



Review

A review of application of carbon nanotubes for lithium ion battery anode material

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ABSTRACT

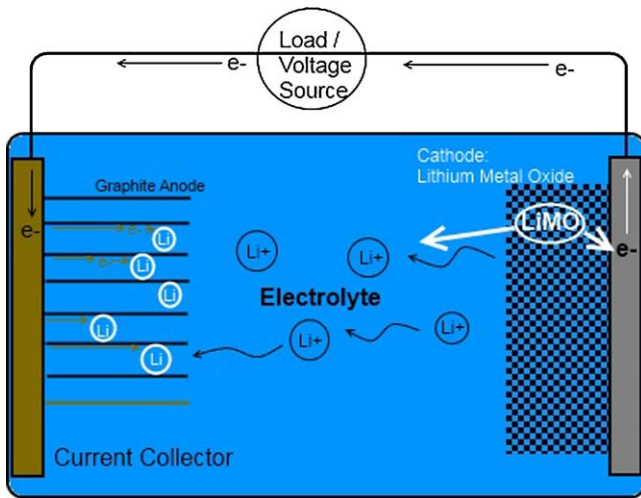
With their unique structural, mechanical, and electrical properties, carbon nanotubes are promising candidates for use as anode material in lithium ion batteries. As an allotrope of graphite, carbon nanotubes have already been presented as a competitive lithium storage material. What is more, carbon nanotubes can be a critical component in nanostructured anode materials with greatly improved capacity and cyclability. Carbon nanotubes have demonstrated to be very effective buffering components, and can serve as the backbone in nanostructured anode materials since they can alleviate the degradation of the structural integrity that often results from the significant volume change associated with the charging and discharging process. In addition, the highly conductive carbon nanotubes offer enhanced electronic transport in these nanostructured anode materials. This paper reviews the recent progress of using carbon nanotubes as components of anode material to improve the performance of lithium ion batteries.

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Lithium Ion Battery: Charging

Fig. 1. Schematic of lithium ion cell.

1. Introduction

With the advent of plug-in hybrid electric vehicles and a new greater political awareness toward the importance of energy storage, batteries and battery related technologies have become an increasingly pivotal part of the modern era. Among the batteries on the forefront of the latest technology, lithium-ion batteries have readily become the most ubiquitous. They are commonplace in consumer portable electronic devices due to their high energy density and safety, and it is well known that they do not suffer from 'memory' effects that plague other batteries. Notwithstanding their popularity and dominance in the market place, great efforts have been made to improve the characteristics of these batteries, particularly with respect to their capacity and its tendency to decay over time. Indeed, the purportedly small lifespan of the battery packs in certain hybrid electric vehicles has caused much concern among car owners and makers alike.

Recently, much research has gone into innovating novel nano-architectures to increase the capacity and improve the lifespan of the lithium-ion cell. Among the possible candidates to do this, carbon nanotubes have emerged as one of the foremost contenders. Their peculiar structure and unique properties such as high electrical conductivity and tensile strength make them well suited as a critical component in novel anode material for enhanced lithium storage. This paper provides an overview of the recent advances in lithium ion storage technologies with respect to the use of carbon nanotubes.

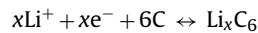
2. Review of current commercial Li-ion battery technology

2.1. Li-ion cell design and components

Lithium-ion batteries are composed of three parts: anode, cathode, and electrolyte. Fig. 1 outlines a rough schematic of a lithium ion cell. The cathode, typically a lithium metal oxide, acts as the positive terminal of the battery (during discharge) and the anode, commercially composed of graphitic carbon, acts as the negative terminal. The cathode reacts according to the following half reaction:



Similarly, the anode reacts according to the following half reaction:



While charging and discharging, Li^+ ions move between the anode and cathode via the electrolyte, which is typically a lithium salt such as LiPF_6 dissolved in organic solvent such as ethylene carbonate. Importantly, the electrolyte does not enable the conduction of free electrons; instead, the electrons that complete the half reaction move via an external wire. Commercially, the most common cathode material has been lithium cobalt oxide since its introduction by Sony in the early 1990s [1], due to its high energy density. Lithium manganese oxide is also commonplace in cathodes where higher current density is a concern [1].

It is now possible to characterize the reactions in terms of charging and discharging. When charging, a voltage is applied across the anode and cathode that drives the half reactions in the forward (left to right) direction. Lithium ions are then formed from the lithium metal oxide in the cathode, diffuse across the electrolyte, and are finally inserted into the carbon/graphite anode. During the ion formation, the metal in the lithium metal oxide is reduced, producing a free electron to maintain charge neutrality. The electrons that are freed in the ion formation are subsequently driven across a wire that connects the two electrodes to finally provide the necessary electrons for the insertion half-reaction to take place. The voltage necessary to accomplish this is determined by the particular metal in the lithium metal oxide and by the material that the anode is composed of, as well as the electrolyte itself. When discharging, the reaction naturally tends in the reverse (right to left) direction, and the potential difference between the two electrodes is used to power devices. And so during discharge, electrons move from the anode to the cathode, positive current originates from the cathode, and so the cathode acts as the positive terminal.

2.2. Advantages and limitations of graphite based anodes

Anodes in many commercial grade lithium ion batteries are composed of graphitic carbon. Graphite is best characterized as a stack of hexagonally bonded sheets of carbon held together by van der Waals forces. The forces between any two given carbons in the same sheet (which share sp^2 hybridized bonds) are much stronger than the forces between any two concurrent sheets. It is because of this disparity in forces that Li^+ ions are able to be inserted in between the planes of graphite. This process, known as insertion or intercalation, is the mechanism through which graphitic anodes are able to store lithium. When lithium intercalates in graphite, it occupies an interstitial site between two planes of graphite. Once inserted, a lithium ion prevents other lithium ions from binding in directly adjacent interstitial sites. In other words, lithium ions can only combine on every 2nd carbon hexagon in the graphite sheet which limits the amount of lithium ions to 1 for every 6 carbon atoms [2]. This is directly linked to the energy storage density of graphite in Li-ion batteries. This storage density, often called capacity, similarly has a theoretical limit; in the case of graphite, it is 372 milliamp hours per gram (mAhg^{-1}) [2]. Fig. 2 shows a diagram of lithium ions intercalating into graphite.

Graphite is commonplace among commercial lithium ion batteries because of their low expansion during lithium insertion. This low expansion is directly linked to their ability to maintain their charge capacity after many charge-discharge cycles. The reasons for this will become clear later, but in any case, their predominance in the market is a result of their cycle over cycle efficiency, not their capacity. The lithium insertion capacity of graphite (372mAhg^{-1}) is a relatively low capacity, and lithium ion cells stand to gain much if this value is increased.

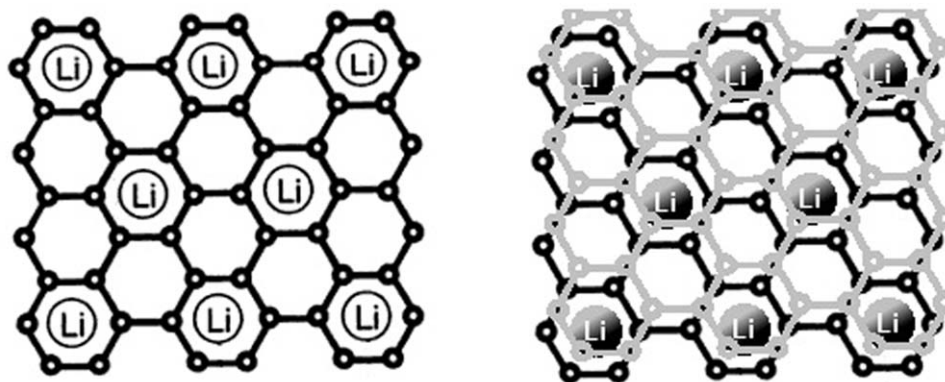


Fig. 2. Schematic of lithium intercalation in graphite. (a) Lithium is inserted in every 2nd carbon hexagon and (b) between the graphite layers.

2.3. Advantages and limitations of metal and alloy based anodes

In fact, metals such as aluminum ($993 \text{ mAhg}^{-1} \text{ LiAl}$ and theoretically 2234 mAhg^{-1} for Al_4Li_9), tin ($994 \text{ mAhg}^{-1} \text{ Li}_{22}\text{Sn}_5$), antimony ($536 \text{ mAhg}^{-1} \text{ Li}_3\text{Sb}$), and several others have capacities that are far greater than that of graphite [3,4]. The difference is that the lithium is not stored through the intercalation mechanism that graphite uses. Instead, these metals are lithium ion storage materials because they are capable of forming an alloy with lithium. By forming alloys, these metals are capable of storing far more lithium per gram than graphitic carbon can. Significantly, whereas it takes 6 carbons in graphite to insert one lithium ion, one aluminum or tin atom can often alloy itself with 2–4 lithium atoms [3,4]. This results in a much higher storage capacity, but also results in a large volumetric expansion of the anode. When the battery is later discharged and the lithium returns to the cathode, the metal alloy reverts to its original metal state and in the process shrinks dramatically back to its original size.

This large change in volume, sometimes an expansion/contraction of 500%, causes the structural integrity of the anode to be compromised, which then causes the anode to physically crumble [5]. This process is called pulverization, and is the primary reason that metal alloys are not used in rechargeable batteries. Once pulverization occurs, it cannot be reversed and the battery permanently loses a fraction of its capacity. When a metal alloy based anode is used repeatedly, it results in an exponential decay of capacity. It is evident then, that to improve the capacity of a rechargeable battery such as the lithium ion cell, a simple metal alloy anode will not suffice.

3. Carbon nanotubes as alternative anode materials

3.1. Qualification of carbon nanotubes for lithium ion battery anode materials

As an allotrope of graphite, carbon nanotubes (CNTs) have been approved to be a good anode material for lithium batteries [6–12] due to their unique structure (one-dimensional cylindrical tubule of graphite sheet), high conductivity (10^6 S m^{-1} at 300 K for single-walled CNTs (SWCNTs) and $>10^5 \text{ S m}^{-1}$ for multi-walled nanotubes (MWCNTs)) [13,14], low density, high rigidity (Young's modulus of the order of 1 TPa) [15,16], and high tensile strength (up to 60 GPa) [17]. SWCNTs can have reversible capacities anywhere from 300 to 600 mAhg^{-1} [18–24]; this means it can be significantly higher than the capacity of graphite (320 mAhg^{-1}), a widely used battery electrode material. Furthermore, mechanical and chemical treatments to the SWCNTs can further increase the reversible capacities up to 1000 mAhg^{-1} [7–10]. To enhance the charge capacity of the

lithium ion batteries and to reduce the irreversible capacity, a practical route could be to synthesize hybrid composite materials with CNTs as a critical component [25–28].

3.2. Advantages carbon nanotubes have over graphite

Carbon nanotubes offer a means of raising the capacity of lithium battery significantly, without being susceptible to pulverization. Their morphology makes them uniquely suited to replace graphite as the de facto anodic material in commercial lithium ion batteries. As previously stated, desirable properties such as their high tensile strength, high conductivity, and relative inertness make CNTs good candidates for this purpose. Carbon nanotubes not only have a higher capacity than graphite, but they can be used as a support matrix to form novel CNT and metal composites that can take advantage of the higher capacity of metals too [29–42].

Metal nanoparticles such as tin and tin antimonide can be deposited on the outside and inner surfaces of the carbon nanotubes [22,43], and these particles are then able to form an alloy with the lithium without impeding the insertion/intercalation of lithium into the CNTs themselves. This effectively gives this type of metal coated CNT composite two mechanisms by which to store lithium. The advantages of such an approach are many. First and foremost, this enables the anode to take advantage of the high lithium capacity that metals have to offer without the problem of pulverization. This is because the highly conductive CNTs act as glue matrix for the metallic nanoparticles. When the nanoparticles suddenly alloy themselves with lithium and increase in size, the anode is able to remain structurally intact because the highly conductive CNTs act as a flexible wire mesh, allowing the metal particles to remain attached to the anode's current collector. The CNTs are then able to transport the electrons to and from the metal nanoparticles when they are alloying and dealloying. Second, the carbon nanotubes themselves are able to store any additional lithium that is not alloyed with the metallic nanoparticles.

3.3. Limitations of carbon nanotubes as anodes for lithium ion battery

Unfortunately, carbon nanotubes are a relatively recent discovery [44], and their production methods have yet to be refined enough for production of CNTs with desired structures such as diameters, number of layers, length, degree of defects, and electronic property, which are important factors and need to be considered for development of CNT based anodes. At present, another issue with carbon nanotubes is their irreversible lithium ion capacity. This is when upon the first charge, more lithium ions are inserted into the carbon nanotubes than ever come out. In

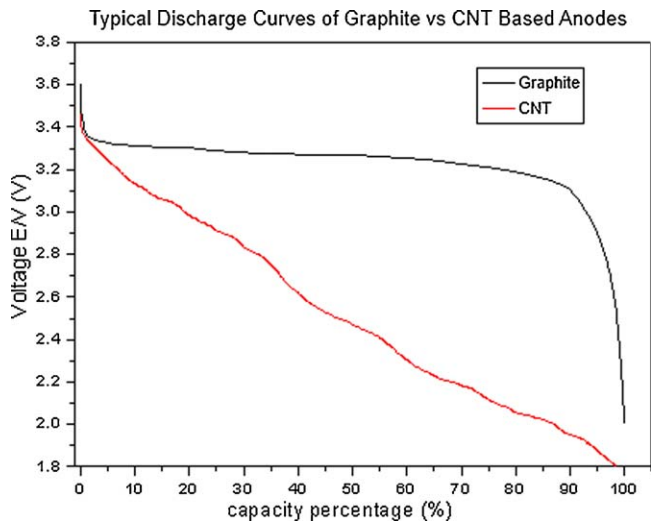


Fig. 3. A schematic representing typical discharge curves of a graphite and CNT based anode. The CNT based anode curve does not represent composite CNT/metal anodes which can have much flatter discharge curves.

effect, a fraction of the lithium ions are consumed instead of stored. Although this happens for graphitic carbon as well, the problem is more pronounced in carbon nanotubes.

A related problem for CNT based anodes is the lack of a voltage plateau while the battery is discharging, as can be seen in Fig. 3. Unlike graphitic anodes, CNT anodes typically have broad changes in voltage as the cell discharges. This can make them difficult to use in most electronics which require a stable voltage source. Moreover, this means that the increased specific capacity (often cited in units of mAhg^{-1}) does not necessarily imply increased specific energy (Jg^{-1}). However the problems of high irreversible capacity and lack of a stable voltage as the battery discharges are both morphology dependent. In particular, CNTs decorated with metal nanoparticles and core/shell composite anodes of CNT and other materials can have much flatter discharge curves than anodes made of just CNTs [32]. In any case, ongoing research continues to bring carbon nanotubes closer to commercial readiness as synthesis methods improve and novel anode structures are tried.

4. Mechanism of lithium ion storage in carbon nanotubes and metals

As previously explained, lithium ions can be stored via two fundamentally different mechanisms: intercalation and alloying. The former is employed by carbonaceous materials such as graphite and CNTs, while the latter is employed by metals. At present, we will go into detail about intercalation. The spacing between unintercalated graphite layers is approximately 3.35 \AA [45]. This interlayer spacing increases to about 3.5 \AA when lithium is inserted. This small expansion (<5%) enables the graphite to keep its structural integrity. When lithium is inserted, graphite's planar conductivity is actually increased [45] which enhances its ability to act as an anode. As previously mentioned, high conductivity is one of the key properties of both CNTs and graphite that enable them to act as good anodic materials. This is because the electrons that are being consumed or freed in the anode half reaction must be able to reach the lithium ions. The graphite acts as a pathway for the electron to reach the lithium ion, or vice versa, for the electron to leave the lithium atom and make its way back to the cathode. It ensures that the electrons are able to move to and from the lithium ions and the current collector.

4.1. Kinetics and mechanisms of Li ion diffusion in carbon nanotubes

In raw carbon nanotubes, intercalation also occurs. However, due to the vastly different morphologies, the insertion level is no longer limited to LiC_6 . In fact, there are varying reports of just how much lithium CNTs are able to store. Shimoda et al. estimated that a density up to around LiC_3 is possible [8], whereas there are some experiments that report capacities even lower than that of graphite's LiC_6 [43,46]. The large variety in reported capacities is strongly linked to the different morphologies of the CNTs investigated in each experiment. In fact, it is surprising how important the exact morphology of the CNTs is to its lithium ion capacity. Particularly important to the capacity is the presence of defects. Defects, which can occur naturally or can be introduced by acid treatment, can be thought of as holes in an otherwise perfect cylinder of graphite sheet. The presence of these holes allows lithium to better diffuse into and intercalate inside the carbon nanotubes, thereby increasing its capacity [7,8,18,19]. By doing this, one effectively lowers the diffusion path length and allows more lithium ions to be inside the CNTs [8]. As previously mentioned, acid treatment such as nitric acid can be used to introduce defects into CNTs [18,19]. Ball milling can also be used to introduce defects into CNTs [7].

To investigate the mechanisms through which lithium ions are stored in CNTs, many ab initio studies have been performed [20,47–50]. Nishidate and Hasegawa used molecular dynamics simulations to test the diffusion characteristics of lithium entering single walled CNTs and quantified the effect of defects on lithium insertion in CNTs [20]. In Figs. 4 and 5 one can observe the effects that defects have on the morphology of the CNT. As carbon atoms begin to be removed, a hole begins to occur in the wall of the carbon nanotube as each of the carbon atoms attempts to remain bonded with its neighbors. The results showed that while lithium rarely diffused into defect free, $n=7$, and $n=8$ defected CNTs, it was able to diffuse readily into CNTs with $n=9$ defect. Once inside, the lithium is able to move through the interior of the CNT and can be absorbed successfully, indicating that lithium ions can be accumulated in the interior of CNTs in addition to the exterior. Ab initio calculations of the molecular interaction potential on CNTs of various chiralities were performed by Garau et al. [47,48]. They concluded that topological defects that were 10-membered rings posed no barrier to lithium diffusion inside the CNT, and that 9-membered ring defects had a diffusion barrier of just $9.69 \text{ kcal mol}^{-1}$. These results seem to agree with Nishidate et al.'s conclusion that lithium readily diffuses into CNTs with $n=9$ defects and greater. Ab initio studies using first principle density functional theory were also conducted by Fagan et al. on lithium intercalation into the channels in between CNTs that occur when they form into bundles [49], and these channels were found to be favorable intercalation sites.

While Nishidate et al. focused on defects introduced through the sidewall of the CNT, it is important to note that lithium can also enter CNTs in other places. Meunier et al. determined through ab initio simulations that lithium could also come in through the ends of open ended nanotubes (as opposed to closed nanotubes that had a buckyball-like cap at the ends) [21]. Meunier et al. noted that to be effective, however, open ended CNTs would need to be relatively short, to allow ions to freely enter and exit. Experimental evidence to support this can be found whenever ball milling open ended CNT samples immediately results in higher capacity. Kumar et al., for example, determined the difference between the capacities of opened and unopened carbon nanotubes to be almost 120 mAhg^{-1} [22]. Shimoda et al. determined that the reversible Li storage capacity increased from LiC_6 in closed ended tubes to LiC_3 after etching, a process that both shortens and introduces defects into CNTs [8]. Meunier et al. concluded that the key factor in determining

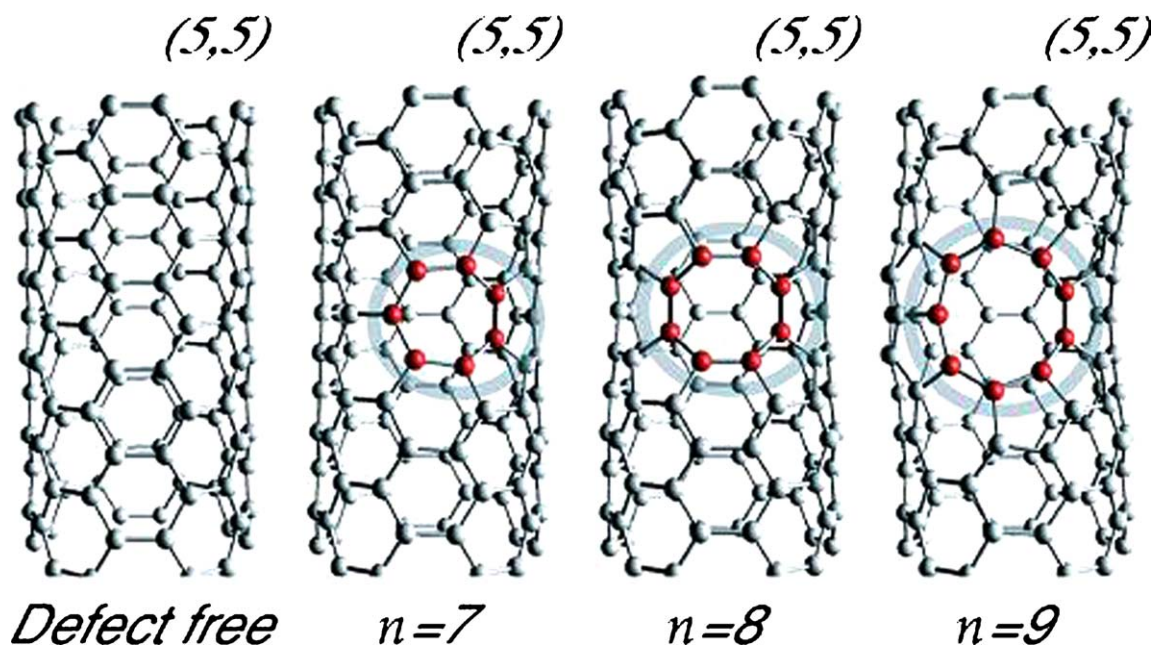


Fig. 4. Types of topological defects (rings of the red dots) in a (5,5) SWCNT. Here $n=7$ means 7 carbon ring defect, $n=8$ means 8 carbon ring defect, and $n=9$ means 9 carbon ring defect. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) From [20] with permission.

the diffusion coefficient of the CNTs is the ability for the Li ions to reach either end of the open CNTs or a 9 sided (9-carbon ring) defect in between [21]. This is because once inserted, the lithium ions undergo a one dimensional random walk inside the tube, and

if the tube is too long, effective diffusion decreases as lithium ions are able to enter but never exit. This is reflected in Wang et al.'s experiment showing the capacity of short (300 nm) CNTs greatly exceeding that of the longer micrometer scale ones [51].

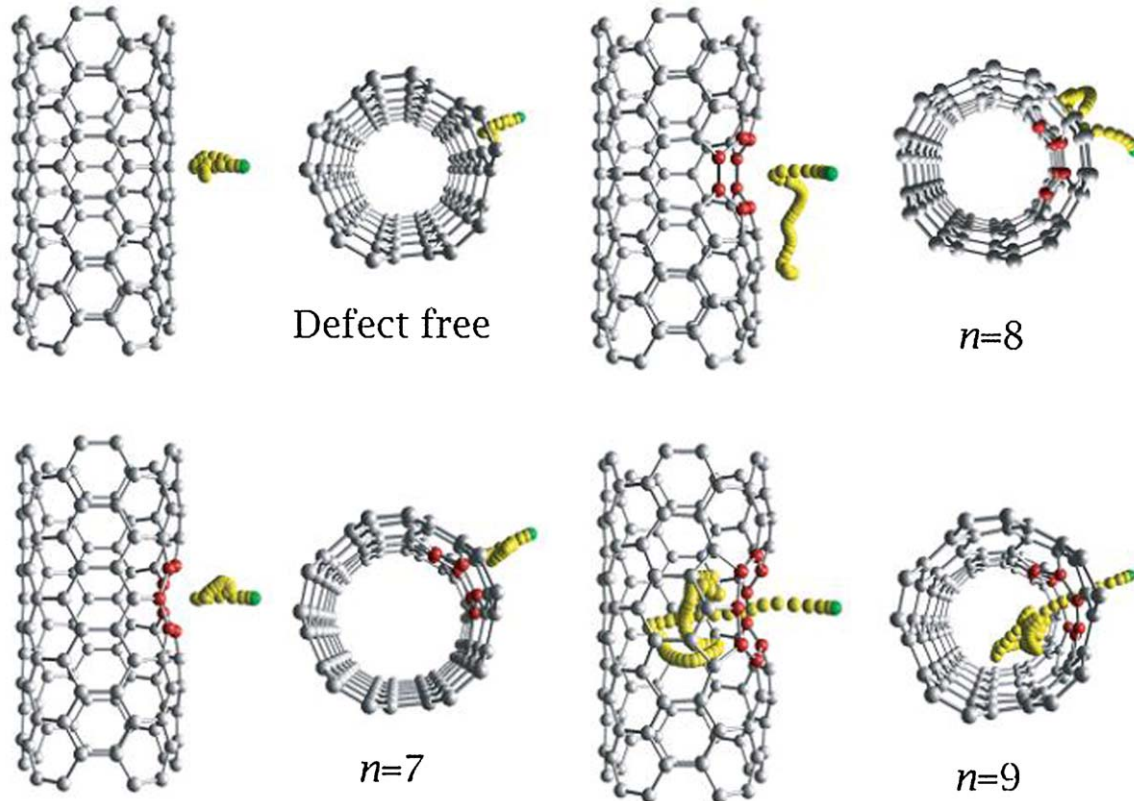


Fig. 5. Effect of defects on Li insertion in (5,5) SWCNT. Red balls indicate the defects, green balls indicate the initial position of the Li, and yellow balls indicate the trajectory of Li. Note: for each nanotube, both the side view and the top view are presented. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

From [20] with permission.

4.2. Characteristics of carbon nanotube lithium ion storage

Kawasaki et al. determined that between semiconducting and metallic CNTs, metallic CNTs are able to store about 5 times as many lithium ions [23]. The difference between semi-conducting and metallic CNTs is in their chirality. When the difference between two components of the chiral vector is a multiple of 3, experimental and theoretical calculations have shown the CNT is metallic; otherwise it is semiconducting [52]. This means that in a random distribution of CNTs, approximately 1/3 of them will be metallic while 2/3 will be semiconducting. Recently, techniques have been developed to separate metallic and semiconducting CNTs from a mixed sample [53–56], though that is not a focus of this paper. Kawasaki et al. proffered two explanations for the different Li storage in metallic and semi-conducting CNTs: one that the difference between their electrical conductivity caused a kinematic effect that altered the effective capacity of Li storage in the CNTs, and two that the lithium ion absorption potentials were inherently different between the two types of CNTs [23].

While the introduction of defects into CNTs generally improves reversible capacity, it also increases irreversible capacity. This means that while more lithium ions are able to be stored and later retrieved, the increased amount of defects also causes a larger amount of lithium ions that are stored on the initial charge cycle to be permanently lost. High irreversible capacity means that lithium ions are essentially consumed by the first cycle and are never returned to the cathode, and so no net work can be done with the lithium ions lost to irreversible capacity.

Something of note, the capacity of the lithium ion anodic cells is often affected by the current that it is being required to deliver. When a cell is measured at a high current density, its capacity is often quite lower than when it is measured at lower current densities. Due to this un-ideal behavior, the reported capacities between different experiments may not be entirely indicative of the superior anode. While most experimenters report their capacities at a current densities of 0.1–0.3 C, some are reported at higher current density. Since capacity is a function of the current density, high current densities are desirable for certain high performance applications of batteries. It should be noted that battery makers often denote their current density in fractional terms of C. C/n is current rate which is the amount of current provided such that the charge (C) stored in 1 g of the anodic material will take n hours to discharge. By extension, a 0.1 C rate corresponds to the amount of current provided per gram of anode material such that it takes 10 h to fully discharge, while a 2 C rate is the amount of current it took to discharge the battery in half an hour. This method is somewhat convoluted, since 1 C is not an easily defined numerical value current density. Fig. 6 highlights the change in capacity fading that occurs when current rate is changed. Ning et al. conducted a study on capacity fading to quantify the effects that different current draws had on how quickly the lithium ion electrodes deteriorated [57]. Most experiments cited here are conducted at a 0.1–0.3 C, primarily because lithium ion batteries in particular are typically used for long discharge cycles. For example, most laptop users are concerned with their battery life, in which a 3–8 h lifespan could be converted into a 0.1–0.3 C current rate.

4.3. Metal alloying for lithium storage

As previously mentioned, metals can be used as anodic material because they are able to store lithium ions via alloy formation. Alloying allows a storage capacity many times greater than graphite is able to store via intercalation, but the process causes the anode to expand greatly and ultimately compromises the structural integrity of the anode which then results in crumbling. This process, called pulverization, is the primary reason why metal anodes are not fit

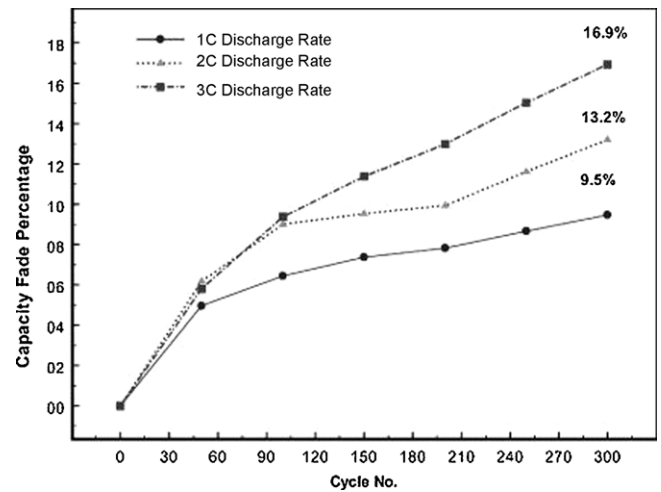


Fig. 6. Effect of current draw on capacity fading. From [57] with permission.

to be used in lithium ion cells, or any secondary (rechargeable) battery [4]. However, recently there have been attempts to mitigate the expansion by using thin films and nanoparticles [29,58]. While these attempts have improved the anode's ability to cycle somewhat, these anodes are still susceptible to systemic and continued decay in capacity and are ultimately incapable of matching the nominal decrease of 0.03% per cycle experienced by commercial graphitic cells [57]. For commercial cells, this slight decrease in capacity is caused by slow degradation of the electrode materials. Even though the graphitic anodes are not plagued by problems of pulverization, repeated charge/discharge cycles can compromise the integrity of the cells. Fortunately, there seems to be no reason why an anode made of carbon nanotube could not improve upon this number and slow the decay of batteries.

5. Carbon nanotubes and carbon nanotube composites for lithium storage

Indeed, some of the most interesting innovations at improving lithium ion cell anodes have come from attempts to combine CNTs with various deposits. Recently, efforts have been made to synthesize core/shell structured CNTs which have either CNTs filled with metallic nanoparticles, metal coatings that have been deposited on CNTs, or some combination of inner/outer CNT/metal core/shell. First however, we will examine anodes composed of pure CNTs for comparisons sake.

5.1. Raw carbon nanotubes

Many efforts have been made to use pure CNTs as a replacement for graphite in Li-ion cells [18–23,59–63], with widely varying degrees of success. Yang et al. reported capacities of 170 mAhg⁻¹ and 266 mAhg⁻¹ for two different samples for unetched SWCNTs [18]; Wang et al. reported a capacity of 340 mAhg⁻¹ [29]; and Kawasaki et al. reported a capacity of 641 mAhg⁻¹ for metallic CNTs [23]. Attempts to intercalate lithium specifically into MWCNTs (as opposed to SWCNTs) have also been widely reported [19,64–66] with varying degrees of success. Recently, Chew et al. created a free standing MWCNT film with the desirable property of being flexible that was able to retain its capacity after many cycles, though its capacity was no better than that of commercial graphitic anodes [67]. There has also been a recent push to creating polymer-carbon nanotube composites for their interesting properties and possible applications outside of battery electrochemistry [68]. Nonetheless,

the wide range of capacities underscores the importance of morphology of CNTs in determining capacity. In the previous sections, the different ways in which CNT morphology might affect lithium capacity were discussed, and the wide range of reported capacities provides evidence of this point. However, raw carbon nanotubes provide only a small improvement to the capacity of graphite, and little if any improvement to their cyclic efficiency. In addition to only slightly improving upon the capacity of graphite, carbon nanotubes face difficulties such as their high irreversible capacity and problems with consistently controlling their structure and morphology during synthesis. As such, it is currently difficult to justify using pure CNTs as a replacement for graphite in lithium ion cell anodes.

5.2. Core-shell structured carbon nanotube-metal oxide anode materials

Recently, novel anodic materials have been made by combining CNTs with high capacity metallic coatings in order to improve the lifespan of the battery. The advantages of this type of composite are the increased capacity of the metal alloying materials while using the CNTs as a scaffold to prevent pulverization and crumbling in the anode. A compound made of both metal and carbon nanotubes has two mechanisms to store lithium with, intercalation and alloying. In addition to increased capacity and better cycling, CNTs can act as a conductive wire to transport electrons to and from the coating in cases where the CNTs are coated with a non-conductive metallic oxide. Thus, both the high tensile strength and the conductivity of CNTs make them uniquely suited for new nanostructured anode composite materials. Reddy et al. described a method where a layer MnO_2 is coated onto CNT using anodized alumina templates [25]. Zhang et al. reported the formation of cross-stacked carbon nanotube sheets uniformly loaded with SnO_2 nanoparticles by hydrothermal synthesis [28]. Fig. 7 shows the TEM images of the cross-stacked carbon nanotube- SnO_2 core-shell nanowires. This type of anodic material holds the most promise out of all the possible candidates to replace graphite in lithium ion batteries. They can easily triple the gravimetric capacity of graphite, and if the appropriate synthesis methods and materials are used, can experience just as minimal a capacity fade over cycles as graphite does. We will continue with a discussion into the various synthesis methods for this type of anode, and the results achieved by the experimentalists.

5.3. Silicon-carbon nanotube composites

Recently, there has been much focus on using silicon as an anodic material, due to its supremely high gravimetric capacity for lithium storage (theoretically 4200 mAhg^{-1} for $\text{Li}_{4.4}\text{Si}$). Like metals that undergo alloying, silicon too suffers from severe volume change during charging and discharging that results in a compromised crystallographic structure and ultimately in crumbling and electrode capacity loss. In order to mitigate the effects of pulverization, novel nanoarchitectures have been used. For example, Chan et al. recently synthesized silicon nanowires capable of repeatable discharges in excess of 3000 mAhg^{-1} [31]. The nanowires are able to avoid crumbling because their small diameter means that the effect of expansion is minimal, allowing the nanowires to grow and shrink both radially and axially without crumbling. However, there are some problems with pure silicon based anodic materials. Silicon has a lower conductivity, particularly amorphous silicon, and in the process of lithium alloying and dealloying, the originally crystalline silicon nanowires become at least partially amorphous. The lower conductivity makes it difficult for current to be drawn by the current collector. This has lead Chen et al. and others to combine the high capacity of silicon with carbon nanotubes. In a later experiment [32] Cui et al. used silane chemical vapor deposition to deposit

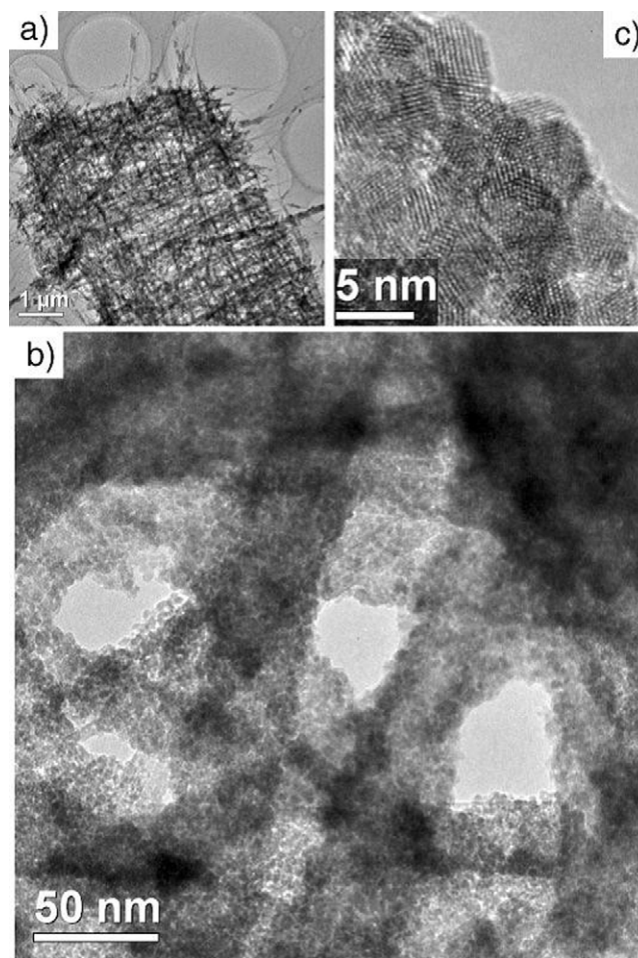


Fig. 7. TEM images of the cross-stacked CNT sheets coated with SnO_2 nanoparticles. (a) A small piece of the cross-stacked CNT sheets loaded with SnO_2 nanoparticles, (b) a close-up of the sample showing the uniform coating of the SnO_2 nanoparticles on the CNTs, and (c) a high-magnification TEM image of the sample showing crystalline SnO_2 nanoparticles with diameter of 4–5 nm. From [28] with permission.

silicon onto commercially purchased carbon nanofibers. The carbon core allowed electrons to easily move between the silicon and the current collector. Shu et al. grew carbon nanotubes using a conventional CVD method; the carbon nanotubes were grown on micron sized milled silicon particles as opposed to a silicon substrate [33].

6. Synthesis methods of carbon nanotube-metal and carbon nanotube-alloy for Li-ion battery application

In this section, synthesis methods of the various anode composites will be discussed.

6.1. Electroless deposition

One of the chemical methods for depositing specific metals onto the surface of carbon nanotubes is the electroless plating method. A form of chemical reduction, electroless (or autocatalytic) plating is the deposition of a metallic coating by controlled chemical reduction that is catalyzed by the metal being deposited. Electroless plating normally involves the chemical reduction of metal onto CNTs introduced by bathing the CNTs in an electroless solution. The metal salt and the reducer react in the presence of a catalyst (the part to be deposited). After the reaction is initiated, the metal

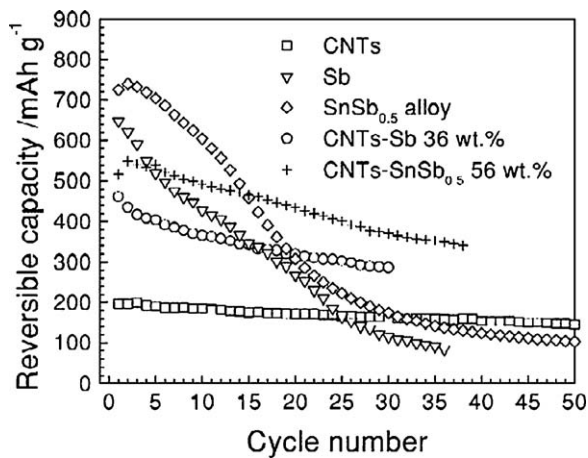


Fig. 8. Reversible capacity vs. cycle number of CNTs, Sb, SnSb_{0.5}, CNT-Sb and CNT-SnSb_{0.5} electrodes at the constant current density of 50 mA g⁻¹ at 0–2.0 V. From [43] with permission.

deposited serves as a catalyst, thus ensuring continuous buildup of the metal on the surface. The reducer is typically a very strong one, either sodium borohydride (NaBH₄), potassium borohydride (KBH₄), sodium hypophosphite (NaH₂PO₂), or the like. An aqueous salt like tin chloride (SnCl₂) might be reduced causing tin to be deposited on the surface of the carbon nanotubes.

Electroless plating is marked by its ease of use and preparation. It is able to evenly coat CNTs even when they are bundles, because the CNTs are in the same chemical bath that the reduction is taking place in. However, the method is limited to plating metals that are easily reduced. Among these, nickel, copper, tin, silver are the easiest and most common to deposit [4], though these metals are not necessarily the best metals for increasing the capacity of a metal/CNT hybrid structure.

It is for the reasons stated above that the method has proved to be the most popular method in recent experiments to improve anodic capacity. Chen et al. used this method to deposit both tin and antimony onto CNTs with moderate success [43,69]. See Fig. 8 for more details. One can see that although the capacity remains substantially over that of graphite, there is a noticeable exponential decay in capacity. It is for this reason that this particular

implementation needs to be improved significantly so that it will work in the commercial field. Also of note is Chen et al.'s reported capacity of 200 mAhg⁻¹ for CNTs, notably smaller than the 320 mAhg⁻¹ capacity of graphite.

A better example of electroless plating would be Kumar et al.'s tin filled carbon nanotubes [22], as shown in Fig. 9. One can see from Fig. 9 the marked difference in capacity fading, with capacity notably leveling out well above 800 mAhg⁻¹ of the Sn-filled (NaBH₄) carbon nanotubes at a discharging rate of 0.1 C. To what can we attribute this success to? For one, Kumar et al. took advantage of a nitric acid treatment to improve the absorption of lithium by the CNTs. Also, by using strictly tin, an element that has a well-known high capacity for lithium, they were able to keep the capacity high. Instead of diluting the capacity with another metal such as antimony, using pure tin seems to have a better effect on the net capacity of the structure. Kumar et al. compared two separate synthesis methods using the same deposition metal to compare the qualities of one with the other. In Fig. 9a and b it is apparent that the electroless plating method resulted in a slightly better sample when compared to the capacity of the tin filled CNTs produced using hydrothermal deposition. We will discuss the hydrothermal method in the next section. Note that in Fig. 9b when there is a higher current draw, the hydrothermally produced sample does better in terms of capacity for the first several cycles, though there is a far more rapid decay in capacity (this is what we expect from Section 4.2). However, there is an unexplained increase in capacity from the electroless deposited CNTs after 20 cycles, at which point their capacity improves over that of the hydrothermally produced sample.

Other successes using the electroless plating method include Huang et al.'s Sn-Co coated CNTs which maintained a capacity above 400 mAhg⁻¹ for 30 cycles [34]. Jhan et al. [35], Lee et al. [40], Zhao et al. [70], Chen et al. [71] and Yang et al. [72] also synthesized CNTs coated with various tin compounds (primarily tin oxides) since tin is favored for its high capacity. The widespread use of electroless plating is primarily a result of its ease and simplicity. It can be used with a variety of different compounds, and experimentalists have not just limited their research to higher capacity metals. Yan et al. used it to create both CNT/Ag and CNT/TiO₂ compounds [41]. A more complicated synthesis method that also uses a chemical bath to coat carbon nanotubes with one or more elements is the hydrothermal method.

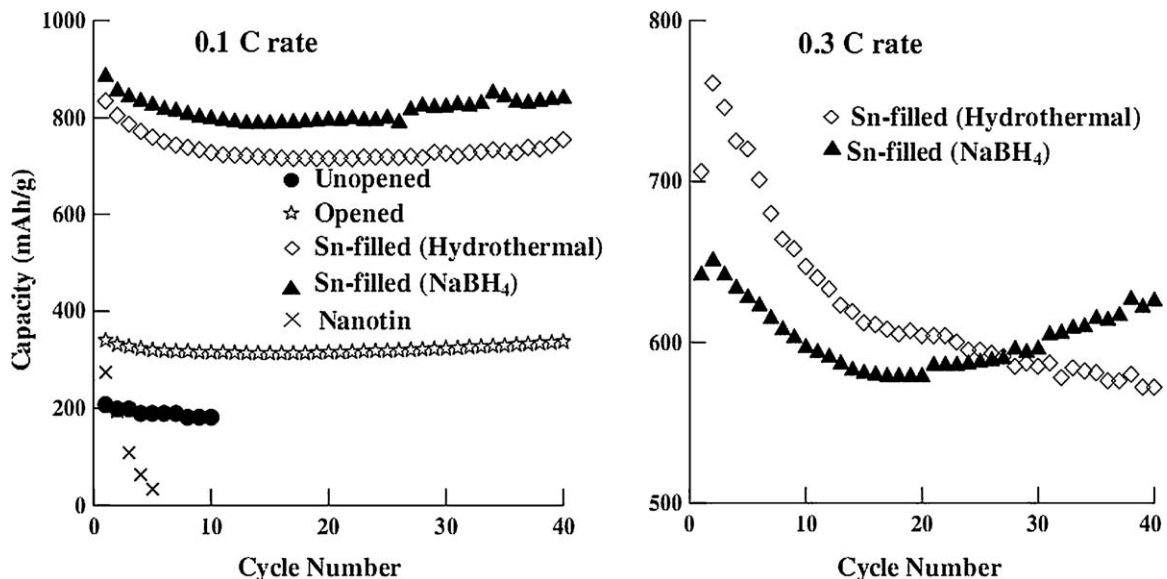


Fig. 9. Cycling behavior of the nanosized tin, unopened, opened but unfilled, and the tin-filled CNTs.

From [22] with permission.

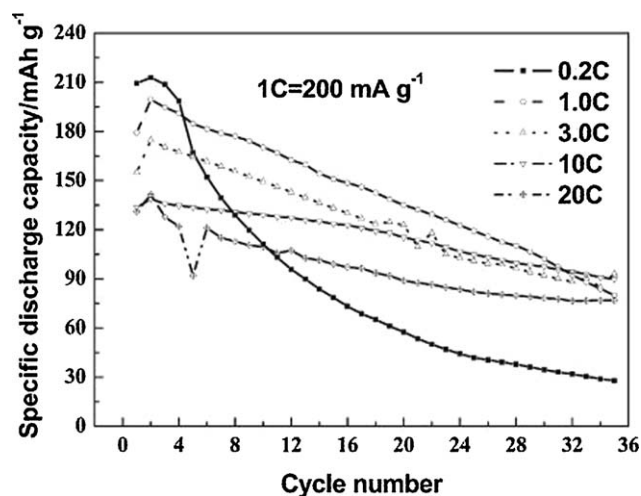


Fig. 10. Specific discharge capacity vs. cycle number of MnO₂ coated CNTs prepared by hydrothermal method.

From [36] with permission.

6.2. Hydrothermal deposition

Like the electroless plating, the hydrothermal method [28,36,37,73,74] involves bathing carbon nanotubes in a chemical bath. Unlike electroless plating, high temperatures and pressures in an autoclave are used to achieve the deposit. Instead of using a chemical reducer to reduce the metal onto the surface, inert Teflon lined autoclaves are able to put aqueous solutions at high temperatures and high vapor pressure in order to crystallize one of the aqueous components onto the carbon nanotubes. Kumar et al. attempted a hydrothermal deposit of tin as an alternative to the electroless route in the same experiment, and found the results to be highly comparable [22]. Although there was a slight edge in capacity for the electroless route, the difference was well within the range of chance and the hydrothermal route should not be thought of as inferior because of this one experiment (see Fig. 9 to compare). Yue et al. performed hydrothermal synthesis of manganese oxide coated on CNTs [36]. This is notable because manganese oxide coated CNTs were also synthesized using AAO templates by Reddy et al. [25], though their results will be discussed in a section below. Yue et al.'s results can be seen in Fig. 10. The low capacity and the significant capacity fading mean that the sample is unsuitable as a replacement for graphite. The use of an autoclave adds an extra step in experimental procedure compared to the electroless method, but allows a larger repertoire of elements that would not otherwise form on the CNTs. Among those to try this method, Wang et al. coated CNTs with cobalt oxide and achieved a capacity in excess of 500 mAhg⁻¹ for over 100 cycles [37]. The disparity between the capacity of Wang et al. and Yue et al.'s results can be explained by the different capacities of cobalt oxide and manganese oxide. Zhang et al. uploaded SnO₂ nanoparticles to cross-stacked CNT sheets to form CNT–SnO₂ network. The SnO₂ nanoparticle loaded CNT sheet, as an anode for a lithium-ion battery, has delivered over 850 mAhg⁻¹ of charge capacity with 100% retention for at least 65 cycles when cycled in the potential window of 0.01–3 V versus Li⁺/Li (see Fig. 11 for details) [28]. Alternatively, carbon nanotubes were coated by Ma et al. with nanosized particles of lithium manganese oxide, a common cathode material for commercial lithium ion batteries, showing possible application for CNTs beyond the anode [73]. This too was done using hydrothermal synthesis.

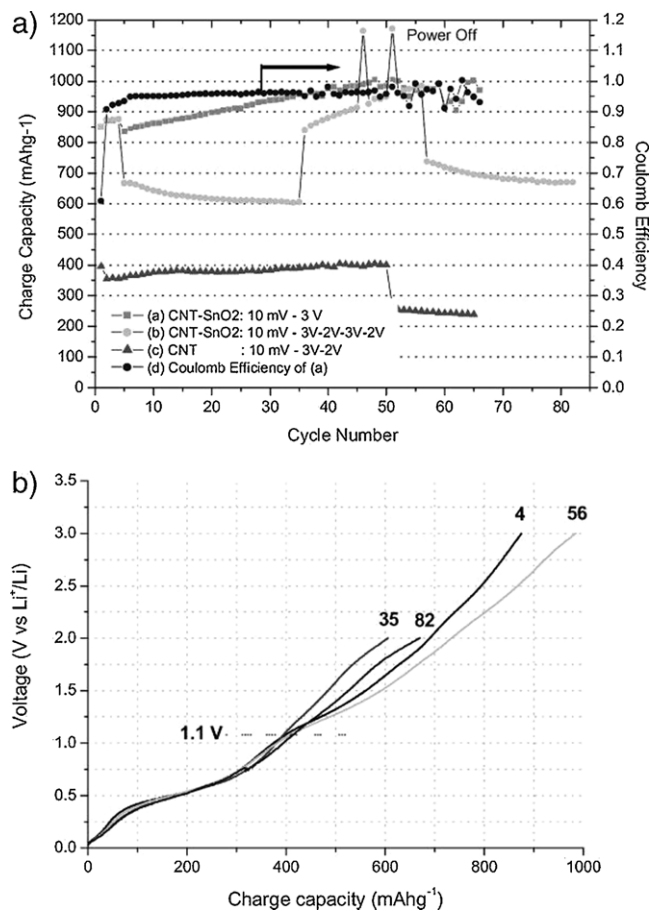


Fig. 11. (a) Cycling performances of the cross-stacked SnO₂–CNT composite sheets with a weight increase of 127% (curves a and b) and the CNT bare cross-stacked CNT sheet (curve c). The Coulomb efficiencies of the cross-stacked SnO₂–CNT composite was shown in curve (d). (b) The galvanostatic voltage profiles of the SnO₂–CNT composite sheet cycled under varied cut-off voltages (corresponding to curve b). The number above each curve indicates the corresponding cycle number.

From [28] with permission.

6.3. High energy mechanical milling

High-energy mechanical milling (HEMM) is a synthesis method in which fine powders are milled together, causing mechanochemical bonds to be formed. It is different from any of the previously mentioned methods because it does not involve a chemical reaction of some sort. Huang et al. used it to synthesize a blended composite of TiO₂ and carbon nanotubes [75]. However, the reported results have a lower capacity than that of graphite. One will note that here the reported capacity of pure CNTs is a mere 125 mAhg⁻¹. Fig. 12 underscores that the capacity of the TiO₂/CNT composite seems to be the mere addition of the capacity of each of the individual components. HEMM methods have been used in a variety of other experiments, with varying degrees of success. For example, Yan et al. combined Mg₂Si with carbon nanotubes using HEMM and found that it stabilized with a capacity of up to 400 mAhg⁻¹ after 30 cycles using various ratios of Mg₂Si to carbon, a marked improvement over anodes of pure Mg₂Si which lose almost all capacity after just 3 cycles [39]. HEMM methods can also be useful when electrochemical deposition is not available. Yuan et al. used HEMM to synthesize sulfur coated CNTs in order to overcome the difficulties specific to the chemical reduction of sulfur onto CNTs [42].

One advantage of this method is that its use is not limited to that of metals or easily reduced elements. Wang and Kumta used it with great success to combine the very high capacity of silicon

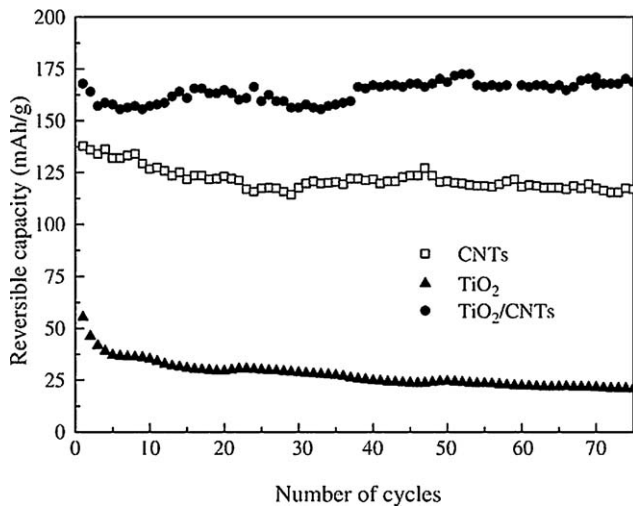


Fig. 12. Cycling performance of the CNTs, TiO₂ and HEMM coated TiO₂/CNTs electrodes at a current density of 50 mA g⁻¹. From [75] with permission.

with the high conductivity of carbon nanotubes, reaching a stable capacity above 1000 mAhg⁻¹ [76]. They described a matrix that is formed by CNTs, amorphous carbon black, and elemental silicon formed using HEMM and postulated that the Si/C particles cause the SWCNTs to bend and wrap around the Si/C particles which enable them to hold together and preserve electrical contact with the anode, thus mitigating any potential loss in capacity due to pulverization. This allows the integrity of the anode material to remain largely unchanged after many charge/discharge cycles. The composite takes advantage of the high conductivity of the CNTs and the super high capacity of the silicon in order to create a high capacity compound with little noticeable fading. Because silicon is not a metal and not easily reduced, it is generally thought to be unsuitable to be used in most of the previously mentioned methods. HEMM is also used to introduce defects into pure CNTs in order to improve their capacity. It is reported, however, that doing such also severely increases the irreversible capacity. In other words, the difference between the initial charge and discharge capacities of the cell widens.

6.4. Anodized alumina template deposition

One of the most novel synthesis techniques employed recently by researchers involves the use of porous anodized alumina as templates. These templates, which provide a mold for which to make cylindrical structures out of, can be filled with nanoparticles of metals or even used as a growth template for CVD deposited CNTs. Through the use of vacuum infiltration, metal nanoparticles are infiltrated into the channels of the porous anodized aluminum oxide. This is typically followed (or in some cases preceded) by CVD growth of carbon nanotubes inside the AAO [25]. This method could be adapted for various other coatings, so long as the substance is capable of being vacuum infiltrated or deposited.

Notably, MnO₂ coated CNTs were also synthesized in a different experiment by Yue et al. using the hydrothermal method [36]. Reddy et al.'s implementation, however, is far superior in terms of both capacity and fading. Whereas Yue et al.'s capacity peaked at roughly 210 mAhg⁻¹ and decayed to 100 mAhg⁻¹ in approximately 10 cycles, Reddy et al. began with a reversible capacity of approximately 1200 mAhg⁻¹, and stayed above 500 mAhg⁻¹ for 15 cycles, a large improvement. The difference in reported capacities can be attributed to the large difference in the morphologies of the two composites. In Reddy et al.'s work, the carbon nanotubes are aligned

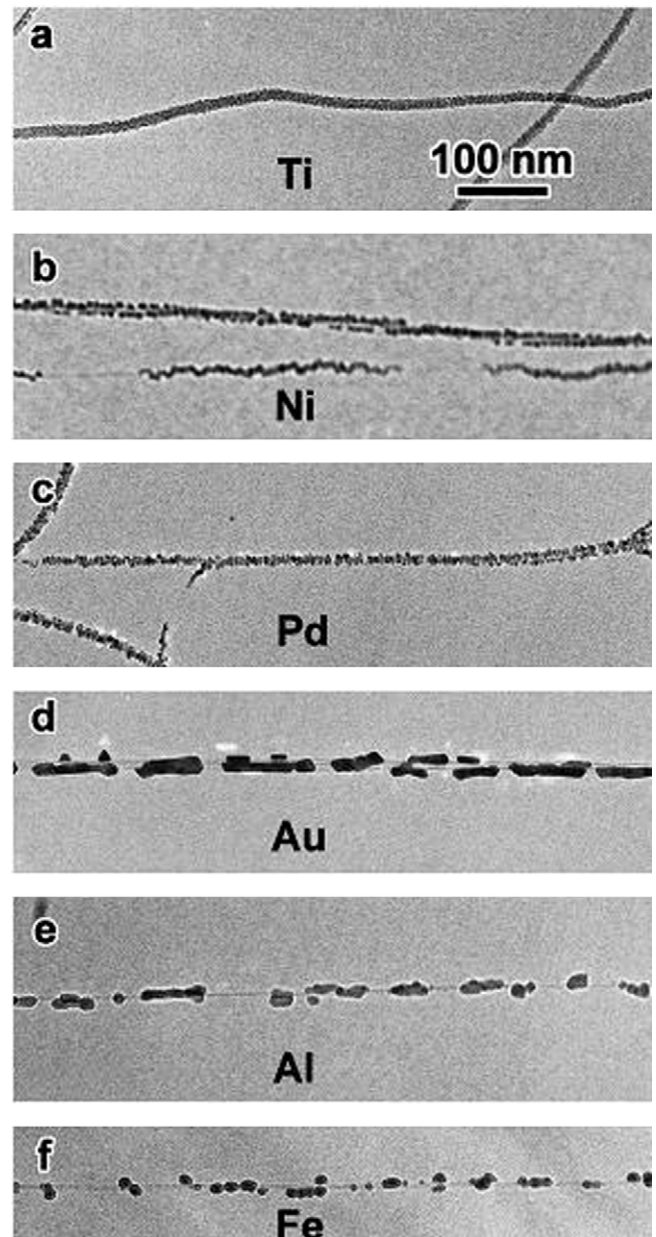


Fig. 13. Metal nanoparticles formed on CNTs using e-beam evaporation. From [80] with permission.

while in Yue et al.'s work the carbon nanotubes are randomly oriented. The structural difference between the two MnO₂/CNT anode materials is no doubt responsible for the distinctive capacity and fading rate.

Attempts at using anodized alumina for templates in CNT and other anodic materials were also done by other groups. Wang et al. filled AAO templates with tin oxide nanoparticles using vacuum infiltration to grow SnO₂ nanotubes and then used CVD to grow a carbon nanotube shell on the SnO₂ nanotubes [77]. Sigurdson et al. studied the effect that the pore diameter has on carbon growth [78]. Interestingly, Yen et al. used the cylindrical pores to synthesize tubes of Si–O–C, though unfortunately did not perform any Li-ion storage capacity tests [79].

6.5. Physical or chemical vapor deposition

One other alternative that could be used to create coaxial CNTs is vapor deposition. By using an electron beam to irradiate metal atoms, a thin layer could conceivably be deposited onto CNTs

using a method called electron-beam evaporation or e-beam deposition. Zhang et al. attempted the e-beam deposition of several different metals onto SWCNTs, and found that the different metals had two fundamentally different ways of interacting with the CNTs [80]. When depositing titanium, nickel, and palladium, Zhang et al. noticed that a continuous or quasi-continuous coating was formed on the surface of the SWCNTs. However, when Zhang et al. used the e-beam to deposit gold, aluminum, or iron, instead they found that the CNTs were covered in discrete particles clumps (see Fig. 13). This difference underscores the complexity of the metal–CNT interaction, and suggests that picking an appropriate metal might not simply be determined by just the metal's natural capacity for lithium. As morphology has shown itself to be of the utmost importance to lithium capacity, the difference in morphology between the discrete particle clump coating and the uniform continuous coating might play just as important a role in the net capacity of the compound as the difference in the lithium capacity of the metals used to coat the CNTs. Unfortunately, Zhang et al. did not test the lithium ion capacity of any of the compounds they synthesized, so it is not known if this method is suited for the purpose of anodic material fabrication.

It is not evident that electron beam deposition could be carried out to evenly and uniformly coat a disordered bundle of CNTs. Given that the CNTs grown using chemical vapor deposition are generally in disordered bundles, this means an alternative production method would likely be used in order to use the e-beam deposition properly. It is possible that the chemical vapor growth of an aligned array of carbon nanotubes might be better suited for e-beam deposition, but such an attempt has yet to be seen.

7. Conclusion and future work

Batteries and battery related technologies have moved to the forefront of the technology field, becoming an increasingly important part of daily life. In a world where Moore's law dictates that the number of transistors in CPUs doubles every 2 years, battery technology is struggling to keep up. It is clear that while lithium ion batteries are very important to consumer electronics and technology in general, there is still much room for improvement. The flurry of research going into various anodic compounds and the constantly improving results reported by researchers in this field are testimony to this. It is the opinion of the authors that perhaps the greatest potential composite for improving the lithium ion battery involves carbon nanotubes. Versatile, strong, and highly conductive, this modern material has the potential to revolutionize not only batteries, but has many applications elsewhere, some that have yet to be realized.

As mentioned above, composites that take advantage of carbon nanotubes and the high capacity of other materials show the greatest potential for improving the lithium ion cell. Of these materials, silicon is perhaps the most interesting. Silicon is so superior to its alternatives in terms of capacity that it seems likely that any sufficiently high capacity anode must use silicon. The authors would like to focus on integrating silicon and carbon nanotubes to create nanocomposites with high capacity and minimal fading. Following the works of Reddy et al. [25], Zhang et al. [28], and Wang and Kumta [76] and others, CNT–silicon and CNT–metal oxide based anodes could stand to revolutionize the battery field.

Acknowledgement

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