Carbon nanotubes' use in energy storage

Jaidev Dhavle
Maastricht Science Programme, Maastricht University, Maastricht, Netherlands
Email: j.dhavle@student.maastrichtuniversity.nl

Abstract – The global energy demands are increasing at a very rapid rate. These high energy demands are resulting in rapid consumption of scarce resources which can lead to major problems in the future. Thus, the development and use of ‘green’ resources must occur as soon as possible. In view of these circumstances researchers are continuously trying to find alternative energy sources to meet our energy demands. In this context, Carbon Nanotubes (CNT) has proved to be very useful in terms of storing renewable energy. This review paper focuses on the role and effect of CNT in popular energy storage devices and also includes information on the synthesis and properties of CNT.

Keywords – Carbon Nanotubes, Hydrogen Storage, Lithium Ion Batteries, Super-Capacitors and Photovoltaic Cells

1. Introduction

Energy demands are increasing at an alarming rate. This demand is reflected in the soaring prices of numerous resources, increasing scarcity of current resources for example fossil fuels. The current resources we are utilizing to fulfill our man-made demands are also not environmentally stable. Thus, it is imperative that we start developing and using renewable sources. One innovative approach which has encouraged and assisted us to commence the usage of renewable energy sources is the development of energy storage devices. Lithium ion batteries, Super-Capacitors, photovoltaic cells (PVC’s) etc. are some of the upcoming energy storage devices. These devices have been implemented in many technologies and have demonstrated considerable efficiency. However, these energy storage devices also have drawbacks which limit their applicative potential. Research has been taking place to improve the performance and applicative prospective of these devices while simultaneously reducing or eliminating the drawbacks that these energy storage devices may possess. Over the past 2 decades a novel material has been implemented in energy storage devices to achieve the aforementioned criteria; Carbon Nanotubes (CNT). Due to its unique composition, properties and modification flexibility, CNT’s have attracted many researchers to utilize it in energy storage devices. Hence in this review paper, my attempt is to explain the synthesis and properties of CNT’s as well as its capability to store various forms of energy and it utilization in related devices. To be more precise, I will be focusing on the use of CNT in electrochemical storage (Super-capacitors, Li-ion Batteries, PVC’s), hydrogen storage (Hydrogen Fuel Cells) and mechanical energy.

2. Carbon Nanotubes: Synthesis and Properties

Carbon is known to exist in 3 forms namely: amorphous carbon, graphite and diamond. The spatial arrangement of Carbon atoms determines it form and thus its properties, for e.g. Graphite is soft, black and the presence of covalent and Van Der Waals forces among carbon atoms. Diamond is hard, transparent and the carbon atoms are arranged in a diamond lattice. CNT’s at a molecular level can be visualized as a graphene sheet rolled up into a tube (at Nano-scale) to form Single Walled Carbon Nanotubes (SWNT). It is also possible to have additional graphene tubes surrounding the SWNT core to produce Multi-walled Carbon Nanotubes (MWNT) [1].

![Figure 1. Graphene rolled up to form SWNT/MWNT’s [1]](image)

2.1. Arc Discharge Synthesis of CNT’s

MWNT’s were discovered by Ijima and Ichihashi whereas, SWNT’s by Bethune et.al through the use of arc-discharge method (Fig.2). This method involves the use of 2 electrodes (graphite in case of CNT) in a chamber filled with an inert gas. The purpose of using an inert gas in this procedure is to prevent any side reaction from occurring. A direct current is then passed through system which causes carbon deposition on the negative electrode. CNT’s in the form of ropes are formed on the electrode. Ijima proposed a topological model for the open ended growth mechanism of these rope like structures in which pentagons and heptagons play an important roles in tube shape. The model proposed that carbons were captured by dangling bonds on the graphite electrode and layer-layer growth occurs which causes thickening of the nanotube. The nucleation of positive (pentagons) and negative (heptagons) disclinations on open-tube end causes changes in growth direction and morphologies of the tube. Bethune et.al synthesis of SWNT through this method involved similar setup as Ijima’s
however, they used thin anode electrode with bored holes filled with pure metal powder (Fe, Ni or Co) and graphite. The electrode were vaporized using a current of 95-105A in 100-500 Torr of He. The result of this procedure was SWNT with uniform diameters of 1.2±0.1nm. [2]

Figure 2. Simplified setup of arc-discharge method [2]

2.2. Laser Abolition Synthesis of CNT’s

In this method (Fig.3), a graphite rod with small amounts of Ni and Co are placed in a horizontal tube which is placed in a furnace set at 1200°C. A laser beam is fired at this rod and vaporizes it in the presence of an inert gas at controlled pressure. The nanotubes are deposited on a water cooled collector located outside the furnace. This method produces SWNT (70% yield) which are in the forms rope or bundle (5-20nm diameter). The SWNT have metallic nature. The growth of these nanotubes can be explained by the ‘scooter’ mechanism. The Ni or Co atom chemisorbs onto the open edge of the nanotube. The metal atom must have high electronegativity to prevent formation of fullerenes and should effectively catalyze nanotube growth. The metal atoms circulates (“scoots”) in the vicinity of the open end tube and adsorbs carbon molecules and arranges them into graphite like sheets. The tube will continue to grow until many catalyst atoms cluster at the end of the nanotube. To end the growth mechanism, the catalyst cluster will detach or be over-coated with carbon atom to stop the catalysis.

Figure 3. Simplified setup of laser abolition [2]

Both the arc discharge method and laser abolition method have high yields of CNT (>70%). However the drawbacks of these methods are: (1) they rely on evaporation of carbon atoms from solid targets at T>3000°C and (2) the nanotubes are tangled sometime which results in complex purification and limits applicative potential. [2]

2.3. Catalytic Growth of CNT’s

Carbon fibers have been produced by the thermal decomposition (a.k.a chemical vapor decomposition (CVD)) of hydrocarbons in the presence of a catalyst. The CVD process involves a catalyst decomposition of hydrocarbons in a tube reactor at 550-750°C and growth of the CNT after cooling the system. The best result can be achieved by using Fe, Ni or Co as catalysts embedded on the appropriate substrate(s). It yet to be determined whether the nanotubes grow out of the catalyst Nano-particles embedded in the pores by tip or base growth, which depends on contact force between catalyst particles and substrate. [2]

2.4. Properties of CNT’s

This section presents the mechanical, bending, toughness and thermal properties of CNT.

2.4.1. Mechanical Properties

CNT are expected to have high stiffness and axial strength due to the presence of carbon-carbon sp² bonding. To determine this magnitude of these properties, research have used to atomic force microscopy (AFM). Through use of the AFM, it has been determined that large displacements can lead to buckling, plastic deformation or fracture of the nanotube. Small displacements can deform the nanotube without any damage. [2]

2.4.2. Bending Properties

The bending strength can be defined as the force per unit area at the buckling point, this is because at this point, the stiffness drops substantially. The average bending strength for CNT’s are 14.2±8.0 GPa. [2]

2.4.3. Toughness of CNT

The parameter toughness can be defined as the elastic energy stored by the material before its failure. Researchers found that CNT’s of length 1µm buckle elastically at large deflection angles, ≈ 10°. In addition they estimated the strain energy stored by a 30nm diameter nanotube to be 300keV. The estimated strain energy of CNT is of greater magnitude than that of SiC rods. Hence, the ability of CNT’s to elastically sustain loads at great deflection angles allows them to store or absorb considerable energy. [2, 3]

2.4.4. Thermal Properties

In SWNT (and SWNT bundles), the specific heat and thermal conductivity is determined by phonons at all temperatures. The thermal conductivity can be determined by the product of the specific heat, (phonon group velocity)² and phonon relaxation time summed over the phonon states. The thermal conductivity of SWNT decreases as T decreases. Linear dependence of thermal conductivity on temperature is observed when T is below 30K. Researchers found that the specific heat of MWNT’s (10<T<300K) was revealed to be linearly dependent on the temperature over a given temperature interval. Thermal conductivity of MWNT measured from 4 to 300K was shown to vary and no maximum value was obtained due to Umklapp scattering. In addition researchers also found that that thermal conductivity of an individual MWNT was 3000W/mK at room temperature. This thermal conductivity was not observed in bulk MWNT. It was also discovered that as the diameter of individual MWNT increases the thermal conductivity is similar to that seen in bulk MWNT. [2]
3. Carbon Nanotubes: Energy Storage

The sections to follow will describe the use of CNT’s in Energy Storage devices. The energy storage devices that will be focused upon are Super- Capacitors, Lithium Ion Batteries, Hydrogen Storage Devices and Photovoltaic Cells (PVC).

4. Carbon Nanotubes: Super-Capacitors

A super-capacitor is a storage device that is between batteries and conventional capacitors in terms of energy density (Wh) and maximum power (W). It can be seen as two non-reactive porous plates or electrodes, immersed in an electrolyte and voltage potential applied across the collectors. A porous dielectric separator between the two electrodes prevent charge from moving between the two electrodes (Fig.4). There are two types of super-capacitors pseudo-capacitor (energy storage is done via Faradic charge transfer) and electric double-layer-capacitor (EDLC) which is non-Faradic. CNT’s can be used in super-capacitors because of their nm distribution size range, accessible surface area, low resistivity and high stability. [4]

![Figure 4. Components of a Super-capacitor](image)

4.1. Factors of CNT that impact capacitance

The electrostatic interactions in EDLC depends on the area of the electrode (CNT)/electrolyte interface which can be accessed by the charge carriers. The higher the surface area of the electrode leads to higher capacitance. Other factors that also determine capacitance are pore size, size distribution and conductivity. Thus, higher capacitance can be achieved by optimizing these factors. The optimal conditions for higher capacitance when utilizing CNT in capacitors are small pore size which is well distributed and larger surface area. [4]

4.2. Heat treatment of capacitors with CNT present

When the capacitors with CNT are heated, the capacitance decreased and temperature increases because of the lower surface area. However, due to heat treatment the equivalent series resistance present reduced resulting in increased power density due to increased graphitization of CNT. The more we heat treat the capacitors, the number of small pore diameter CNT increases as well as its specific surface area which contributes to an increased capacitance. [4, 5]

4.3. Functionalization of CNT’s in capacitors

Capacitance of CNT-based super-capacitor can also be enhanced through chemical activation and functionalization. To illustrate an example, researchers introduced surface carboxyl groups to MWCNT’s based capacitor. This resulted in a 3.2 times larger capacitance in an aqueous electrolyte when compared to the addition of alkyl groups. Fluorination + heat treatment of CNT, adding KOH to CNT and Pyrrole functionalized CNT are some of the other methods used to increase capacitance. [4]

4.4. CNT Shape Engineering in capacitors

The shape of the CNT in the capacitor can also impact the amount of capacitance of the capacitor. Ion diffusivity is an important parameter to optimize to obtain high energy and power density in CNT based capacitors. Usually electrolyte ions diffuse through the pores of the interstitial region within SWNT packing structure (non-aligned) and thus their accessibility is limited to the inner regions of the SWNT solid. Aligning the SWNT pore structures has shown fast and easy ion diffusivity. High power density super-capacitors can also be achieved by aligning CNT’s and electrophoretic deposited CNT films (EPD). The EPD film has a uniform pore structure formed by open space between tangled nanotubes. This allows for ions from the electrolyte to easily interact with the electrode/electrolyte interface and hence greater charging of the electric double layer. [4]

4.5. Manganese Oxide and CNT Composite

The use of CNT and metal composites in electrochemical capacitors (EC) especially the use of MnO$_2$ and CNT’s, MnO$_2$ is a low cost material however, when used as an electrode shows low efficiency in EC’s. However when combined with a CNT/TA array (CNTA) displays superior efficiency in EC’s. The CNTA exhibits regular pore structure, good conductivity and homogenous properties. Ta foils are used so that they don’t influence mass load of MnO$_2$ (Nano-flower) when deposited on CNTA. This system has four key advantages over a regular CNT super-capacitor system: (1) The MnO$_2$ Nano-flowers are connected to the Ta foil by two electron highways (CNT’s) which allows for a superior conducting network thus, resulting efficient charge transport and conductivity. There are no need for conductive additives which eliminates extra resistance and weight to the system (2) Nanometer sizes present in the system reduce diffusion length of ions in MnO$_2$ phase during charge/discharge process resulting in utilization of electrode material and high capacitance. (3) Porous structure increases ionic conductivity of composite greatly. Ion buffering reservoirs can be formed in macro-pores to minimize distances to interior surface MnO$_2$ oxide. (4) The CNT provides mechanical support to the system thus eliminating mechanical/volume problems and prevent Nano-particle aggregation (Fig.5). [6] Apart from MnO$_2$/CNTA composites, CNT and polyaniline composite electrodes in EC’s have also been very effective in delivering high capacitance [7].
5. Carbon Nanotubes: Lithium Ion Batteries

Lithium ion batteries are one of the most popular energy storage device (Fig. 6).

They possess a great applicative potential and as such used in cars, mobile devices etc. However, despite its popularity these batteries do have disadvantages which reduce their efficiency. Some prominent disadvantages include: (1) the electrolyte(s) present in the battery cannot function at low temperatures and formation of unwanted products is possible; (2) Cannot allow moisture to come in contact with Li+ ions otherwise an explosion can occur; (3) If the surface film (a.k.a. SEI) formed on electrodes during charge/discharge process are very thick, then ion/electron transfer is impeded [8]. CNT’s has proved to be very useful in increasing the efficiency and reducing the main drawbacks of Li-ion batteries. The use of MWNT-metal (Sb) composites when used as an anode material in Li-ion batteries demonstrated higher reversible and specific capacities than MWNT alone after multiple cycles. This improvement is because of the Nano-dimension of the metal particles as well as the MWNT relieving mechanical stress due to Li+ insertion and extraction [9]. The limitations of using CNT as electrodes are: (1) The formation of SEI at electrodes; (2) Voltage hysteresis during charging and discharging which impacts Li+ de/intercalation into anode; and, (3) Not enough contact between CNT and electrolyte thus, limiting ion diffusivity [1]. Limitation (1) was shown to be true by researchers while characterizing MWNT tubes when they observed a discharge plateau in the discharge curve (Fig 7). This phenomena was accounted for by the formation of the SEI at the anode [10].

6. Carbon Nanotubes: Hydrogen Storage

Hydrogen is considered a possible energy carrier because it is the most abundant element in the universe, has the highest energy density per unit mass and it burns “green” producing only water. However, there are many difficulties with its efficient production, storage and transport. Currently hydrogen is stored in high pressure tanks or in cryogenic tanks (H2 is liquid). This is not an efficient method of storage because they can’t be used commercially and there are significant energy costs involved. Thus, sorbent material such as CNT’s have shown considerable promise in storing hydrogen [11]. CNT’s are chemically stable and have low mass density. It has been demonstrated that H2 can be stored in SWNT’s displaying 5 to 10% wt. They achieve this by physisorbing to the exterior or interstitial space (Fig 8). SWNT’s maximum hydrogen storage capacity increases with tube diameter. In contrast, for MWNT’s hydrogen storage capacity is independent of tube diameter (Fig.9). It was also shown that H2 molecules can exist stably in vacant spaces present in the nanotube [12]. It addition as the internal pressure in the CNT increases the H2-H2 and C-H2 spacing decreases but CNT radius increases which allows for more H2 storage [13]. There are also repulsive forces present between the H and C atoms. This energy tends to become larger as the diameter of tube increases and which results in failure of the nanotube wall. Hence, the repulsive energies determine the maximum storage capacity (for H2) and stability of the CNT [12, 13]. The optimal dimensions for CNT to meet the Department of Energy demand for 62kg/m3 and 6.5wt% H2 are as follows: SWNT: (14,14) and (30,30) with no strain and MWNT’s: (22,22) to (30,30) [13].
6.1. SWNT hydrogen storage

This section intends to provide more insight into SWNT hydrogen storage due to its vast experimental research.

1. A low pressure, smaller pores result in higher storage due to enhanced absorption in the pores. At a high pressure, this trend is the opposite because larger pores provide better storage capabilities.

2. A lower bulk density of the adsorbent results in better gravimetric storage densities because a sizeable portion of the system weight is due to absorbent. Lower volumetric storage capacities is observed since more space is required per unit mass.

3. Doping occurs between interstitial channels of tubes. This results in tubes being forced apart. The dopants can be removed by heat treatment and thus allow for more H$_2$ storage.

4. The presence of metals in CNT’s can help stabilize H$_2$ at room temperature. [14]

7. SiC Nanotubes H$_2$ storage

According to computer simulations Si-CNT are excellent candidates for H$_2$ storage. The reason is due to the presence of point charges upon the material surface which improves the storage capacity and binding energy of H$_2$. A charged induced dipole (arises from hetero-polar Si-C bond) interaction further stabilizes H$_2$. A hydrogen molecule can approach the nanotube walls from the inside and outside to towards various binding sites in many orientation. Molecular hydrogen can be stored internally or externally between the tubes. The amount of hydrogen stored is dependent on the attraction force between the tube and the H$_2$. In accordance with a GCMC simulation it has been shown that Si-CNT can store twice as more H$_2$ than regular CNT, particularly at low pressures (Fig.10) [15]

8. Carbon Nanotubes: Photovoltaic Cells

Organic photovoltaic (OPV) technologies demands are increasing because they are devices made from abundant elements which are flexible, light and hence has high applicative potential. SWNT’s have been used as electron acceptors with the donor polymer being P3OT. A large open circuit voltage of 0.75V was observed due an ohmic contact between the SWNT and metal electrode. Conductive coatings have also been made using layer-by-layer assembly of SWNT to be used in CdTe solar cells (Fig. 11). These films has conductivities of $10^2$-$10^3$S$m^{-1}$ with low loading ≈ 10% hence, indicating effective usage of SWNT percolation pathways. The use of CNT’s in OPV is still an upcoming area of research (A.C.Dillion, 2010)

9. Conclusion

CNT’s, due to their unique properties have been able to improve the efficiency and properties of energy storing devices. There is still an immense scope to research and understand the importance of utilizing CNT’s in energy storing devices. The usage of CNT- metal oxides , CNT-based fuel cell , CNT-polymer solar, CNT- quantum dots and CNT’s integrated into dye sensitized solar cells are among the many energy storage devices, which are demonstrating promise to be efficient and applicable to meet the growing energy demands of mankind. CNT in one of the most important fields of study that is proving to be a success in helping us to eliminate the current energy problems to pave a path towards a greener world.
10. References


