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Carbon Nanotubes: Applications to Energy Storage Devices

Ruhul Amin, Petla Ramesh Kumar and Ilias Belharouak

Abstract

Carbon nanotubes (CNTs) are an extraordinary discovery in the area of science and technology. Engineering them properly holds the promise of opening new avenues for future development of many other materials for diverse applications. Carbon nanotubes have open structure and enriched chirality, which enable improvements the properties and performances of other materials when CNTs are incorporated in them. Energy storage systems have been using carbon nanotubes either as an additive to improve electronic conductivity of cathode materials or as an active anode component depending upon structural and morphological specifications. Furthermore, they have also been used directly as the electrode material in supercapacitors and fuel cells. Therefore, CNTs demand a huge importance due to their underlying properties and prospective applications in the energy storage research fields. There are different kinds of carbon nanotubes which have been successfully used in batteries, supercapacitors, fuel cells and other energy storage systems. This chapter focuses on the role of CNTs in the different energy storage and conversion systems and impact of their structure and morphology on the electrochemical performances and storage mechanisms.

Keywords: carbon nanotube, energy storage, nanocomposite, batteries, fuel cells, supercapacitor

1. Introduction

Carbon is one of the most important elements on earth and it plays a crucial role in living organisms and modern technological world either as complex compounds or in its elemental form. Carbon has several allotropes (e.g. graphite, diamond, lonsdaleite, Buckyball and amorphous carbon etc.) and different morphological textures (nanotube, nanowire and graphene). Specific applications in devices and other uses are highly specific to the textures and nature of the allotrope of desired properties. Notably, ever since graphite and diamond were discovered for the first time in 1779, their innovative applications have been growing until the present. Leveraging the benefits of these carbon morphologies, the journey towards innovation and discovery has continued to advance at a steady pace and almost two centuries later, Sumio Iijima discovered for the first time the existence of multi-walled carbon nanotubes (MWCNTs) and in 1992 he observed single-walled CNTs (SWCNTs) [1]. The synthesis and characterization of CNTs is beyond the scope of this chapter. It should be noted that graphite and CNTs have some characteristic properties and features, that enable them to be used in the energy storage and conversion systems. It is worth mentioning that the carbon nanotubes (CNTs), have

been envisioned to potentially impact different areas of science and technology due to their unique properties and structural features [2–4]. Specifically, CNTs have very high tensile strength of 60 GPa and high electronic conductivity reported to be 10^8 Scm^{-1} and 10^7 Scm^{-1} for single-walled and multi-walled carbon nanotubes, respectively [5, 6]. Besides the potential practical applications in chemical and bio sensors [7, 8], field emission materials [9], catalyst [10], electronic devices [11], CNTs have been used in energy storage and conversion systems like, alkali metal ion batteries [12], fuel cells [13], nano-electronic devices [14] supercapacitors [15], and hydrogen storage devices [16]. The extraordinarily high electronic conductivity of CNTs enable CNT and graphite as an additive to composite electrodes and facilitate activation of poorly conducting electrode materials making them electrochemically active. In this chapter, we emphasize the applications of CNTs in four different areas: alkali metal ion (Li, Na and K) batteries, alkali metal air batteries, supercapacitors, and fuel cells. The underlying governing structural features and morphological impact on the electrochemical performances have been discussed and the specific storage mechanisms are also highlighted.

2. Structure and properties of carbon nanotubes

Carbon nanotubes can be either as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). Simply a wrapped graphene sheet with a hollow fiber is the single-walled CNT. On the other hand, a combination and collection of SWCNTs is the multi-walled CNTs. It should be noted that carbon nanotubes are designated as one-dimensional (1D) structures because of the long length-to-diameter ratio (aspect ratio) [17]. The electronic properties of CNTs are associated with the geometrical structure of them which is uniquely specified by a pair of indexes called chiral indexes (n, m). There are three typical types of CNTs can be obtained: armchair (n, n), zigzag ($n, 0$), and chiral (n, m), depending on the orientation of the graphene lattice with respect to the tube axis they are twisted [18–20]. The formation of a single-walled CNT is shown in **Figure 1** by rolling a single graphene sheet in different directions. It is worth to mention that the rolling introduces strain into the carbon bonds oriented circumferentially while the single graphene sheet is made into a tube. This strain will be greater for smaller diameters; therefore, the armchair will be more strained than zigzag single-walled CNTs [21].

Properties of CNTs: Importantly, the local electronic character of carbon nanotubes is highly dependent on the carbon framework arrangements either zigzag or armchair. Also, there is a long-range defect which is formed by displacement or disorientation of standard nanocarbon structures, including hybridization of carbons, vacancies creation, and bond rotations (*Stone – Wales*). These imperfections are responsible for the chemical, mechanical and optoelectronic properties of CNTs. Noting that this imperfection can modify the electronic properties of CNTs by creating Fermi levels variation and the resulted charge diffusion processes can be affected [22, 23].

The resistivity of CNTs resulted from the electrical conductivity is determined by their carbon framework (graphite) and the one-dimensional character which is regulated by the quantum mechanical properties. The resistance of CNTs is independent of the length of the tube and act as a good conductor in which the highest current density can be as high as 10^9 A cm^{-2} . This important property of CNTs may improve the rate capability of electrochemical devices like batteries and capacitors. The helicity and diameter of CNT determines either it would be metallic or semiconducting in nature [24]. It should be mentioned that the strong C=C double

bonds in the carbon nanotubes makes them having high Young’s modulus in its axial direction and highest tensile strength. Of course, the presence of imperfection/defects in the tube wall reduces the Young’s modulus and tensile strength remarkably. However, reported experimental data are significantly smaller than the theoretical predictions which is most probably resulted from the high flexibility and aspect ratio [25, 26]. At room temperature the thermal conductivities of individual SWCNTs is reported up to 6600 W/(m K) which is almost double than the pure diamond [27]. Besides these, the CNTs have many others useful properties such as electro-optic effect, saturable absorption and *Kerr effect* etc. [28, 29].

The favorable and beneficial electrical, mechanical and thermal properties of carbon nanotubes are promising for various electrochemical applications like batteries, supercapacitors, fuel cells and hydrogen storage. Some important properties of SWCNTs and MWCNTs are listed in **Table 1**.

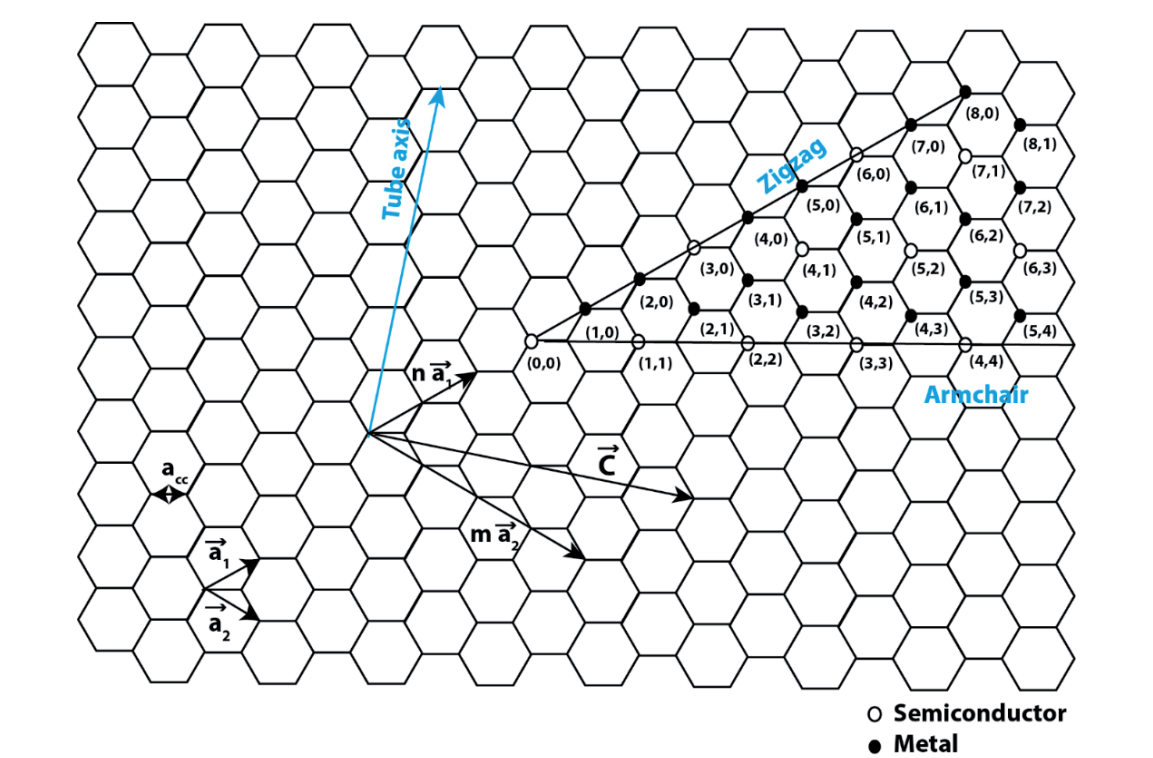


Figure 1. Lattice, two off-set triangular sublattices of graphene and graphene sheet rolling vector map. Reproduced from Ref. [21] with permission from the Royal Society of Chemistry.

Property	SWCNT	MWCNT
Specific gravity	0.8 g cm ⁻³	<1.8 g cm ⁻³
Elastic modulus	~1.4 TPa	~0.3–1 TPa
Resistivity	5–50 μΩ cm	5–50 μΩ cm
Thermal conductivity	3000 W m ⁻¹ K ⁻¹	3000 W m ⁻¹ K ⁻¹
Magnetic susceptibility	22 × 106 EMU g ⁻¹	22 × 106 EMU g ⁻¹
Thermal expansion	Negligible	Negligible
Thermal stability	600–800°C (air) 2800°C (vacuum)	600–800°C (air) 2800°C (vacuum)
Strength	50–500 GPa	10–60 GPa

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Table 1. Properties of single walled and multi walled nanotubes.

The values of Young's modulus and tensile strength of CNTs are around 1.2 TPa and 160 GPa, respectively. These unique mechanical properties make CNTs one of the toughest materials and play a vital role in protecting electrode integrity during the charge–discharge cycle of alkali-metal ion batteries. Furthermore, CNT based paper can be used as active material and current collector in supercapacitors, which can reduce the contact resistance as well as electrode weight. The thermal stability of CNTs is also an important property, which can help the composite electrode for stable battery operation at high current rates. SWCNTs and DWCNTs are showing a positive thermal expansion coefficient of $1.9 \times 10^{-5} \text{ K}^{-1}$ and $2.1 \times 10^{-5} \text{ K}^{-1}$, respectively, at room temperature. This negligible thermal expansion coefficient makes CNTs feasible for high energy density battery applications.

3. Storage mechanism of carbon nanotubes in electrochemical applications

CNTs have showed high performance as anode materials and cathode additive for alkali metal ion batteries because of their favorable properties (electrical, mechanical, and structural). The battery electrode based on CNTs attracted attention of many research groups around the world. Recently different modifications in the CNTs have been made for the deployment as a promising electrode material regarding alkali metal ion intercalation, adsorption, and diffusion [31]. In Lithium ion Batteries (LIBs), it has been well established that Li^+ ions are stored via two mechanisms, one is intercalation and other one is alloying [32]. The lithium ion storage mechanism in CNTs have been investigated by many research groups. First, let us go into detail about intercalation mechanism in pure carbon nanotubes. Because of different morphologies, the amount of Li^+ ion insertion is not limited to LiC_6 . The capacities (Li ion storage capacity) is highly dependent to the CNT morphology, especially defects and diameter of the carbon nanotubes [33].

Defects (n-rings) can be occurred naturally or introduced by treatment (nitric acid treatment or ball milling) as shown **Figure 2**. The theoretical studies (DFT total-energy calculations using local-density approximation (LDA) and the

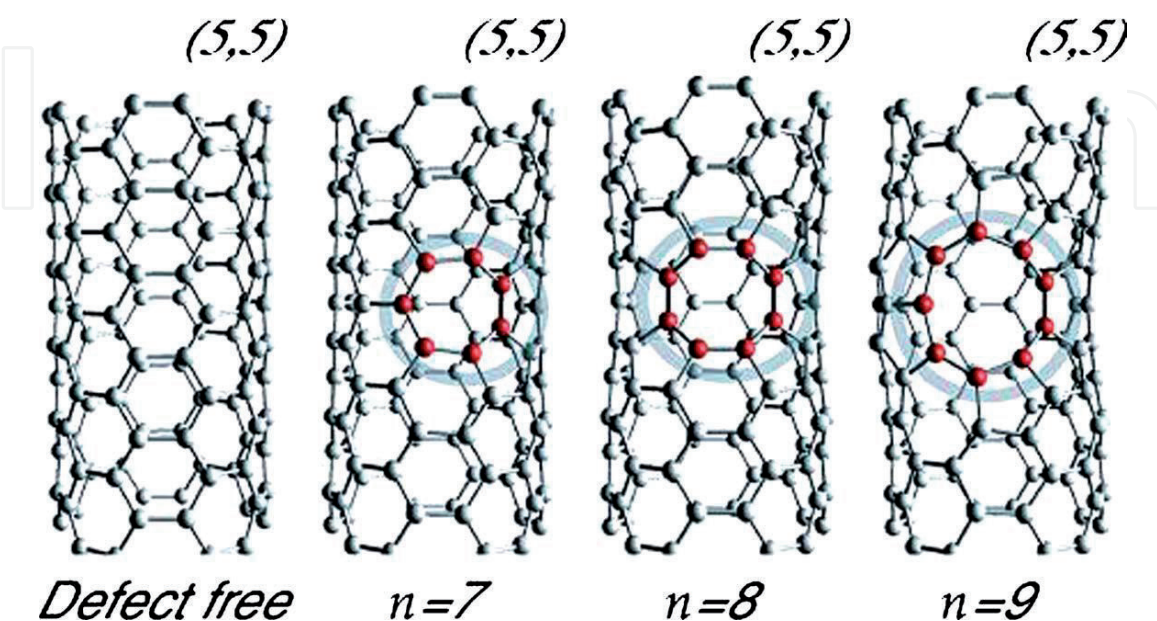


Figure 2. Types of defects (rings of the red dots) in a (5,5) SWCNT. Reproduced from Ref. [34] with permission from the American Physical Society.

generalized-gradient approximation (GGA)) were employed to investigate the detailed energetics of lithium ion adsorption on the defective single-wall carbon nanotubes [34]. It turned out that the presence of the holes on CNTs wall increase their capacity which is most likely favorable diffusion of lithium ion into the inside of the carbon nanotubes and reduces the diffusion path length [35, 36].

Another important note is that Li^+ ion can also penetrate the CNTs from its ends. Meunier *et al.*, adopted *ab initio* simulations for investigating the lithium ion migration through the ends of open-ended carbon nanotubes [37]. It is obvious that the CNTs should be short in size to allow Li^+ ions to freely intercalate/de-intercalate. The theoretical studies indicated that the capacity difference between opened and closed carbon nanotubes was almost 120 mAh g^{-1} [38]. It is also reported that the reversible Li storage capacity increased from LiC_6 in closed ended tubes to LiC_3 after etching which might be due to the short and highly defective CNTs generation [33]. Once Li^+ ion entered CNT either from the end of tube or through defects, it undergoes one 1D random walk in the tube. Provided that if the tube is very large the Li^+ ion will be able enter, however, it will be difficult to exit or never exit. It is indirectly proved by Wang *et al.*, showing that capacity of a short (300 nm) CNTs is much higher than the longer CNTs (micro-meter) [39]. On the other hand, Yang *et al.*, investigated the impact of length on electrochemical properties of CNTs. It was observed that the small size CNTs exhibit relatively less charge-transfer resistance than longer CNTs. It is not clearly explained why the lithium ion diffusion coefficients (D_{Li}) of both the long and short CNTs reduces as the intercalation is on progress and voltage drops. It might be due to repulsive interactive as lithium concentration increases in the tube. However, in short CNTs the difference between initial and final value of diffusion was smaller than longer CNTs. Therefore, the investigation indicates that shorter the CNTs length better will be the electrochemical performances [36]. In addition, Wang *et al.*, developed solid state cutting method to prepare the short CNTs from micro-meter long CNTs using Nickel Oxide (NiO)

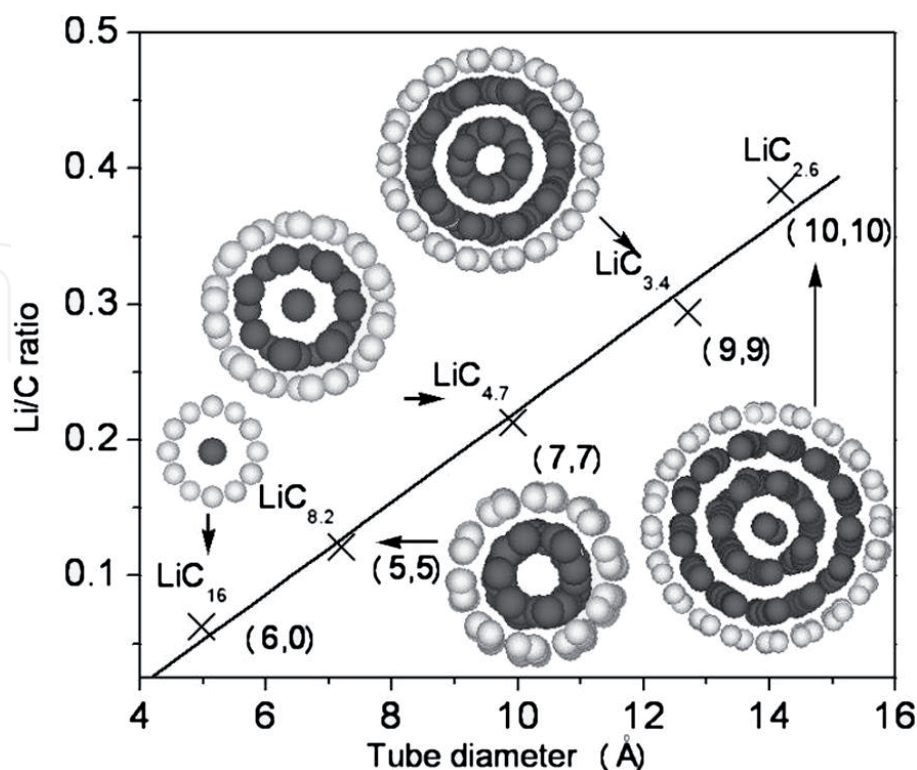


Figure 3.
 The variation of Li/C ratio as a function of tube diameter [White and grey balls represent C and Li atoms].
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particle as a cutter at 900°C. They successfully obtained short CNTs around 200 nm in length and the measured electrochemical reversible capacities increases as the length of CNT is decreases [40]. The same research group used Iron (II) sulfide (FeS) as a catalyst to produce the short CNTs as well as directly grown short CNTs with length of 200–500 nm. They are able to show that the long CNTs exhibited 188 mAh g⁻¹ while short CNTs 502 mAh g⁻¹ capacity [39].

Furthermore, there is significant relationship between the ratio of lithium-carbon (Li/C) and the diameter of tube. If the tube diameter is bigger, the intercalated lithium atoms gravitated to form multi-shell structural feature when the system is at the equilibrium state (**Figure 3**). These structures with a linear chain in the axis will improve the lithium capacity. It was also reported that the interaction potential at the central region is varied with the diameter of the nanotubes and diameter of 4.68 Å has higher interaction energy, that made CNTs better candidate for lithium ion battery anode material [41, 42].

Another important factor for lithium storage in CNTs is conducting nature of CNTs. There are two different types of CNTs, as mention above, one is semi-conducting another one is metallic CNTs based on their chirality. The experimental measurements and modeling studies indicated that if the chiral vector is a multiple of 3, the CNT behaves like metallic; otherwise it would be semiconducting. The metallic CNTs is able to store approximately 5 times more lithium ions than semi-conducting CNTs [43].

4. Electrochemical applications

4.1 Carbon nanotubes and their composites for alkali metal ion batteries (Li, Na and K) and other batteries

As it is discussed above, the one-dimensional carbon nanotube can be obtained as single-walled carbon nanotubes and multiwalled carbon nanotubes. Last 20 years, applications of CNTs are emerging in energy storage research on carbon structures and nano composite materials because of their excellent electrochemical properties including lower density, higher tensile strength, and higher rigidity [44].

Li-Ion Batteries (LIBs): Both single walled and multi walled carbon nanotubes are highly investigated in lithium ion battery either as an anode material or as a conductive additive in the composite electrodes. It is worth mentioning here that the one-dimensional CNTs enable to store higher amount of lithium than the conventional graphitic carbon (specific capacity of 372 mAh g⁻¹). The CNTs exhibits reversible capacities range between 300 and 1250 mAh g⁻¹, depending on structure and morphology and defect concentration [44–47]. The SWCNTs show first discharge capacity around 2500 mAh g⁻¹ with a voltage plateau between 1 and 2 V vs. Li/Li⁺. However, after first charge–discharge cycle the voltage profile varies based on the quality of CNTs and their pre-treatment [48]. Yang *et al.*, prepared unetched SWCNTs by co-pyrolysis method and the measured capacity was 170 mAh g⁻¹ and 266 mAh g⁻¹ for differently treated two samples [36] although the theoretical studies indicates that the reversible capacities should be more than 1116 mAh g⁻¹ (LiC₂ stoichiometry) as it is possible for single walled CNTs [49].

Along with SWCNTs, researchers successfully demonstrated the lithium ion intercalation into MWCNTs [50] (**Figure 4**). It is interesting to note that the specific capacities around 8500 mAh g⁻¹ was reported for multi-walled CNTs at slow current rate (0.1 mA cm⁻²). On the Contrary, however, most of the carbon nanotubes show capacities typically less than 4000 mAh g⁻¹ [44]. A comparative study has been carried out on highly conductive, binder-free, free-standing flexible films

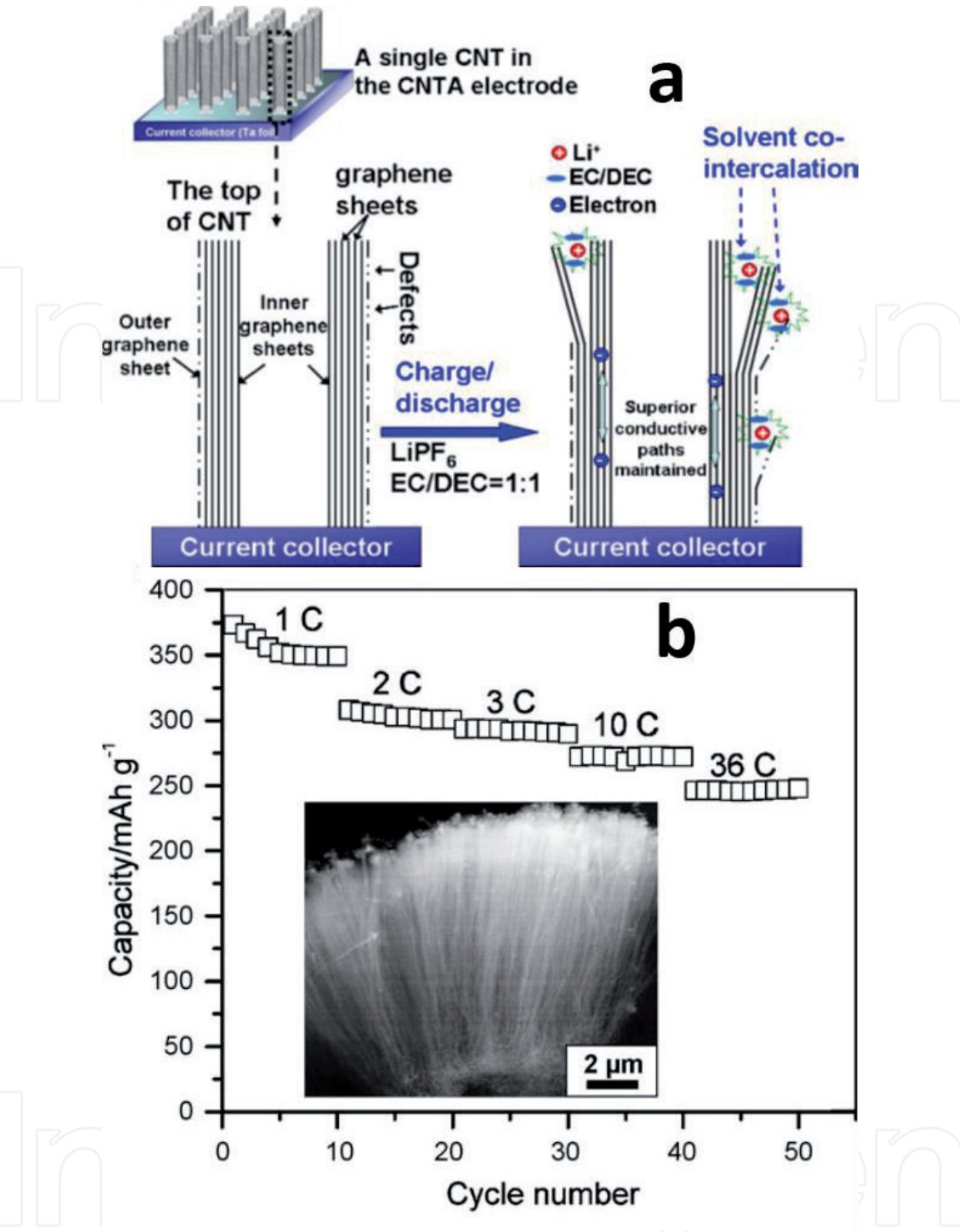


Figure 4.
(a) Schematic representation of the microstructure of nanotube array and energy storage mechanism and (b) cycle performance of carbon nanotube array (CNTA) electrodes. Reproduced from Ref. [50] with permission from Elsevier.

made from three different types of carbon nanotubes (SWCNTs, DWCNTs and MWCNTs). They were able to show that the free standing MWCNT film was retain its capacity after hundreds cycles, which is better than other CNTs films [51]. Lahiri *et al.*, prepared directly deposited MWCNTs on cooper current collector by chemical vapor deposition (CVD). It exhibits better specific capacity, at high current rate of 3C and good cyclic stability over 50 cycles [52].

Charan *et al.*, prepared aligned multiwalled carbon nanotubes (MWNTs) on stainless-steel foil and obtained high stable specific capacity of 460 mAh g^{-1} for 1200 cycles at 1C rate [53]. Li *et al.*, synthesized stacked multiwall carbon

nanotubes (MWCNTs) by floating catalyst chemical vapor deposition (FC-CVD) method and observed a stable discharge capacity of 310 mAh g^{-1} at 0.5 C rate for 300 cycles [54]. Brian *et al.*, obtained highest capacity for SWCNT electrodes with using 1 M LiPF_6 in Ethylene carbonate: Propylene carbonate: Dimethyl carbonate (EC:PC:DMC) as the electrolyte and capacity retention is more than 95% after 10 cycles [55]. Researchers have using different surface functionalization and doping (N, B) processes for getting efficient Li ion storage in CNTs [56] and highly concentrated N doped CNTs was developed and presented reversible capacity of 494 mAh g^{-1} which is almost double conventional CNTs capacity [57]. On the other hand, when flexible and free-standing pyridin-B-CNTs film was prepared using one-step floating catalyst chemical vapor deposition method, it delivers high specific capacity with excellent cycle stability of 548 mAh g^{-1} after 300 cycles at 0.1 A g^{-1} [56].

Up to now discussion was concentrated on the raw CNTs utilization in lithium ion battery as an anode material. Hereafter the discussion will be focused on the collective data for hybrid nanocomposites by incorporating CNTs into Li-storage compounds as new electrode (anode & cathode) materials. In this composite electrode, significance of π -orbital overlap in metallic type CNTs where electrons can transfer with mean free paths along the length of the nanotube (ballistic transport). So, when it is used as an additive, it will increase rate performance, especially combined with the poor electronic conductive cathode materials. Furthermore, CNTs have the mechanical and electrical properties along with a large surface area which is beneficial for lithium ion battery composite electrode [48]. The CNT was employed in silicon based anode consisting of silicon nanowire/graphene sheet (SiNW@G) which was intertwined architectures [58] where CNT can act either as conductive additive or active component depending on the operation voltage of the cell. The molybdenum dioxide was embedded with multiwalled carbon nanotubes ($\text{MoO}_2/\text{MWCNT}$) by hydrothermal process where hybrid composite consists of spherical flowerlike MoO_2 nanostructures interconnected by MWCNTs and exhibits reversible lithium storage capacity of 1143 mAh g^{-1} at a current density of 100 mA g^{-1} . The zinc oxide was covered by N-doped carbon freestanding membrane electrodes for lithium ion batteries and the hybrid material shows the high performance with a specific capacity (850 mAh g^{-1} at a current density of 100 mA g^{-1}) and excellent cycling stability [59]. The polymer-derived silicon oxy-carbide/carbon nanotube (SiOC/CNT) composites exhibit stable lithium anode material [60].

The application of carbon nanotubes as an additive for anode or cathode has huge advantages compared to other carbon form like amorphous carbon, acetylene black etc.. As discussed above the CNTs have a high electrical conductivity at room temperature and very small amount ($0.2\% \text{ w/w}$) of CNTs will be able to create a percolation network for electronic conductivity [61] and therefore, could increase orders of magnitude in electrical conductivity of composite electrodes and form better percolation network. CNTs have been employed as an conducting additive for LiCoO_2 , $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, LiFePO_4 , LiMnPO_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes; showing better in the reversible capacity of the composite electrodes compared to other carbon polymorphs [62–65].

Lithium Sulfur Batteries (Li-SBs): After LIBs, Lithium sulfur batteries are drawing much attention due to the high energy density of lithium-sulfur (Li-S) batteries (2600 Wh kg^{-1}) and is natural abundance of sulfur. Beside the potential advantages, the major challenge is the electronically insulation behavior of sulfur. In addition, during the cycling processes, the polysulfides are formed which are soluble, and discharge intermediate and products migrate towards Li anode. This impacts the columbic efficiency, accelerates battery self-discharge and cycle life. Several research groups are using CNTs for sulfur encapsulation to overcome above

mentioned problems [66]. The sulfur is incorporated carbon nanotubes, nano pores and/or in between nano wires for Li-S battery cathode. The electrode delivers discharge capacity of 669 mAh g^{-1} after 300 cycles with a low capacity fading rate of 0.166% per cycle at 0.1 C rate [67]. Sometimes functional groups were grafted on the modified multi-walled carbon nanotubes which can adsorb the dissolved polysulfides and enhance the redox reaction of lithium polysulfides and in parallel provides the electronic conduction pathway.

Sodium Ion Batteries (SIBs): Off significance, CNTs cannot be used as anode for Na ion batteries, like LIBs, because of large radius of Na ion (1.02 \AA) which cannot be intercalated comfortably into the layer structure. The Na ion intercalation into graphite is thermodynamically unstable and it cannot form primary stage structures of NaC_6 or NaC_8 . The Pure graphite can deliver a maximum capacity of $\sim 31 \text{ mAh g}^{-1}$ by forming NaC_{70} [68]. The defect-rich and disordered carbon nanotube structures have been synthesized for enhance the sodium storage as an anode for SIBs, which exhibits reversible capacities over 130 mAh g^{-1} . Very recently, Han et al., prepared high defective and disorder mesoporous carbon nanotubes by ethanol flame method. The electrode displays a remarkable rate capability of 145 mAh g^{-1} at 1 A g^{-1} , with excellent cyclability [69]. Another approach to obtain defective CNTs is doping of heteroatoms, such as nitrogen, which can also enhance the electrical conductivity of carbon nanotubes [70].

CNTs have been using as an additive for lower electronic conductive electrode materials in SIBs. It was reported that porous FePO_4 nanoparticles were electrically connected by single-wall carbon nanotubes synthesized by hydrothermal reaction. The fabricated composite electrode shows discharge capacity of 120 mAh g^{-1} at a 0.1 C rate with unprecedented cycling stability [71]. The CNTs have been using as a promising additive for polyhedral cathode materials like $\text{NaTi}_2(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, $\text{Na}_2\text{FePO}_4\text{F}$, NaVPO_4F , $\text{Na}_4\text{VMn}(\text{PO}_4)_3$, $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$, $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}(\text{SO}_4)_2$, $\text{Na}_2\text{MnSiO}_4$, $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$, $\text{Na}_4\text{Co}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$, Prussian blue analogues ...etc. [72]. Our group published the impact of MWCNT on particle growth as well as electrochemical properties of $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$ cathode. Among three carbon sources (Carbon, MWCNT & rGO), MWCNT is more effective to obtain moderate particle size with enhanced electrochemical properties (**Figure 5**). The prepared $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$ -MWCNT composite delivers the stable capacity of 98 and 89 mAh g^{-1} in half cell and full cell with $\text{NaTi}_2(\text{PO}_4)_3$ -MWCNT configurations, respectively [73]. It should be noted that most of the alloying and conversion anode materials lose their electron conducting path due to the pulverization during charge-discharge cycles. In this case, CNT can be used as conductive additive as well as electrode integrity protector. The battery research community has been encapsulated metal based (e.g. Sn) anode with the CNTs to accommodate the volume expansion during Na insertion to avoid the pulverization. The reported results indicate that the carbon encapsulated, Sn@N-doped, nanotubes is beneficial to get good reversible capacity of 398 mAh g^{-1} at 100 mA g^{-1} , with capacity retention of 67% over 150 cycles [74, 75]. The ultrathin MoS_2 nanosheets was developed on the surfaces of CNTs by a hydrothermal method MoS_2/CNTs , which exhibit excellent electrochemical performance as conversion anode materials for SIBs. The MoS_2/CNTs , shows a reversible capacity of 504 mAh g^{-1} at a current rate of 50 mA g^{-1} over 100 cycles [76]. Many alloying and conversion anode materials have used CNTs as conductive additive, examples TiO_2 , MoS_2 , CuS , Fe_2O_3 , & FeO .

Potassium Ion Batteries (PIBs): Unlike sodium, potassium ion can be intercalated into graphite structure without requiring a special electrolyte solvent for K-ion batteries (PIBs). It was reported that theoretical capacity of K battery is 279 mAh g^{-1} (KC_8) by stepwise potassiation through KC_{36} and KC_{24} phases based on

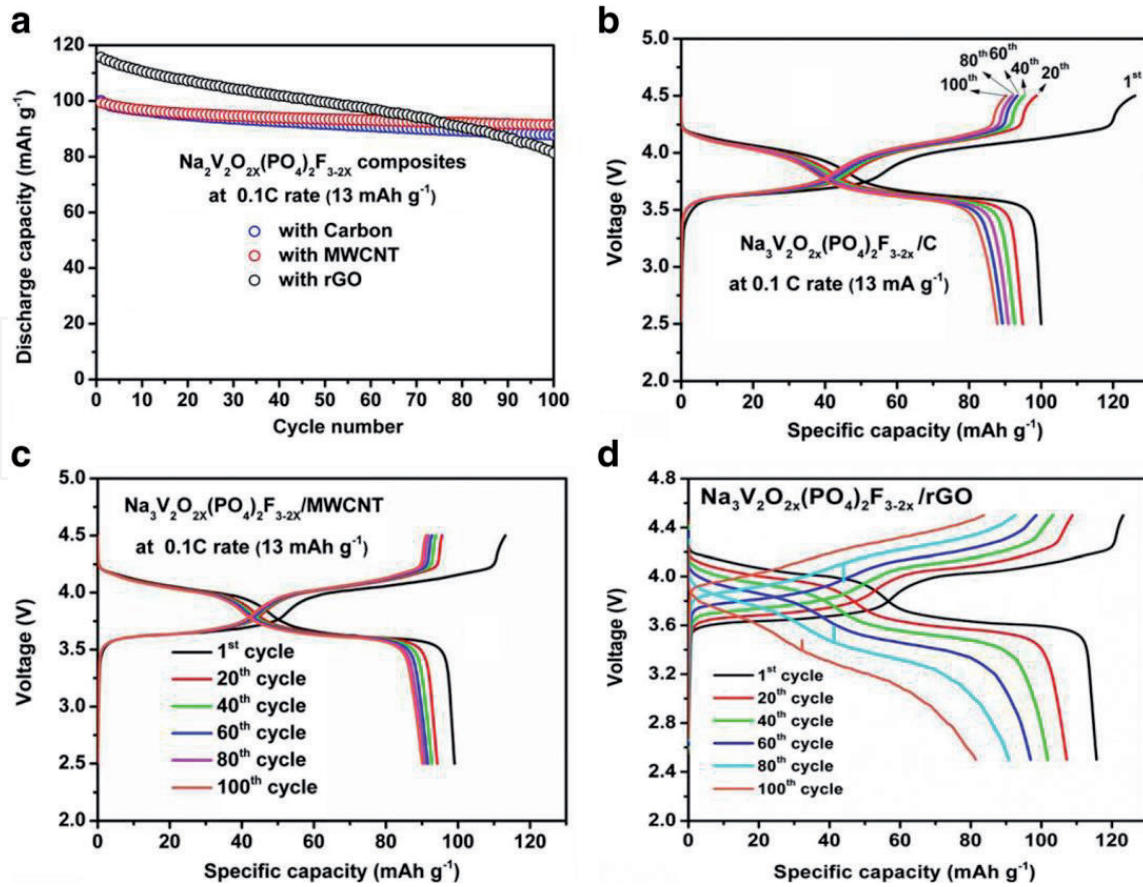


Figure 5.

(a) Cyclability of $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$ along with three different carbon materials. Charge-discharge curves for the $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$ with (b) carbon, (c) MWCNT, and (d) rGO. Reproduced from Ref. [73] with permission from Springer Nature.

intercalation/deintercalation mechanism [77]. Noting that the insertion potential of K^+ into the graphite structure is little higher than that of Li^+ , which could make more secure battery systems. However, the biggest obstacle is the poor cycle stability of graphite as the anode for PIBs. Battery community have been trying to improve the performances of PIBs and fulfill the requirements of commercialization [78]. Liu *et al.*, prepared N-doped bamboo-like carbon nanotubes by simple pyrolysis method and the unique structured material shows a high reversible capacities of 204 mAh g^{-1} and 186 mAh g^{-1} at 500 mA g^{-1} and 1000 mA g^{-1} , respectively [79]. The science behind the better performance is not well understood yet.

The analysis of electron density difference demonstrates the interaction between the K ion and the nitrogen doped CNTs which has strong ionic bonding, and the electron re-distributions between N5 & N6 CNTs. It is shown, in the K ion –N5 CNT systems (**Figure 6A**), the net gain of electronic charge on the pyrrolic N atom plays more significant role than those of the other two pyridinic N atoms. The N6 CNT (**Figure 6B**), the alkali metal atom associates strongly with two pyridinic N atoms, therefore, the overlapping of the corresponding peaks in **Figure 6** (bottom) is seen. The bonding with the third pyridinic N atom is relatively weaker [80]. The theoretical studies predicted that inner carbon of CNT is dense while outer carbon of CNT is loosely bind. The hierarchical carbon nanotubes structures in the inner dense part act as skeleton while the outer loose-CNT effectively accommodates the K-ion accommodation, which are showing a better specific capacity of 232 mAh g^{-1} and good cyclic stability [81]. Like other electrode systems these carbon nanotubes are expected to act as a conducting additive assuring the electrical percolation in the composite electrode and to protect the integrity of electrode using their mechanical properties [82, 83].

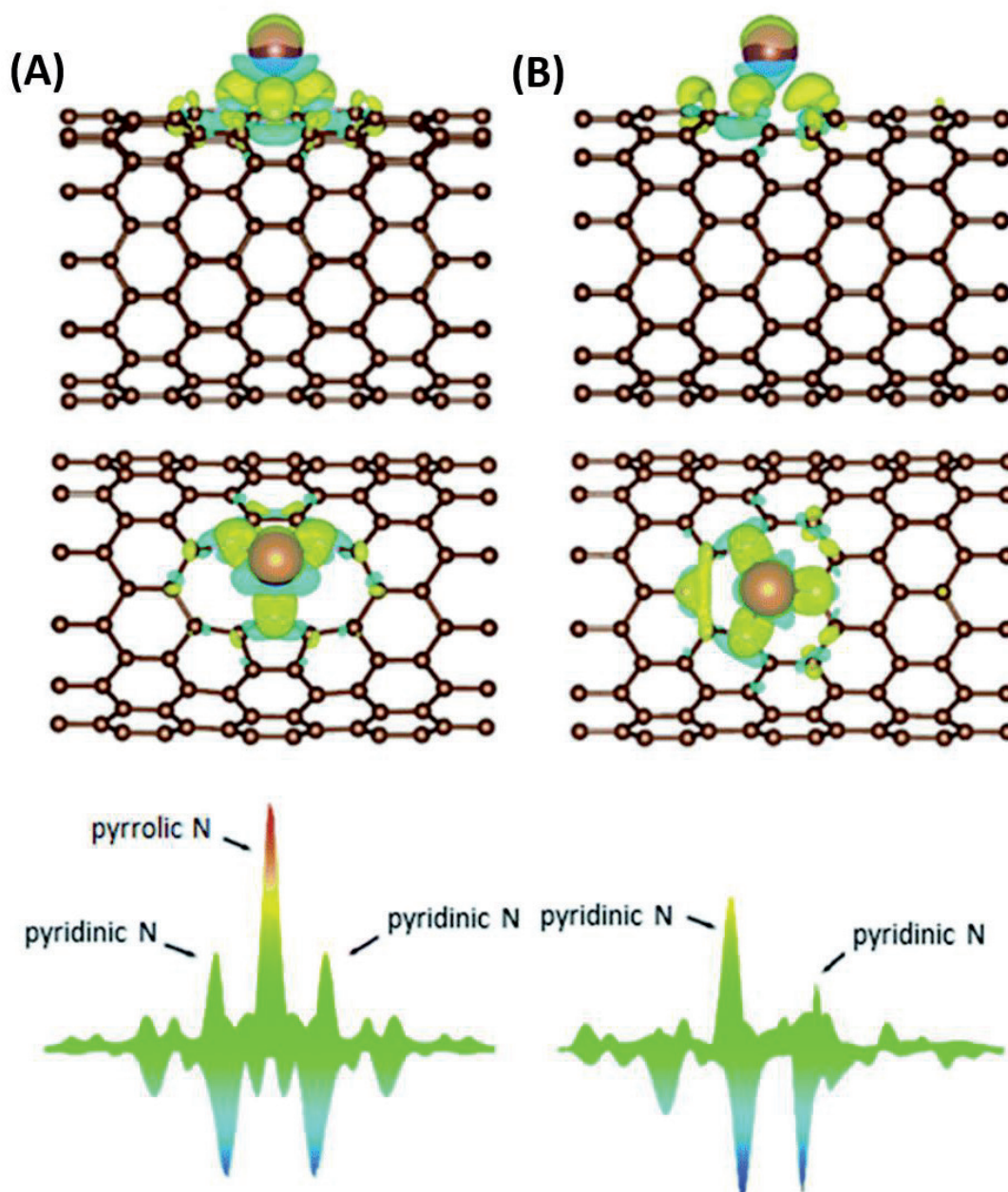


Figure 6. Differential electron densities (A) K-ion on N5 CNT, (B) K-ion on N6 CNT: top, side view; middle, top view; bottom, electron density differences in the plane. Reproduced from Ref. [80] with permission from the Royal Society of Chemistry.

Lead acid batteries: Lead acid battery is one of the most popular electrochemical storage systems for the last 150-years, however, it has been suffering from poor lifecycle. The limited lifecycle is most probably originated due to the formation of large non-conducting uncontrolled lead sulfate (PbSO_4) crystals both the positive and negative plates. The deposition of insulating PbSO_4 crystals lower the electrical conductivity and accessibility of electrolytes to active material in both plates [84, 85]. Various research groups studies different amorphous carbons as a sulfation-suppressing additive in negative plates, because the sulfation is more prominent in negative plate than positive plate due to slower kinetic reaction. Recently, Prof. Aurbach and his group used SWCNTs as a suppresser of uncontrolled sulfation processes in lead-acid battery electrodes. The carbon nanotubes additive would be uniformly distributed throughout the composite electrode and capable of boosting charge acceptance at low concentrations [86, 87].

4.2 Metal-air batteries

Lithium-Air Batteries (LABs): Recently battery community focused on the metal-air battery due to higher theoretical density. It is just an alternative to LIBs. The most popular and promising metal-air batteries are lithium-air and zinc-air batteries. The energy density of rechargeable lithium-air batteries very high energy ($\sim 1700 \text{ Wh kg}^{-1}$) comparable to gasoline and much higher than secondary Li-ion batteries ($\sim 160 \text{ Wh kg}^{-1}$). The reaction mechanism of lithium air battery is appeared to be very simple, at discharge state oxygen in air reduced by lithium ions to form lithium peroxides via $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2$ and/or $4\text{Li}^+ + 4\text{e}^- + \text{O}_2 \rightleftharpoons 2\text{Li}_2\text{O}$, and formation of lithium and oxygen from decomposition of lithium oxides during charge processes. The thermodynamic equilibrium cell voltage for the discharge reaction in LABs is 2.96 V vs. Li/Li⁺ [88]. In practical realization, the reported cell voltage is less than 2.96 V which is due to the cell polarization resulted from the oxygen reduction and evolution reaction during discharge and charge processes. However, breaking the discharge products during the charge processes, it requires much more than 2.96 V to drive the reverse electrochemical reaction. Either pure catalyst or carbon-supported catalyst particles have been used to accelerate the electrode reactions [89]. It should be mentioned that most of the time CNTs have been used as conductive supporting materials for metal and metal oxide catalyst particles in the metal-air batteries. The functionalized CNTs can also be used as air electrodes. It was reported that the flexible multiwalled carbon nanotube exhibited very high specific capacity of $34,600 \text{ mAh g}^{-1}$ at a current density of 500 mA g^{-1} in the Li-O₂ batteries [90]. It is indicated that CNTs have huge prospectuses as in the Li-air battery cathode component.

Zn-Air batteries (ZAB): Zinc-air batteries are very safe for electrical vehicles which is fabricated by non-flammable and non-explosive materials. They can be used for other safe applications. As mentioned above, the electrocatalysts is required in air electrode to efficiently accelerate the kinetics of the oxygen reactions [91] and increases the battery performances and efficiencies. It is demonstrated that the nitrogen-doped carbon nanotubes (N-CNTs) promoted notable ORR activity in acid and alkaline solutions. This is because of the inserted heterogeneous nitrogen which might activates the reaction sites and can induce in breaking the O-O bonds of O₂ molecules [92].

Another critical role of CNTs in batteries is the current collector. Present, flexible CNTs based carbon papers can be fabricated from all CNTs and used as anode and current collector for aqueous battery systems. Conventional current collectors, such as carbon cloth and metal foils (stainless steel, Titanium), are low surface area and highly corrosive in aqueous media. Also, these CNTs can be used as a pure binder in primary thermal battery electrode fabrication. The electrode with the CNTs binder has better thermal stability than conventional organic binders. The traditional organic binders were decomposed before reaching the operating temperature of 500°C, and its residual material can act as an insulator.

5. Fuel-cells (FCs)

The reaction mechanism in Li-air battery and fuel cells has great similarity where oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are important for fuel cells efficiency. To enhance the efficiency of the fuel cell, a catalyst is needed. Instead of using expensive Pt as a catalyst, researchers started using a supporter, which can improve the capability of low-cost catalyst. Commonly used catalysts supporters are porous carbon, carbon nanotubes, graphene, and

other carbon polymorphs. It was demonstrated, at higher current density, CNT supported FCs, exhibited better electrochemical performances than the carbon black supported FCs [93]. Doping with heteroatoms or loading of transition metal catalysts on CNTs substantially enhance the activity of highly efficient fuel cells. There are few reports on encapsulation of Ag, Fe, Co, CuSe (Figure 7) & Ni based compounds in pure CNTs, which are showing the high ORR performance in fuel cells [94]. It is also reported that the higher oxidation state of Ni is very active for OER and inactive to ORR. However, Ni encapsulated N doped CNTs are showing very high ORR activity and less OER active. Several studies are compared the performances of the platinum catalyst with non-noble metal catalysts with the CNT support and they exhibit better catalytic activity and it reduces the cost of whole cell. Furthermore, CNTs can make the fuel cell highly stable and high resistive against corrosion during electrochemical reaction [94, 95]. CNTs not only increase the catalytic activity; enhance the corrosion resistance. Besides, CNTs improve the mass transmission capability of both electrodes in a fuel cell.

5.1 Supercapacitors

The morphology of electrode materials and fabrication process plays an important role for the performance of a supercapacitor. The capacitance value of a supercapacitor is highly dependent on electrode surface-area and porosity. The basic principle of a capacitor is to store energy by separation of charge at the electrode and electrolyte interface (i.e., double layer capacitance). The ions transfer between the two electrodes is mediated by diffusion across the electrolyte [96]. Supercapacitors exhibits better reversibility, higher power density, and longer cycle life which made it attentive and promising for energy-storage devices. It is worth to mention that supercapacitors exhibit the highest known power capability ($2\text{--}5\text{ kW kg}^{-1}$), but they suffer from a moderate energy density ($3\text{--}6\text{ Wh kg}^{-1}$).

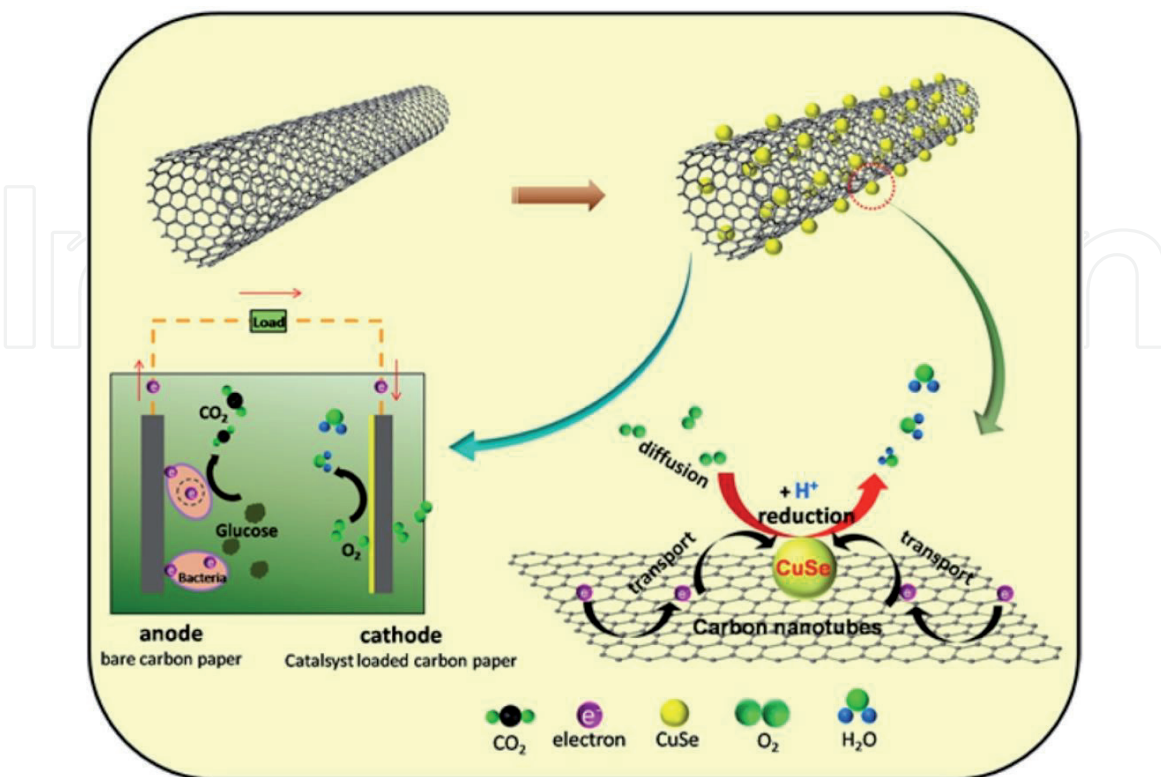


Figure 7. Carbon nanotubes decorated with copper selenide (CuSe) nanoparticles for microbial fuel cells. Reproduced from Ref. [94] with permission from Elsevier.

Carbon nanotubes (CNTs) are very promising as supercapacitor electrode materials because of their excellent electrical properties and one-dimensional nanostructures. Noting that defect free or less defect CNTs has smaller surface area and micropore content than conventional activated carbon (AC), which made them insufficient capacitance in CNT-based electrodes. However, it is reported that the formation of defects on surface and open ends by alkaline solution activation increases the surface area of CNTs [97] and exhibits better capacitance value. The SWCNTs show enhanced specific capacitance than those of MWCNTs which results from large surface area of SWCNTs. However, that MWCNTs could generate capacitance twice as high in comparison to SWCNTs which is attributed to the presence of mesopores and entangled tube structure, facilitating the transport of the ions [98]. The flexible aligned SWCNTs with high surface area and better electrical conductivity is beneficial for capacitors applications [99]. It should be mentioned that contact resistance reduces the performance of supercapacitor and therefore, polished metal foils is used as current collectors to grow the carbon nanotubes for lowering contact resistance. The better discharge efficiency can be obtained through the electrostatics and can result high power density [100]. The cell resistance can be lower either by fabricating carbon nanotubes as thin film electrodes which has coherent structures with highly concentrated colloidal suspension or fabricating CNT based thin film electrodes using an electrophoretic deposition (EPD) method. It is reported that these flexible CNTs films are binder free and forms network with negligible electrode resistance [101]. As we mentioned in above applications, N doped CNTs may contribute to improving the power characteristics of supercapacitors their own way. The doped nitrogen modifies the conduction band and the modified electronic structure which helps to enhance the quantum capacitance and electrical conductivity of CNTs [102]. Recently researchers have started the fabrication of a high-performance wire-type supercapacitor with CNTs to get the high voltage and high energy density (**Figure 8**). It should be noted that the carbon nanotube sheets were wrapped to make a fiber shaped supercapacitors on elastic polymeric fibers with moderate stretch ability [103, 104].

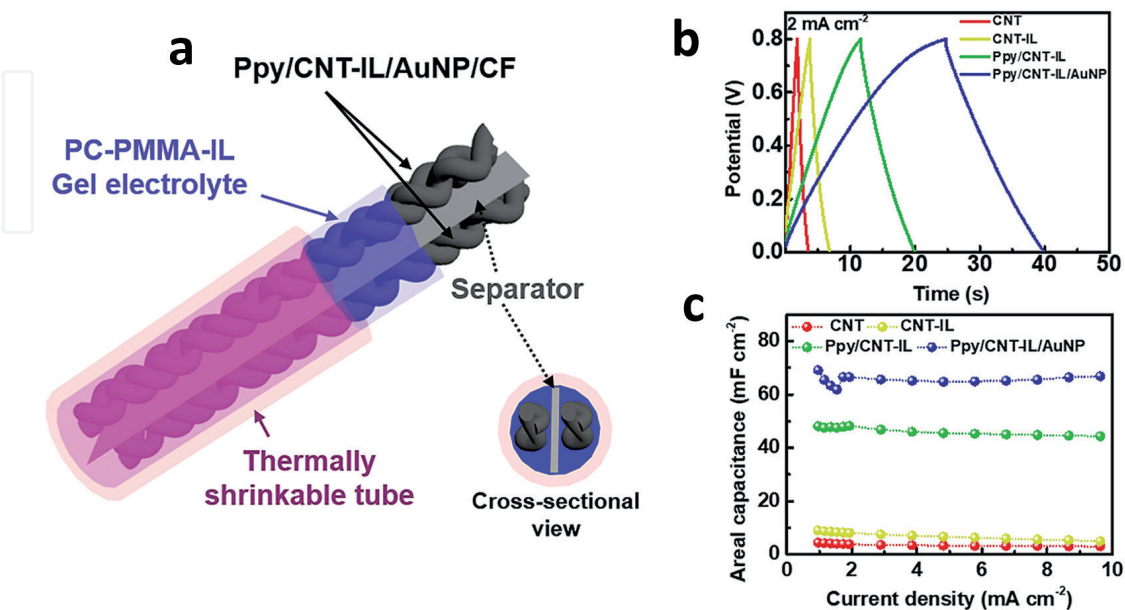


Figure 8.

(a) Schematic representation of the wire-type supercapacitor, (b) galvanostatic charge/discharge curves and (c) Comparison plots of areal capacitance versus current density for CF electrodes coated with CNT, CNT-IL, Ppy/CNT-Ionic Liquid, and Ppy/CNT-Ionic Liquid/AuNP. Reproduced from Ref. [104] with permission from Elsevier.

Graphitization and pore size distribution of CNT are also significant factors for supercapacitor application. While heating, the specific surface area increases, but the capacitance decreased due to the average pore diameter decreases and saturated at high temperature. Furthermore, chemically activated of CNTs also shows tubular morphology with defects on the surface that gave a significant increase in pore volume. Aligned CNTs can also significantly improve the capacitance and power density of supercapacitors. It is also reported that the highly packed and aligned CNTs showed higher capacitance and less capacitance drop when compared to other thick CNT based electrodes.

6. Conclusions

One-dimensional carbon nanotubes (CNTs) have been considered as potential candidates for the development of energy storage materials based on their unique chemical and physical properties. The architecture and quality of the CNTs plays a vital role on the electrochemical performances exhibited by both batteries and supercapacitors. It is observed that a slight modification (defects creation, hetero-atoms doping & controlling the distribution of pore sizes) in the CNT structure brings out complementary properties that translate to excellent electrochemical performances. Anchored and directly grown aligned structure of CNTs trends to have high stability and fast ion transportation. The composite electrode with incorporated CNTs is being benefited from the high surface area, excellent conductivity, enhanced specific capacity, better cyclability and rate capability. CNTs can be used as an electrochemically active and inactive electrode component in energy storage systems. It turns out that all types of CNTs can serve as flexible supporting materials and can also enable next generation flexible energy storage devices. The future of advanced energy storage systems (either batteries or supercapacitor) can certainly be benefited from the incorporation of CNTs. The extraordinarily high electronic conductivity also enables CNTs and graphite as an additive to the composite electrode and enable to activate poorly conducting electrode materials to make them electrochemically active. Moreover, the structures and morphologies of CNTs are beneficial for supercapacitors and as catalyst support for fuel cells.

Acknowledgements

This manuscript has been supported by Oak Ridge Nation Laboratory (ORNL) managed by UT-Battelle, LLC, under contract DE-AC05-00OR22725 with the US Department of Energy (DOE).

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