence the conductivity and electrolyte absorption capacity and thus the overall capacity of the cell. The large electrochemically accessible surface area of por- ous nanotube arrays and their high conductivities make them an ideal anode material for LIBs.

Apart from Si, intermetallic compounds, transitional-metal oxi- des (MO, where M is Co, Ni, Cu or Fe) and Sn/C nanostructured composites have also been studied, showing that they possessed high electrochemical capacities with 100% capacity retention for up to several hundred cycles and high recharging rates [87–91]. One of the disadvantages of these materials was that their syn- thetic routes were very complicated and expensive.

CNTs as anode materials

CNTs possess a unique shape and a high capacity that are useful characteristics for use in LIBs, particularly if Li ions can be interca- lated into the tube. Template-synthesized CNTs can be fabricated

as free-standing nanoporous carbon membranes, and narrower, highly ordered graphitic CNTs can be prepared within the mem- brane's tubules [92]. Both the outer and inner tubules are electro- chemically active for intercalation of Li ions. Electrochemical test results showed that the CNT membrane electrodes exhibited a reversible intercalation capacity of 490 mA Hg—1. The CNT struc- ture and the degree of graphite crystallinity play a major role in determining both the specific capacity and cyclic life of CNT mem- branes [11–15,92,93]. The cycleability of highly-graphitized MWCNTs was more stable than that of slightly graphitized MWCNTs, whereas the slightly graphitized MWCNTs had a higher specific capacity than the highly-graphitized MWCNTs. This obser- vation is attributed to the fact that Li tended to be doped preferen- tially into the regions with less organized graphitic structures, microcavities, edges of graphitic layers or the surface of single gra- phitic layers. Nevertheless, graphitized CNTs in general showed a higher capacity of Li intercalation than amorphous CNTs [94]. The electrochemical performance of CNTs during Li insertion corre- lates well with their micro-texture and chemical compositions that are affected by the synthesis conditions [94–96]. The rather dis- couraging results on Li insertion capability of MWCNTs in an ear- lier paper [97] further confirmed the importance of CNT structure.

MWCNT (mA Hg—1)	The initial capacity (mA Hg—1)			Cyclic performance (cycles)	Residual capacity		
Ref.	Charge	Discharge			Charge	Discharge	
Pristine	312						[99]
Chemically Etched	422	2087	100				[99]
Purified	351	641	50		311		[101]
Ball-milling			50		616		[101]
Short CNTs	502	1295	50			230	[104]
Long CNTs	188	615	50			142	[104]

Instead of using CNTs as the main anode material, studies have also been made on incorporation of CNTs as additive into the otherwise graphite dominant anode in anticipation to improve the capacity due to the CNT's higher electrical conductivity and specific surface area than graphite. The electrochemical perfor- mance of LIBs relies largely on the efficient cyclic insertion/extrac- tion of Li ions between the cathode and anode, where rapid charging, high ionic storage and slow discharge constitute ideal de- vice characteristics. Coin-cell batteries constructed using purified SWCNT 'paper' as the anode and LiNi0.2Co0.8O2 as the cathode material were reported [98]. An overview of the components used to fabricate the battery is shown in Fig. 14a: they are from left to right (1) cathode mixture in aluminum cap, (2) Celgard separator, (3) O-ring, (4) SWCNT anode, and (5) stainless steel cell base. Fig. 14b shows the typical charge– discharge behavior for the SWCNT anode coin cell. The first discharge cycle had a capacity of 166 mAhg—1 under these conditions, demonstrating the viability of SWCNT anode material.

Factors affecting performance of MWCNT anode materials

There are several important factors that affect the electrochem- ical performance of CNT anode materials, among which the surface condition and length of CNTs have been extensively studied. The MWCNTs were modified through chemical etching, ball-milling and shortening, and their influences on the initial and residual capacities are summarized in Table 5 and the details are discussed in the following.

A large number of defects and pores were introduced to MWCNTs as a result of chemical etching by HNO3, which were cor- related to enhancements of the capacity in the voltage range above 1.0 V and the reversible capacity [99,100]. These observations were related to preferential doping of Li ions onto the reactive defect sites rather than the perfect carbon structure. Although the ball- milling treatment also increased both the reversible capacity and Coulombic efficiency of MWCNTs, a large voltage hysteresis oc- curred

because of the large amount of surface functional groups formed on MWCNTs [101]. The voltage hysteresis of MWCNTs was partly related to the kinetics of Li diffusion into the inner cores of MWCNTs, which could be reduced by cutting the MWCNTs into shorter segments [102].

Extensive research has been made to evaluate the effect of MWCNT length on the performance of anode material [103–105]. A new approach was developed to cut conventional micrometer- long entangled MWCNTs into about 200 nm long segments that could give rise to excellent dispersion. The reversible capacity of LIBs increased, whereas the irreversible capacity decreased upon shortening the MWCNT lengths because the insertion/extraction of Li ions into/from the short MWCNTs were easier than long MWCNTs. Moreover, short MWCNTs had a lower electrical resis- tance and Warburg prefactor, resulting in better rate performance at high current densities [103]. It can be seen from Fig. 15 that short MWCNTs had a higher Li extraction capacity than the long MWCNTs, and the specific capacities became stable after 30 cycles for both electrodes. The retention of reversible capacities after 50 cycles was also higher for short MWCNTs (77%) than long ones (60%).

A basically analogous conclusion has been drawn in another study on the effects of CNT type and length synthesized by two dif- ferent methods [105]: short CNTs or carbon nanorods, a few hun- dred nm in length, were synthesized by oxidation and carbonization of carbon-encapsulated iron carbide/iron nanorods,

whereas long CNTs, a few lm in length, were synthesized by cata-

lytic pyrolysis of C3H6 using Fe as catalyst. The reversible capacities of the electrode made from short CNTs were 266 and 170 mA Hg—1 at current densities of 0.2 and 0.8 mA cm—1, respectively, which were almost twice those of the electrodes containing long CNTs. Both the surface film and charge-transfer resistances of the short CNTs were significantly lower than those of the long CNTs; and the Li diffusion coefficient of the electrodes made from both CNTs decreased with decreasing voltage, the reduction being more seri- ous in long CNT electrodes than short ones. These observations fur- ther confirmed a higher electrochemical activity and more favorable kinetic properties during the charge–discharge process in the electrodes made from short CNTs.

Li ion insertion in MWCNTs occurs only in the low potential re- gion and clearly differs from the case of graphite. While the typical discharge curve of the latter usually shows a staging phenomenon characterized by several potential plateaus, such a behavior is not observed in MWCNTs. Because of the morphological complexity of the CNTs, the identification of Li storage sites in general remains the main hindrance for elucidating the mechanism of Li insertion. Indeed, different from graphite, Li storage in CNTs is much more af- fected by the presence of so-called ''3D defects'', such as cavities and pores of different shapes and dimensions [106]. Therefore, unexpected results are often obtained when CNTs with unique structures are used as the anode material of LIBs.

As important members of the carbon nanotube family, bamboo- shaped carbon nanotubes (BCNTs) and quadrangular carbon nano- tubes (q-CNTs) were thought to be suitable for anode material in LIBs, due to better improved cyclic stabilities and higher electric conductivity than common MWCNTs [107,108]. BCNTs that pos- sess a high percentage of edge-plane sites on the surface exhibited better electrochemical characteristics with a faster electron trans- fer rate than their straight CNT counterparts with smoother and more basal plane regions. Fig. 16 presents the EIS of the BCNT, MWNT and CB samples. The significantly reduced resistance arose from the higher electron transfer kinetics of the BCNTs than those of CB and MWNTs due to the better wettability, more edge sites and more oxygen functional groups, and easier formation of 3D electrical conduction networks in BCNTs.

Novel q-CNTs were prepared on a large-scale production and investigated as the anode material for LIBs [108]. Compared with traditional CNTs, the q-CNTs possess a novel nanostructure, such as quadrangular cross section, one open end and ''herringbone''- like walls, as shown in Fig. 17. The unique nanostructure of q-CNTs could shorten the diffusion time by both increasing diffusion coef- ficient and decreasing the diffusion pathway, resulting in an excel- lent rate capability.

Doping of CNTs using a heteroatom is also found to be efficient in improving the electrochemical performance of CNT anodes: boron- and nitrogen-doped MWCNTs as anode materials have been

studied. Boron-doped MWCNTs exhibited a discharge capac- ity of 180 mA Hg—1, which is higher than 156 mA Hg—1 for the un- doped counterparts [109]. Prepared from pyridine as a precursor, nitrogen-doped MWCNTs were shown to have a reversible spe- cific capacity of 340 mA Hg—1 [110]. The improved electrochemi- cal performance is attributed to boron or nitrogen doping leading to a breakdown in in-plane hexagonal symmetry of CNT walls, resulting in an increase in electrical conductivity [111,112]. Composites are often the only way to maximize the performance of the constituent materials. A nanocomposite of CNTs and gold particles in a block copolymer matrix sustained more than 600 cycles at rates ranged from C/1.8 to 8.8C [113]. The composites had enhanced Li-ion diffusion through improved electronic conductivity.

MWCNTs are particularly attractive because they possess sites, where Li ions can be intercalated: spacing between the graphene layers, local turbostatic disorders arising from the highly defective structures, and the central core [92–96]. The large capacities are of- ten ascribed to defects and shortened length of the nanotubes, which can improve Li diffusion properties [114]. Other advantages of MWCNTs, such as high electrical and thermal conductivities, en- dow MWCNT electrodes with high power outputs and good heat dissipation, improving the safety of the devices. One typical disad- vantage of using CNT anodes is the irreversible capacity charge loss in the first cycle due to the SEI formation on the nanotubes that needs to be overcome during the battery charge phase. The other is the difficulty of uniform dispersion into the electrodes.

Nanocomposite anode materials containing CNTs as conductive additive

Previous studies have shown that the reversible capacity of CNTs varied widely depending on the synthesis method and treatment technique employed. The irreversible capacity, how- ever, was too high to realize practical applicability. Furthermore, the reduction in capacity upon charge–discharge cycles was very high due to the detrimental surface reactions with solution spe- cies [115]. The formation of intense surface films may increase the electrode impedance and even electrically isolate part of the active mass [116]. In order to overcome these issues, several methods have been developed, including the use of MWCNTs as additive. Many different CNT composites with a variety of Li stor- age materials have been studied, such as Sn/MWCNT [117,118], Bi/MWCNT [119], SnSb/MWCNT [120,121], CoSb3/MWCNT [122], CoSn3/MWCNTs [123], Ag/Fe/Sn/MWCNT [124], TiO2/MWCNT [125,126] and SnO2/MWCNT [127,128] for use as anode materials. Li storage metals and metal oxides, such as Sn, Sb, TiO2 and SnO2, easily develop cracks during the charge–discharge process in spite of their significantly high electrochemical Li intercalation capaci- ties. The breakdown of the electrode is a major cause of rapid degradation of their capacities as a consequence of the large spe- cific volume change during the lithiation and de-lithiation reac- tions. The combining of MWCNTs that can hinder the agglomeration and enhance the electronic conductivity of the ac- tive materials is responsible for the enhanced cyclic performance. Table 6 summarizes the electrochemical parameters, such as ini- tial charge and discharge capacities and residual reversible capac- ities, of various anode materials with and without CNT additives, undeniably confirming much enhanced cycle performance of the nanocomposites containing MWCNTs as compared to the neat an- ode materials. The details of the changes in electrochemical prop- erties affected by the presence of CNTs are discussed in the following.

Table 6
Electrochemical parameters of anode materials consisting of various types of MWCNT-based nanocomposite.

Electrode type	Current rate	Initial charge capacity	Initial discharge capacity	Cycle	Residual reversible capacity	Charge transfer	Ref.

Material	Rate	(mA Hg—1)	(mA Hg—1)	number	(mA Hg—1)	resistance (X)	Ref
Sn/MWCNT	0.1 C	643	1590	40	627		[117]
Sn-MWCNT	50 mA g—1		570	30	442	16.4	[118]
SnNi-MWCNT	50 mA g—1		512	30	431	17.3	[118]
Bi/MWCNT	25 mA g—1	308	570	50	315		[119]
Sb	50 mA g—1	648	1023	30	115		[120]
SnSb0.5	50 mA g—1	726	951	30	171		[120]
Sb/MWCNT	50 mA g—1	462	1266	30	287		[120]
SnSb0.5/MWCNT	50 mA g—1	518	1092	30	348		[120]
CoSb3/MWCNT		312	915	30	265	7.2	[122]
Ag/Fe/Sn/MWNT	0.2 mA cm—2	530		300	420		[124]
TiO2	50 mA g—1	52	287	75	21	123	[125]
TiO2/MWCNT	50 mA g—1	168	830	75	165	75	[125]
SnSb/MWCNT	50 mA g—1	680	1408	50	480		[121]
Ag-	0.2 mA cm—2	500	250	30	172	15.8	[126]
TiO2/MWCNT	0.2 mA cm—2			30	>400		[127]
SnO2/MWCNT	37.2 mA cm—2		728.3	40	126.4		[128]
SnO2	37.2 mA cm—2		665.1	40	505.9		[128]
SnO2/MWCNT	850 mA g—1	100	100			60	[129]
Li4Ti5O12	850 mA g—1	145	145	500	142	38	[129]
Li4Ti5O12/MWCN	50 mA g—1		819	50	279		[147]
Si/MWCNT (7:3)	50 mA g—1		1770	50	1250		[147]
Si/MWCNT (5:5)	50 mA g—1		1182	50	889		[147]
Si/MWCNT (3:7)	0.25 mA cm—2	960	1882	30	1066		[151]

Li4Ti5O12/MWCNT composites

Spinel Li4Ti5O12 has long been considered as a promising alter- native to graphite anode material for LIBs. The combination of zero strain insertion properties and high Li mobility makes it an ideal anode material. However, its rate performance is severely limited due to its low electronic conductivity. The introduction of MWCNTs into Li4Ti5O12 particles showed an ameliorating effect on rate capability and capacity retention [129]. The charge transfer resistance of Li4Ti5O12 and Li4Ti5O12/MWCNT electrodes was 60 and 38 X, respectively. The cycling stability of Li4Ti5O12/MWCNT composite shown in Fig. 18 indicates that the discharge capacity was quite stable during the charge–discharge process at low cur- rent rates. Even after 500 cycles at 850 mA g—1 the discharge capacity was standing at 142 mA Hg—1, which was 97.9% of the ini- tial discharge capacity. It is worth noting that the anode could be charged at an extremely high rate of 3400 mA g—1. These results confirmed that the Li4Ti5O12/MWCNT composite electrode had a high rate capability and capacity retention, which can be attributed to the improvement in conductivity and the smaller size of Li4- Ti5O12 crystals in the Li4Ti5O12/MWCNT composite electrode.

Transitional metal oxide/MWCNT composites

It is proven that transitional metal oxides could deliver revers- ible capacities as high as 1000 mA Hg—1 [130–132]. However, their applicability is limited by the large hysteresis in their charge–dis- charge curves and the relatively low electronic conductivity. Nano- composites containing CNTs for energy storage applications are prepared by simply mixing MWCNTs with the functional metal or metal oxide particles based on various techniques. The resultant composites have a compositional variation across the radial direc- tion and a constant concentric arrangement of each participating component along the axial direction, resembling an electric cable configuration. A general approach to produce MWCNT/metal oxide nanocomposites via self-assembly was developed recently [133]. Schematic illustrations of the self-assembly of MWCNT nanocom- posites are shown in Fig. 19. The self-assembly technique allows preparation of binary composites as well as more complex sys- tems, such as ternary and quaternary composites. The nanoparti- cles of active phase, e.g., metals and metal oxides, serve as the primary building block to form various types of composites, including TiO2/MWCNT, Co3O4/MWCNT, TiO2/Co3O4/MWCNT and Co/CoO/Co3O4/MWCNT. It was shown that the self-assembled TiO2/MWCNT composites were sufficiently robust and their elec- trochemical performance was significantly enhanced compared to neat TiO2.

1D nanostructured electrode materials showed strong potential for LIBs due to their good electrochemical performance. Co3O4/CNT composites were synthesized using a hydrothermal method as an- ode material [134]. Nanocrystalline Co3O4/CNT composite anodes exhibited a reversible Li storage capacity of 510 mA Hg—1 over 50 cycles. Fe3O4/CNTs composites were also studied as anode material [135]. Fe3O4 nanoparticles were attached onto the sidewalls of modified CNTs by chemical coprecipitation of Fe2+ and Fe3+ in an alkaline solution. The electrochemical test results indicate that the initial discharge and charge capacities of the 66.7 wt.% Fe3O4/ CNTs nanocomposite electrodes were 988 mA Hg—1 and 661 mA Hg—1, respectively. The charge capacity retained after 145 cycles was 645 mA Hg—1, which outperforms that of commer- cial graphite materials. The excellent cycleability and the high capacity retention of the electrodes are attributed to the frame- work of CNTs and deposition of nanosized Fe3O4 particles onto CNTs.

Incorporation of CNTs as an additive to active anode materials is an effective strategy to form conductive networks in the electrode at a content much lower than other carbonaceous materials, like carbon black and graphite. Many applications including aerospace, transportation and portable electronics require lighter weight and longer life batteries for electrochemical energy storage [136], which in turn depend on the weight and volume of the electrode, except for its energy content. New techniques have been devel- oped to meet this requirement. CNTs have the capability to be assembled into free-standing electrodes as an active Li-ion storage material or as a physical support for ultra-high capacity anode materials like silicon or germanium [137]. The major advantage arising from utilizing

free-standing CNT anodes is the removal of the copper current collectors, which can translate into an increase in specific energy density by more than 50% for the overall battery design. However, major challenges, such as the first cycle charge loss and paper crystallinity for free-standing CNT electrodes, need to be overcome through further research.

TiO2/MWCNTs nanocomposites

Fig. 20 shows representative images of the TiO2/MWCNT nano- composites and their starting building blocks. The as-prepared TiO2 nanoparticles used in the composites had a narrow size distri- bution of 3–4 nm. The MWCNT nanocomposite exhibited a rough surface after decoration with uniformly dispersed TiO2 nanoparti- cles (Fig. 20c and d). The corresponding XRD spectra (Fig. 20e) indi-cate that although the (101) diffraction of the metal oxide phase overlaps with (002) of MWCNTs, the TiO2 nanoparticles maintain their pristine phase even after decoration onto the MWCNTs. All diffraction peaks can be indexed to tetragonal anatase TiO2 nano- rods (JCPDS file No. 21-1272).

The performance of the TiO2/MWCNT system was tested in real working environments for LIB applications. To increase the elec- tronic conductivity of anode materials, carbon black are normally mixed with the host material. However, a simple mechanical mix- ing cannot provide a uniform mixture, causing general problems like polarization of the active component and high resistance to electron transfer. When MWCNTs are evenly distributed between the active TiO2 nanoparticles, the TiO2/MWCNT nanocomposites may solve these problems. Although MWCNTs could serve as the major anode material, their discharge only occur at a potential of about 0–0.2 V (vs. Li/Li+) [138,139] that is much lower than the limit of 1.0 V in this particular study. Therefore, it was assumed that the MWCNTs in the as-prepared TiO2/MWCNT nanocompos- ites did not participate in the charge–discharge reactions, and acted only as oxide carrier and charge conductor.

A drop of 26.8% was observed. However, from the 3rd to 15th cycle and onwards, the specific capacity showed only a marginal reduction, and the Coulombic efficiency (i.e., the ratio of Li extraction to Li intercalation capacity) was close to unity (>98%), indicating an excellent cyclic stability. The reversible capacity maintained stably during these cycles was about 225 mA Hg—1, which is approximately 17% higher than the capacity of hydrogen titanate nanowires (~191.8 mA Hg—1) [140], 32% high- er than that of nanosized rutile TiO2 (~170 mA Hg—1) [141] or 50% higher than that of anatase TiO2 (~150 mA Hg—1) [142].

To increase the ionic and electronic diffusion and thus to achieve a high rate capability, unique nano- architectures were syn- thesized and electronically conductive phases were introduced into the nanocomposite. Nanocomposites consisting of brookite TiO2 nanoparticles attached to MWCNTs [143] were also investi- gated as the anode materials for LIBs. Brookite TiO2 crystallizes in the orthorhombic system which is different from the anatase and rutile forms of TiO2 discussed in Section 4.3.2. The brookite crystallites had an average diameter of 7 nm, which was smaller than those obtained from pure brookite due to the homogeneous nucleation onto the MWCNT surface. Fig. 22 shows that the brook- ite/MWCNT composite gave rise to a remarkably high capacity and stable cycleability, useful attributes for anode materials in LIBs. The composites exhibited a high discharge capacity of 151 mA Hg—1 even after 100 cycles at a rate of C/5 (Fig. 22a). The beneficial effect of MWCNTs in the composite electrode was fur- ther evidenced by the large difference in charge–discharge profiles between the neat brookite and brookite/MWCNT composites Recently, well-organized CNT/TiO2 core/porous-sheath coaxial nanocables were synthesized by controlled hydrolysis of tetrabutyl titanate in the presence of CNTs as anode material for LIBs [144]. The morphology of the CNTs was well maintained even after calci- nation, although their surface became slightly rough (Fig. 24a). A uniform sheath with a thickness of about 25 nm can be clearly seen from the image. The 0.34 nm spacing observed in the core of the coaxial nanocable corresponds to the (002) crystalline planes of the MWCNTs (inset in Fig. 24b). Lattice fringes with a spacing of 0.35 nm are clearly visible from the HRTEM image taken from the nanocable edge (Fig. 24c), which is in good agreement with the spacing of the (101) planes of anatase TiO2, thus demonstrat- ing the presence of nanocrystalline TiO2.

Compared with neat CNTs or neat TiO2, the CNT/TiO2 coaxial nanocables showed a much improved rate capability and cycle per-formance. As shown in Fig. 24d, both the specific capacities of the CNT core and the TiO2 sheath were much higher than that of the TiO2-free CNT or that of the CNT-free TiO2 sample. In addition, the capacity retention and the Coulombic efficiency kept almost 100% (Fig. 24e). It is thought that the coaxial cable morphology provides an ideal solution to the ionic-electronic wiring problem in LIBs as well as the synergism of the two cable wall materials. The storage of TiO2 was improved by the contact with CNTs and, even more remarkably, the storage in CNT was improved by the presence of TiO2.

New nano-sized TiO2 rutile has been used as active material in LIBs. MWCNTs were added into the slurry formulation to partly re- place Super P and the resulting electrodes were electrochemically characterized [58]. Fig. 25 shows the rate capability of TiO2 ru- tile-based composite electrodes containing Super P as unique con- ductive agent and a Super P + MWCNTs combination at different current rates. The 1 wt.% MWCNTs in TiO2 rutile-based anodes was efficient in enhancing the rate capability when the electrodes were cycled in the potential range 1.0–3.0 V, as well as increasing both the energy and power densities of LIBs.

SnO2/MWCNT nanocomposites

SnO2 has received much attention as an alternative anode mate- rial due to its high specific capacity of 782 mA Hg—1. However, it experiences a large volume expansion of 260% during the charge–discharge cycles [145] and the incorporation of CNTs is one of the most well-established methods to reduce the volume expansion as well as to improve the electronic conductivity of the electrodes [127,128]. Instead of randomly mixing the active SnO2 particles with CNTs, a new technique was developed to syn- thesize a co-axial SnO2 tube/CNT nanostructure [146]. The porous SnO2 nanotubes were formed first, and a uniform CNT overlayer was grown on the external surface of the SnO2 nanotubes through a confined-space catalytic deposition process. The coaxial nano- structure delivered a reversible capacity higher than that of CNTs in the voltage window of 5 mV–3 V at a current rate of 0.5 C, as shown in Fig. 26. The capacity retention of 92.5% after 200 cycles is deemed similar to the performance of commercial graphite an- odes. The outstanding electrochemical properties are likely to be related to several unique features of the nanocomposite: (i) tubular organization of SnO2 nanoparticles, (ii) stress absorption by the CNT matrix, and (iii) the existence of a hollow interior allowing freedom of expansion, increased electrical contact, and enhanced Li-ion transport.

A novel mesoporous-nanotube hybrid composite was prepared by a simple method that involved in situ growth of mesoporous SnO2 on the surface of MWCNTs through a hydrothermal method [147]. The electrochemical test results indicate that the mesopor- ous-tube hybrid composites displayed a higher capacity and better cycle performance than the neat mesoporous SnO2, as shown in Fig. 27. The improvement was attributed to the synergistic effects of favorable properties, including the 1D hollow structure, high strength with flexibility, excellent electric conductivity and large surface area, which in turn facilitated the reduction in volume expansion, shortened Li ion diffusion path, easy transmission of electrons and stable structure after long cycles.

Other conducting elements are often added into the otherwise two-component SnO2/CNT composite anodes. For hexample, 1D hy-brid nanocables of Au–SnO2/MWCNTs have been developed using a facile one-pot route and their electrochemical performance was studied [148]. The introduction of a small amount (0.9 wt.%) of Au species enhanced the conductive properties. Fig. 28a displays the XRD pattern of the Au-SnO2/MWCNT nanocables confirming

their crystallographic structure. The peak positions at 33.9 and

51.8° were assigned to tetragonal rutile SnO2 (JCPDS Card No. 41- 1445). However, the diffraction peaks corresponding to Au were

not found. The TEM images (Figs. 28b) present that the MWCNTs were coated with a Au–SnO2 hybrid layer of uniform thickness about 10–15 nm, forming nanocables of a diameter about 30– 50

nm. The grain size of the coating material was very small and no lattice fringe was observed. Fig. 28c shows the rate performance of SnO2/MWCNT nanocables with and without Au for rates up to 7.2 Ag—1. The nanocables containing Au exhibited higher reversible

capacities both at low and high rates than those without. The for- mer nanocables with Au had stable reversible capacities of 467 and 392 mA Hg—1 at rates of 3.6 and 7.2 Ag—1, respectively, correspond- ing to 62% and 52% of the capacities obtained at 0.18 Ag—1. In con- trast, the capacities were reduced to 370 mA Hg—1 (3.6 Ag—1) and 242 mA Hg—1 (7.2 Ag—1) for the nanocomposites without Au, corre- sponding to 60% and 39% of the capacities at 0.18 Ag—1, respec- tively. The existence of Au species in the coating and the unique 1D architecture of CNTs as the template were mainly responsible for the enhanced reversible capacities of Au–SnO2/MWCNT nanocables.

The Au-SnO2/MWCNT nanocables had much lower charge transfer resistance in the medium frequency range than for the SnO2/MWCNT nanocables, as shown in Fig. 29. The faradic reaction is determined by ion transfer and electron conduction indicating that the reduction in charge transfer resistance was likely attrib- uted to the improved electronic conductivity of Au–SnO2/MWCNT electrodes arising from the Au nanoparticles. Au, an excellent elec- tronic conductor, helped improve the Li ion insertion/extraction reversibility as well as reduce the cell polarization. On the other hand, the hybrid nanostructure enhanced the electrolyte/SnO2 con- tact area, shortened the Li ion diffusion path in the SnO2 coating layer, as well as accommodated the strains induced by the volume change occurring during the electrochemical reactions. Another material that has been studied recently along with the SnO2/CNT composite anodes is graphene or graphene oxide. Incorporation of 2D graphene sheets to form SnO2/CNT/graphene hybrid compos- ites in the form of powder or paper further improved the specific capacity as well as the cyclic performance due to the increased sur- face area and pore volumes [149].

Si/MWCNT nanocomposites

Silicon is one of the most attractive and widely investigated candidate anode materials due to its high theoretical specific capacity of 4200 mA Hg—1 corresponding to the fully lithiated com- position of Li4.4Si, which is 10-fold higher than that of graphite [75]. However, large crystallographic volume changes and several phase transitions occur during the Li insertion and extraction pro- cesses, leading to the generation of large mechanical strains. These strains cause cracking and breakdown of the electrode, which re- sults in the failure of the anode after only a few cycles due to the loss of electronic contacts between the active particles [150].

In an attempt to improve the cycleability of Si-based anodes, second phase components have been introduced to serve as buffer so that a large volume change during cycling can be accommo- dated. Si/MWCNT nanocomposites with a unique core/shell struc- ture [151] were fabricated, which showed superior anodic performance to that observed in electrodes made from bare Si or Si/MWCNT mixture. The results shown in Fig. 30 indicate that the specific capacities of the composites with a core/shell structure were at least twice higher than the other materials. It was pro- posed that the void space and the flexible characteristics in MWCNT buffer layer on the Si surface allowed volume expansion of Si core without severe electrode swelling. The electronic conduc- tive networks formed by MWCNTs also helped reduce the charge transfer resistance. The relatively poor performance of the Si/ MWCNT mixture compared to that with a core/shell structure sug- gests that the composites with active particles of intimate contacts is more advantageous than simple mixing.

The concept behind the enhanced electrochemical performance by the Si/CNT composites with a core/shell structure is illustrated schematically in Fig. 31, which is compared with the Si powder electrodes consisting of a random mixture of Si particles and CB. The electric conductive networks are easily broken during cycling of the conventional anode material because the Si particles tend to be debonded and separated from the binder after discharging (Fig. 31a). Once the CNTs are fully integrated with the Si particles to form a core/shell structure, the composite electrode can deliver much better electrochemical performance (Fig. 31b). The CNT layer can accommodate the volume

expansion of core Si particles to minimize the electrode swelling. As a result, the electrical conductive network is maintained even after a large volume change in Si particles. The performance of the electrode made from a Si/CNT simple mixture was not equally improved (Fig. 31b) because the CNTs played essentially the same role as the CB.

Si/MWCNT composites with different weight ratios were pro- duced using purified MWCNTs and Si powder through high-energy ball-milling [152]. The electrochemical tests on Li/(Si/MWCNT) cells indicate that the highest Crev and the lowest Cirr were ob- tained 1770 and 469 mA Hg—1, respectively, for the composite an- odes made with a ratio of 50% MWCNT: 50% Si. The ball milling contributed to decreasing the sizes of MWCNTs and Si particles, and thus to increasing the electrical contact between these compo- nents, which in turn enhanced the Li capacity and cyclic perfor- mance. Similarly excellent results have also been reported of the Si/CB/SWCNT nanocomposites that were prepared by dispersing SWCNTs via high power ultrasonication into a pre-milled Si/C com- posite mixture, followed by a subsequent thermal treatment [153]. The nanocomposite with a nominal composition of 35 wt.% Si/ 36 wt.% SWCNTs exhibited a remarkable reversible discharge capacity of ~900 mA Hg—1 with a negligible capacity loss of 0.3% per cycle up to 30 cycles.

The capacity of pure CNT anode can be increased by filling the CNT interior with high-capacity Li-storage compounds, such as those derived from Sn, Sb, alloys and metal oxides, see e.g. co-axial SnO_2 tube/CNT nanostructure [142] discussed in Section 4.3.4. The nanocomposites of CNT filled with Sn_2Sb alloys showed an impres-sive capacity for Li storage through alloy formation, but were significantly less cycleable than graphite: their first cycle discharge capacity was 1250 mA Hg—1 while the corresponding charge capac- ity was 580 mA Hg—1 [154]. It is believed that a carefully crafted combination of CNTs and high-capacity Li-storage compounds may work synergistically to deliver both high capacity and good cycleability. Sn-filled MWCNTs were synthesized using two differ- ent methods, including an $NaBH_4$-reduction process and a hydro- thermal process, as anode material [117]. At a current rate of

0.1 C, the hydrothermally-filled CNTs gave a first-cycle discharge and charge capacities of 1916 and 834 mA Hg—1, respectively; while the $NaBH_4$-reduced samples gave much higher values of 2474 and 889 mA Hg—1. It is also interesting to note that the charge–discharge capabilities of the Sn-filled CNTs nanocompos- ites were much higher than the corresponding values, 1281 and 340 mA Hg—1, respectively, of those containing open-ended CNTs. These observations indicate that the electrochemical performance of CNT-metal composites is related to their structural characteris- tics: metal-filled CNTs are superior to metal-CNT composite mix- tures, when used as the anode material for LIBs.

CNT arrays as anode material

MWCNTs consist of more than two graphene sheets rolled into closed and concentric 1D cylinders. The graphene sheets have an inter-planar spacing of ca. 0.34 nm, which is wide enough for the intercalation/extraction of Li ions. MWCNT arrays have received much attention for use as anode material due to their large surfacearea and ordered electrode configuration [155]. A few studies have been reported on the fabrication and evaluation of ''free-standing'' CNT paper electrodes without substrate. The free-standing CNT pa- per electrodes are light, flexible, highly conductive, and can be fab- ricated using a simple filtration method under a positive pressure without having to use a metal substrate or binder [156,157]. An added advantage is that the electrode made from buckypaper is much lighter than conventional electrodes that are normally fabri- cated by coating a mixture containing an active material onto a metal substrate.

There have been increasing interests in flexible and safe energy storage devices based on both batteries and supercapacitors to meet stringent requirements driven mainly by high-power and high-energy applications. One of the potential solutions to these demands is combining the storage capabilities of LIBs together with the excellent power discharge characteristics of capacitors, making the device highly capable of storing useful quantities of electricity that can be discharged very quickly. Once the

integrated structure of the electrochemical devices containing three essential components, namely electrodes, spacer and electrolyte, is made mechanically flexible, they can be embedded into various func- tional systems in a wide range of innovative products such as smart cards, displays and implantable medical devices. A paper- thin and flexible energy storage device was successfully fabricated

[158] by incorporating nanoporous cellulose as the main constitu- ent of paper with CNTs. The novelty of this device lies in its mechanical flexibility allowing to change its shape to meet the space requirements of modern devithe design, where all components, i.e. electrodes, electrolyte and separator, are integrated into a single unit that acts as a building block for the final battery structure. CNT films of uniform thick- nesses were grown vertically on a silicon substrate, which were then impregnated with cellulose to form a nanocomposite paper. The paper was assembled into a battery by (i) evaporating a thin layer of Li metal as the anode, (ii) using a Li conducting organic solution as the electrolyte, and (iii) attaching aluminum foil on both sides to collect the current. It was claimed that the superca- pacitor could be combined with batteries to make hybrid devices. The charge–discharge cycles of the battery were measured be- tween 3.6 and 0.1 V, at a constant current of 10 mA g—1. A large irreversible-capacity (~430 mA Hg—1) was observed during the first charge–discharge cycle (Fig. 32a), and further charge–dis- charge cycles resulted in a reversible capacity of 110 mA Hg—1 (Fig. 32b). The laminated battery device was able to light up a red light emitting diode (LED) (Fig. 32c) several tens of cycles, dem- onstrating its excellent discharge performance.

Although they can be used to produce innovative functional

nanostructures, aligned CNTs (ACNTs) grown on a substrate suffer from a lack of good electrical connectivity between them [159]. To avoid the lack of lateral connectivity, a novel approach was devel- oped to form a nanostructured ACNT/conducting polymer compos- ite, where the ACNTs were held together by a conducting polymer layer. The ACNTs remained vertically oriented and protruded from the conducting polymer layer with 90% of the tube length being ex- posed. These free-standing ACNT/poly(3,4-ethylenedioxythio- phene (PEDOT)/poly(vinylidene fluoride) (PVDF) membrane electrode was not only lightweight, flexible, highly conductive and mechanically robust, but also could be fabricated into a rechargeable battery without having to use a metal substrate. In addition, the capacity of the ACNT/PEDOT/PVDF electrode was 50% higher than that observed for a free-standing SWCNT paper. This study has important implications in the development of ACNT/conducting polymer composites as a new class of electrode material for flexible rechargeable LIBs and may find niche applica- tions of CNTs in flexible electronic devices.

Concluding remarks and future prospect

As LIBs find a diverse range of new applications, such as EVs, HEVs and power tools, they must have excellent rate charge–dis- charge performance, as well as high energy and power densities To achieve this ultimate goal, there have been enormous research efforts aimed at improving LIB technology, especially the electrode performance. Nanoscaled materials represent a rapidly growing area in the field of LIBs because of their substantial advantages in terms of mass transport. Transport in nanoparticle systems typi- cally encompasses shorter transport lengths for both electrons and Li ions, larger electrode–electrolyte contact area and better accommodation of the strains arising from Li ion insertion/extrac- tion [3,88,97,160–163]. However, a large surface area may also in- crease the solvent decomposition occurring at both the anode and cathode during charge–discharge cycles, resulting in a large, irre- versible capacity loss. In addition, poor packing of nanoparticles may also lead to a low volumetric energy density. Therefore, it is important that the particle size and morphology be optimized so as to maximize the performance of the electrode material. The addition of CNTs in conventional electrodes, both cathodes and an- odes, can enhance the electronic conductivity, improve Li diffusion and maintain morphological stability, which in turn result in high- er reversible capacities, rate capability and battery cycleability. However, there are also challenges in the synthesis of CNT- based nanocomposites, which include: (i) poor adhesion of nanoparticles with CNTs; (ii) difficulties

in uniform dispersion; and (iii) a low CNT content that can be incorporated without agglomeration. Other important challenges include the development of environ- ment-friendly, low-cost, high-volume synthesis and fabrication techniques for nanocomposites, as well as the significant improve- ment in safety characteristics for their use in the battery systems. As has been verified for many electrode materials, such as Li4Ti5O12 and LiMn2O4 [164–166], an electronic conductive medium, such as Ag, could greatly improve their discharge capacity and cyclic sta- bility at high rates. However, Ag is very expensive and the syn- thetic route of the composites is difficult to control for homogeneity of the components. While carbon materials are more cost effective than Ag, the graphitizing process influences the yield of the composites. As a key new material, CNT–based nanocompos- ites have been studied extensively due to their excellent multi- functional characteristics as electrode materials. Graphene, a one-atom-thick planar sheet of carbon that is den- sely packed in a honeycomb crystal lattice, has emerged recent years as an alternative to other carbon allotropes, including CNTs, after the development of various routes for synthesis [167–170]. Due to its combination of unique physical, electrical, mechanical and other functional characteristics, graphene will surely contrib- ute to achieving the ultimate performance of future LIBs and other energy storage devices. Indeed, the application of graphene or graphene oxide in electrode materials for LIBs and supercapacitors has already appeared in the literature [171–174]. Because it is highly conductive, mechanically robust, non-toxic, chemically and thermally tolerant, and has a large electrochemical stability window, graphene is particularly suited for Li ion storage to re- place the traditional graphite anodes, for serving as template sup- porting the active anode particles [149,172], and acting as conductive additive in LIBs [173]. The most obvious impediment to commercial exploitation of graphene materials for LIBs is the ab- sence of reliable methods for large-scale production of processable graphene sheets. Commercially viable synthetic strategies must be explored in order to translate laboratory findings into devices.

The rational design of novel electrical energy storage systems with a high energy density will benefit from a combined experi- mental and theoretical approach. Nanostructuring the electrode materials together with incorporation of conducting fillers like CNTs for larger surface areas and thus higher intercalating capaci- ties is a promising strategy in advanced LIBs. This gives rise to var- ious advantages, including (i) fast rate capabilities due to shorter lengths for both electronic and Li ionic transport, (ii) high energy density and excellent cyclic life arising from the large electrode.

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References

1. Scrosati B. Challenge of portable power. Nature 1995;373:557–8.
2. Tarascon JM, Armand M. Issues and challenges facing rechargeable batteries. Nature 2001;414:359–67.
3. Arico AS, Bruce P, Scrosati B, Tarascon JM, Van Schalkwijk W. Nanostructured materials for advanced energy conversion and storage devices. Nat Mater 2005;4:366–77.
4. Bruce PG, Scrosati B, Tarascon JM. Nanomaterials for rechargeable lithium batteries. Angew Chem Int Ed 2008;47:2930–46.
5. Kang K, Meng YS, Breger J, Grey CP, Ceder G. Electrodes with high power and high capacity for rechargeable lithium batteries. Science 2006;311:977–80.
6. Whittingham MS. Lithium batteries and cathode materials. Chem Rev 2004;104:4271–301.
7. Jiang C, Hosono E, Zhou H. Nanomaterials for lithium ion batteries. Nano Today 2006;1:28–33.
8. Whittingham MS. Materials challenges facing electrical energy storage. MRS Bull 2008;33:411–9.

9. Wallace GG, Chen J, Mozer AJ, Forsyth M, MacFarlane DR, Wang C. Nanoelectrodes: energy conversion and storage. Mater Today 2009;12:20–7.
10. Li H, Wang Z, Chen L, Huang X. Research on advanced materials for Li-ion batteries. Adv Mater 2009;21:4593–607.
11. Frackowiak E, Gautier S, Gaucher H, Bonnamy S, Beguin F. Electrochemical storage of lithium multiwalled carbon nanotubes. Carbon 1999;37:61–9.
12. Chen J, Minett AI, Liu Y, Lynam C, Sherrell P, Wang C, et al. Direct growth of flexible carbon nanotube electrodes. Adv Mater 2008;20(3):566–70.

Claye A, Fischer J, Huffman C, Rinzler A, Smalley RE. Solid-state electrochemistry of the Li single wall carbon nanotube system. J Electrochem Soc 2000;147:2845–52