

Chapter

Applications of Carbon Based Materials in Developing Advanced Energy Storage Devices

*Maria Tariq, Tajamal Hussain, Adnan Mujahid,
Mirza Nadeem Ahmad, Muhammad Imran Din,
Azeem Intisar and Muhammad Zahid*

Abstract

With the increasing pressure of population, the energy demand is growing explosively. By 2050, it is expected that the world population may reach to about 9 billion which may result in the increase of energy requirement to about 12.5 trillion watts. Due to increasing pressures of population, industries and technology, concerns to find possibilities to cope with increasing demand of energy resources, arise. Although the renewable energy resources including fossil fuels, wind, water and solar energy have been used for a long time to fulfill the energy requirements, but they need efficient conversions and storage techniques and are responsible for causing environmental pollution due to greenhouse gases as well. It is thus noteworthy to develop methods for the generation and storage of renewable energy devices that can replace the conventional energy resources to meet the requirement of energy consumption. Due to high energy demands, the sustainable energy storage devices have remained the subject of interest for scientists in the history, however, the traditional methods are not efficient enough to fulfill the energy requirements. In the present era, among other variety of advanced treatments, nano-sciences have attracted the attention of the scientists. While talking about nano-science, one cannot move on without admiring the extraordinary features of carbon nanotubes (CNTs) and other carbon based materials. CNTs are on the cutting edge of nano science research and finding enormous applications in energy storage devices. Excellent adsorption capabilities, high surface area, better electrical conductivity, high mechanical strength, corrosion resistance, high aspect ratio and good chemical and physical properties of CNTs have grabbed tremendous attention worldwide. Their charge transfer properties make them favorable for energy conversion applications. The limitation to the laboratory research on CNTs for energy storage techniques due to low specific capacitance and limited electrochemical performance can be overcome by surface functionalization using surface functional groups that can enhance their electrical and dispersion properties. In this chapter, ways CNTs employed to boost the abilities of the existing material used to store and transfer of energy have been discussed critically. Moreover, how anisotropic properties of CNTs play important role in increasing the energy storage capabilities of functional materials. It will also be discussed how various kinds of materials can be combined along CNTs to get better results.

Keywords: Energy storage, CNTs, Capacitors, Batteries

1. Introduction

With the increasing pressure of population, the energy demand is growing explosively. By 2050, it is expected that the world population may reach to about 9 billion which may result in the increase of energy requirement to about 12.5 trillion watts. Due to increasing pressures of population, industries and technology, concerns to find possibilities to cope with increasing demand of energy resources arises. Although the renewable energy resources including fossil fuels, wind, water and solar energy have been used for long time to fulfill the energy requirements, but they need efficient conversions and storage techniques and are responsible for causing environmental pollution due to greenhouse gasses as well. It is thus noteworthy to develop methods for generation and storage of renewable energy devices that can replace the conventional energy resources to meet the requirement of energy consumption.

In this chapter, we want to grab attention of the readers towards the applications of CNTs in energy storage devices. The basic principle of energy storage devices is briefly explained. Also role of carbon nanotubes as cathode and anode in different types of energy storage are discussed in this chapter.

There are two fundamental ways of storing electrochemical energy. One is the energy storage via faradic process while the other one is a non-faradic process. In the non-faradic devices, electricity is stored in electrostatic way while the faradic devices store energy electrochemically by redox reactions of active reagents. Pseudocapacitors and batteries are the examples of faradic devices while supercapacitors are the non-faradic energy storage devices.

2. Basic principle

In general, electrochemical energy storage devices involve three main steps:

- Electro sorption of ions
- Redox reaction at electrode/electrolyte interface
- Insertion of ions in to the electrodes

The energy storage devices usually store energy at the electrode/electrolyte interface in the form of accumulation of charge at the positive and negative electrodes as ions [1]. The ability of energy storage of devices is greatly affected by the electrochemical reaction that occurs at electrode electrolyte interface [1, 2].

2.1 Charging-discharging mechanism

The basic mechanism of charging and discharging of batteries as well as capacitors are discussed below.

2.1.1 Battery

Battery is composed of three main components; (i) an anode (ii) a cathode and (iii) an ionic conductor acting as an electrolyte. In order to avoid short circuit, a rigid separating medium is placed between the two electrodes (anode and cathode)

[3]. In a charged cell, movement of ions takes place from cathode to anode and reduction occurs due to ionic conduction. This electrons transportation occurs through an external circuit [4]. When a cell is discharged, oxidation occurs at anode which results in the formation of ionic species. Then these ions travel through the electrolyte and recombine at the cathode. The work is done in the process of ions transport as the ionic species produced at anode are unable to travel through the insulating electrolyte, thus they are conducted through an external circuit towards the cathode [5].

2.1.2 Capacitor

Electrochemical capacitors are divided into two main categories which are (i) electric double layer capacitor (EDLC) and (ii) pseudocapacitors. Similar to the battery, all electrochemical capacitors have a pair of electrodes which stores electrical energy [6]. An aqueous solution of acid or alkali such as that of sulfuric acid or potassium hydroxide or any other ionic liquid acts as an electrolyte [7].

There is a dielectric medium present between the electrodes of pseudocapacitors. The applied voltage produces dipoles in which electrical charges are stored. On other hand, in EDLC, electrical charges are arranged at the electrodes/ electrolyte boundaries as 'electric double layer' also known as helmholtz plan [8]. The energy is delivered quickly in EDLC because of quick response of materials to the potential change and physical reactions. It is different from the behavior of battery because, the electrode potential is a continuous function of degree of charge, which is different from thermodynamic behavior of reactants of battery. It is more advantageous over battery due to its environmental friendly materials, long life span and rapid charge/discharge ability [9]. Charging-discharging pattern of the super capacitor with the time is shown in **Figure 1**. The EDLC stores charge without chemical reaction thus no heat is generated leading to high efficiency and long life. The energy stored due to fast redox reactions results in faster charging and discharging of capacitor than that of the battery. Nevertheless, due to the confined electrode surface of EDLC, the amount of energy stored in it is limited and much lower as compared to that of pseudocapacitors and batteries [10].

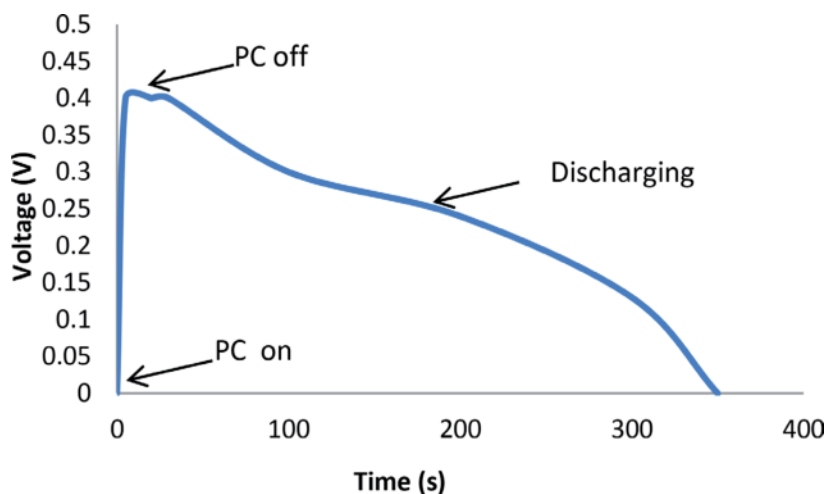


Figure 1.
Charging-discharging curve of supercapacitor.

The electric double layer can be shown in the form of equation as:

$$C = Q \ / \ V = \epsilon_0 \epsilon_r \ A \ / \ d \quad (1)$$

Where,

C = capacitance of electrode

Q = charge transferred at potential V

ϵ_r = dielectric constant of electrolyte

ϵ_0 = dielectric constant of vacuum

d = distance between electrodes

A = surface area of electrode

There are three main parameters that affect all the electrochemical energy storage devices. These include (i) specific capacitance, (ii) power, and (iii) energy density.

The total amount of electric charge that can be stored in capacitor is called the capacitance whereas the maximum amount of power that can be supplied per unit mass is called power density. The energy density can be defined as amount of energy stored per unit mass. EDLC possess lower energy densities as compared to batteries but have many advantages like high power density, faster charging and discharging, long life cycle and no change in chemical structure during charging and discharging [11].

3. CNTs for energy storage devices

Over the past many years, several advancements have been introduced in the primary conception and modification of electrode materials used for energy storage devices. Carbon-based materials, such as activated carbons (ACs), carbon nanotubes (CNTs) and graphenes have proved to be good electrode materials for energy storage devices [12, 13].

CNTs are on the cutting edge of nano science research and finding enormous applications in energy storage devices. Excellent adsorption capabilities, high surface area, better electrical conductivity, high mechanical strength, corrosion resistance, high aspect ratio and good chemical and physical properties of CNTs have grabbed tremendous attention worldwide [14, 15]. Their charge transfer properties make them favorable for energy conversion applications. The limitation to the laboratory research on CNTs for energy storage techniques due to low specific capacitance and poor electrochemical performance can be overcome by surface functionalization using surface functional groups that can enhance their electrical and dispersion properties [16]. Also the use of CNTs for energy storage devices is cheap due to easily available precursor carbon material for synthesis of CNTs. The researches on various energy storage applications of CNTs include Li-ion batteries, hydrogen storage, fuel cells and energy conversions etc.

4. Li-Ion batteries

Li-ion batteries show high energy density as compare to other rechargeable batteries. They have grabbed attention for various applications extending from electronic portable devices to electronic vehicles [17]. Among many other rechargeable batteries, LIBs have low cost, are safe for use and have least side reactions. They can offer maximum energy, high voltage, good capacity and density [18].

During the charging process, Lithium ions move from cathode to anode through an aqueous electrolyte present between the electrodes. The required driving force for this process is the chemical potential difference of Li between the electrodes. During discharging, reduction occurs at the cathode by intercalating Li-ions, while oxidation occurs at the anode simultaneously. In this way, electric current flows through external circuit to perform the required work [19, 20].

The properties of LIB such as energy density, cycle durability, rate of charging and discharging and flexibility is greatly affected by selection of suitable materials for the anode, cathode and the electrolyte [21]. The use of nanostructured materials adds many advantages over the conventional materials, such as larger contact area with electrolyte, short transport pathway for Li ions insertion and reversible Li intercalation. CNTs have been proved to be most suitable additive materials for Electrodes in LIBs and role of CNTs in LIBs is explained in the **Figure 2**. As compared to conventional LIBs, the maximum energy storing capacity of CNTs based Li-ion batteries is 1000 mAh/g (three times higher than conventional) [22].

4.1 CNTs based anode

An anode can be made of pure CNTs or composite metals, which acts as the negative electrode of the LIB during charging while cathode is composed of Li metal oxides or transition metals oxides that acts as the positive electrode of LIB in discharging. The electrochemical performance of Li ion batteries depends largely on the effective cyclic intercalation of Li ions between the electrodes. The ideal characteristics of the battery include fast charging, higher ionic storage and slow discharge [23].

Normally the metallic Lithium used as an anode in Li ion batteries causes safety issues and they have short lifetime and high cost. Carbon based materials and Li-based alloys can replace metallic Li as anode. Use of these materials reduces the activity of Li as compared to lithium metal thus results in decreasing reactivity with electrolyte, reducing the voltage of cell and improving safety. The unique structure of CNTs allows the rapid movement of Li ions through insertion and de-insertion [24, 25]. LIB anodes can be replaced by single wall carbon nanotubes as well as multiwall carbon nanotubes either by simply their deposition on a current collector or by their direct growth on a catalytically modified current collector. SWCNTs and

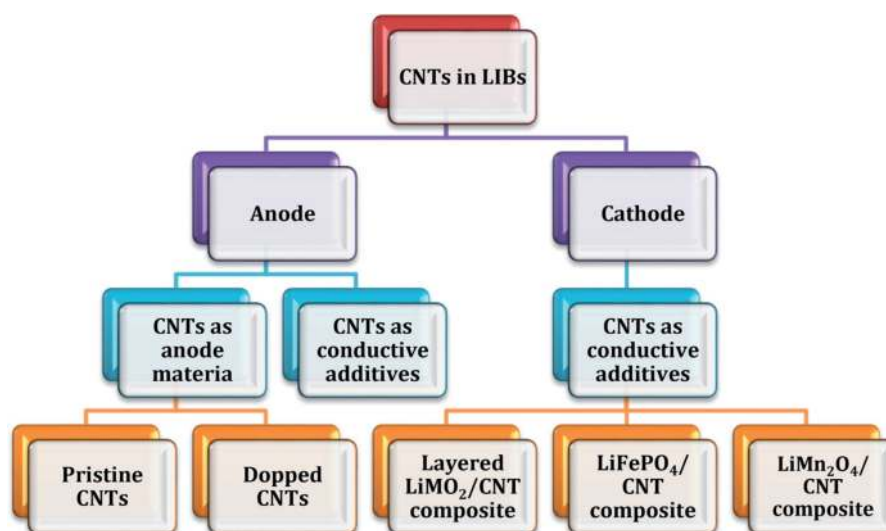


Figure 2.
Incorporation of CNTs in LIBs.

MWCNTs possess higher theoretical electrical conductivities (approximately 106 and 105S/m, respectively) and a good elastic strength ($\gg 60$ GPa) [26, 27].

The factors which affect the kinetics of lithium inside CNTs include radius, length, chirality and structure defects. These factors can be optimized to obtain maximum capacity results. The Li insertion capacity of carbon nanotubes in LIBs depends on chirality. The metallic CNTs show higher insertion capacities as compared to semiconductor CNTs [28].

The intercalation capacity of Li in CNT based Li-batteries is directly associated with the morphology of CNTs. Any structural defect in the morphology of CNTs affects its capacity. If there are holes in the side wall of CNTs due to defect, Li ions diffuse into them easily as compared to defect free CNTs. Li ions move randomly inside the nanotubes such that longer the length of nanotubes, slower the effective diffusion [29].

A limitation in the use of CNT anodes in LIBs is the non-reversible loss of charge after first cycle because of formation of a layer of solid electrolyte inter-phase on the CNTs. This issue can be resolved by using CNTs as conducting additives. The CNT composites with Li material have been proved to be very efficient as they resist the agglomeration as well as increase the conductivity of anode [30].

4.2 CNTs based cathode

In Li-ion batteries the active cathode material play key role in determining their performance. A variety of materials are discovered as the suitable materials for cathode of LIBs, comprising LiCoO_2 , LiNiO_2 , LiMnO_2 , spinel LiMn_2O_4 , LiFePO_4 , LiMPO_4 and elemental sulfur [31–33].

The selection of appropriate cathode material greatly affect the performance of the Li-ion batteries [34]. Carbon nanotubes have been proved to be the most efficient cathode composite materials as they can reduce resistance thus increase the electrochemical performance of composite cathode. The high aspect ratio and geometry of MWCNTs provide continuous conductive network allowing efficient electron transport through material [35]. The large surface area of CNTs provides close contact with active material.

CNTs as additives for cathode materials have been reported by many researchers. Among them most widely used is the nanostructured LiFePO_4 with carbon nanocomposites containing monodispersed nanofibers of LiFePO_4 electrode [36].

For CNT based cathode, nanoparticles should have firm chemical bonds with the active materials so that CNTs act as the current-collectors for faster transport, better strength and larger surface area. CNTs can be introduced into the active material in a number of ways, including simply adding to the forerunner at the early stage of processing of active materials or by their growth in the active electrode material.

5. Super capacitors

Electrochemical capacitors, also recognized as super capacitors, are the rechargeable energy storage devices that store charge of thousands of Farads in the electrode-electrolyte interface. In contrast with other energy storage devices, super capacitors provide high power, low weight and high rate of charging-discharging [37].

Super capacitors are divided into three main types:

- Symmetric
- Asymmetric
- Hybrid

In all types of SCs, carbon is the most commonly used electrode material because they are easily available, less costly, have larger surface area and possess excellent electrical, electrochemical and mechanical properties [38].

Super capacitors are also differentiated into different types depending upon the charge storage mechanism.

- Electric double layer capacitor (Non-faradic)
- Pseudocapacitor (faradic)

The electrochemical double layer capacitor (EDLC) stores energy in a double layer of ions of electrolyte (helmholtz layer) formed on the surface of electrodes surface. The Helmholtz layer stores the charge physically. Pseudocapacitors contain electrodes of active material that store charge by faradic mechanism. Pseudocapacitors possess double the energy density as compared to EDLCs because it includes the bulk as well as the surface of the electrodes [37].

The performance of supercapacitors can be upgraded by increasing the electrode surface area or using appropriate material for electrodes. Comparison of the different features of EDLC and pseudocapictors is given in **Table 1**.

5.1 Electrode material for supercapacitors

Electrode materials play fundamental role to determine the efficiency of a supercapacitor. CNTs can be used as active materials for electrodes as well as incorporated with other additive materials. Many forms of carbon materials are proved to be effective electrode material for electrochemical capacitors. They help the ions to diffuse at the surface and also help to increase change in volume during charging-discharging.

The mostly used CNT based electrodes for supercapacitors include: [39].

- Bare CNT electrode
- Polymer/CNT composite electrode
- Metal oxide/CNT hybrid electrode

5.2 Bare CNT electrode

CNTs are frequently used as electrode material for EC capacitors due to high surface area. The capacitance of electrochemical capacitors is significantly higher

Electric double layer capacitor (EDLC)	Pseudocapacitor
Non-faradic	Faradic
Highly reversible charge–discharge	Quite reversible charge–discharge
Higher power density	Lower power density
Lower energy density	Higher energy density
20–50 mF cm ⁻²	200–500 mF cm ⁻²

Table 1.
Comparison of EDLC and pseudocapacitor.

than other capacitors; SWCNT electrodes show a capacitance of 180.0 F/g, a power density of 20.0 kW/kg and energy density of 7.0 Wh/kg [40].

CNTs can be modified for fabrication to electrode material by attachment of chemical groups through covalent bond or by wrapping the functional groups non-covalently [41]. To improve the power densities and energy, dopants are also used such as N-CNTs [42]. Furthermore, larger surface area can be obtained by oxidation. However it is difficult for bare CNTs, to obtain high energy density and power density simultaneously because of dependence of storage mechanism on physical process.

5.3 Polymer\CNT composites electrodes

Conducting polymers are grabbing the attention as supercapacitors electrode materials owing to higher specific capacitance, high conductivity in charged state, thus reduced equivalent resistance and improved power density. The randomly arranged carbon nanotubes with polymer matrix have a synergistic effect on the capacitance [43].

Among the conducting polymers, CNT composites are the most commonly used polymer composites including polyaniline [PANI] [44, 45] and polypyrrole [PPy] [46] and polythiophene (PTh) composites. We have reported in our work, electrical and thermal properties of polymethyl methacrylate CNTs composites with polyaniline-multiwalled carbon nanotubes (PANI-CNTs) as filler. Theoretically calculated percolation threshold was found to be 1.3 wt% [47]. We have also found from research that PANI had lower thermal stability than its composites with MWCNTs and Ag-MWCNTs [48].

These polymer composites exhibit several advantages like flexibility, stability, and lower cost, good electrical conductivity, more stable capacitance, and large scale production. The modification of composite due to added constituents depends upon the factors such as conductivity, accessibility and diffusion distance in electrode [49].

In one of our reported studies, Polystyrene adsorbed multi-walled carbon nanotubes incorporated polymethylmethacrylate composites have been synthesized with alleviated electrical properties. The calculated value of percolation threshold was 0.1 wt% [50].

5.4 Metal oxide\CNT composites electrodes

Metal oxides are frequently used as electrodes for electrochemical capacitors due to high densities and high strength [51]. Transition metals are more effectively used because they exhibit more than one oxidation states that results in high capacitance [52]. The faradic behavior of metal oxides depends upon the hydration properties and crystalline structure. CNTs are introduced to metal oxides so that when the composite is added to the electrode, it restricts the volume change. Among many metal oxide/CNT composites, the most widely used as electrode material is MnO_2 . MnO_2 possess high theoretical capacitance, found abundantly in nature, and is environmental friendly, easily affordable and easily processed [53, 54]. Ramezani et al. reported the specific capacitance of MnO_2 -CNT composites at a high scan rate of 20 mV/s, to be 180 F/g and possessed a high rate capacity [55]. Reddy et al. also reported Au doped MnO_2 -CNT hybrid coaxial composites having capacitance of 68.0 F/g, energy density (4.5 Wh/kg), power density to be 33.0 kW/kg, and the cycle stability up to 1000 cycles. Effect of CNTs based metal oxide composite on the efficiency of the electrode is best explained in **Figure 3** and **Table 2** [59].

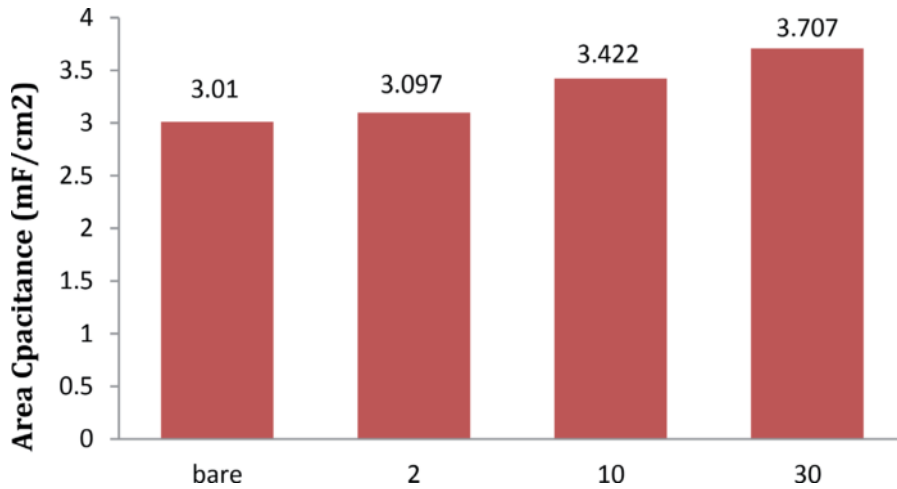


Figure 3.
 Areal capacitance of CNTs fibers electrodes with different MnO₂ coating.

Sr. no.	Electrode	Specific capacitance (F/g)	Scan rate	Reference
1	MnO ₂ /CNT	150	20	[55]
2	MnO ₂ /CNT	325.5	...	[56]
3	Mn ₂ O ₃ /CNT	508	...	[57]
4	Ni(OH) ₂ /CNF	2523	5	[58]

Table 2.
 Data od CNTs based metal oxide composites as electrodes and their efficiency.

6. CNTs as flexible and separate electrodes

The energy storage devices including LIBs and super-capacitors are weighty, bulky and rigid. Therefore, they are now being replaced by the flexible storage devices due to their distinctive advantages such as less weight, flexibility and diversity of shapes etc. Therefore the flexible energy storage devices are most wanted [60].

The CNTs play an important role due to their manipulating capabilities in making flexible electrodes for flexible storage devices. CNTs play a dual role as current collector as well as active material. The CNTs thin films reduce the electrodes size and also increase flexibility and stability [61].

For the fabrication of CNTs as flexible electrodes, few aspects must be taken in account, such as young modulus of the thin film, to make sure that it may not degrade during bending or expanding. Secondly, during the charging discharging process, heat is released which may cause expansion of the material, effecting the working of the device. Thus it is also important to confirm the thermal stability of the active material [62].

6.1 CNT paper for energy storage

CNT papers having improved energy storage capabilities, have grabbed the attention for useful applications. CNT thin films are proved to possess excellent electrochemical performance due to having good conductivity, flexibility and fast heat dissipation capability [63]. With the improving technologies, CNT

electrodes are being modified into CNT paper for the energy storage [64]. A number of CNT papers have been reported as electrodes for storage devices. In 2004, Morris et al. reported a free standing single walled CNTs paper electrode and its application in LIBs as initiative. This SWCNT paper is capable of showing energy of 600.0 Wh/kg and power density of nearly 3.0 kW/kg [65]. A CNT bucky-paper was invented by filtration of DWCNTs which was mechanically stable and flexible [66]. Another free flexible SWCNT paper was made by the chemical vapour deposition method, having the specific capacitance (35.0 F/g) and power density (197.3 kW/kg) [67].

The performance of energy storage of CNT paper can be enhanced by adding pseudocapacitance [68]. Xiao et al. utilized vacuum filtration method to prepare a flexible free-standing carbon nanotubes films and also used electro-chemical method in order to join redox functional groups to the CNT films [69]. The active groups containing CNT films revealed high capacitance of 150.0 mF/cm. Yang's group introduced oxygen functional groups to CNTs thin film through an acid treatment. The film showed elevated volumetric energy of approximately 200 Wh/kg and power of approximately 10 kW/kg [70].

6.2 CNT fibers

The typical weaving technology is used for making fiber shaped CNT electrodes. The fiber shaped electrodes are highly stretchable and flexible with good integration capability [71, 72]. The prime properties of electrode such as conductance, heat resistance and stability etc. are determined by the core material of the fiber. Thus, it is very important to select an appropriate material for the fiber [73].

Novel approach reported by Lu, Zan, et al. included development of super elastic hybrid CNT/graphene fiber accompanied by electro deposition of polyaniline to obtain high performing fiber supercapacitor. It was observed that the specific capacitance of prepared fiber was increased to 39% [12].

Chen, Tao, et al. invented a CNTs-based wire shaped electrode for batteries and supercapacitors and found excellent electro-chemical performance of prepared wire shaped devices with outstanding mechanical and electric properties of core CNTs [74].

6.3 CNT and polymers composites

All polymer based energy storing devices are more useful than batteries and supercapacitors due to their environmental friendly nature, flexible, low cost and versatility. In the novel approaches of flexible energy storage devices, many different ways have been used in which the electrode materials include conducting polymers [75–77] or polymers/CNTs composites [78–81].

The significance of using these polymer composite electrodes is the excellent mechanical properties and structural strength along with high tensile strength of electrode. In addition the densities of polymer-based electrodes are equivalent to that of composite electrodes [82].

Many polymer composite materials have been reported having higher electro-chemical performance like Poly-pyrrole (PPY) on CoO nanowires [83], Poly-aniline (PANI) hybrid electrode [82], PPY on free CNTs bucky-paper [84] etc. Adding polymers to CNTs to form flexible composites electrode is a promising approach to obtain better electrochemical performance along with flexibility for flexible energy storage devices.

7. Flexible energy storage devices

There is a great demand of elastic energy storage devices owing to their flexibility, portability and less weight. **Figure 4** shows the importance of such flexible energy storage devices. These energy storage devices are used as wearable devices, soft electronic devices and roll up display [85, 86]. In order to achieve flexible energy storage devices, the main challenge is to select appropriate material having high capacity and conductivity. There are two main types of elastic energy storage devices:

- Flexible LIBs
- Flexible supercapacitors

7.1 Flexible Li-ion batteries

In order to design portable electronics such as smart cards, wireless sensor, wearable devices, roll up displays etc. flexible Li ion batteries are required which have high energy density and excellent rate capabilities [87]. Flexible batteries have been developed by many routes including cellulose based batteries [88], polymer batteries [89], soft packing batteries [90], and paper based batteries [91, 92]. The performance of flexible batteries highly depends upon the type of electrode material thus a soft flexible nanostructured material is highly recommended to construct a flexible battery. Carbon nanotubes, owing to their unique properties like extremely flexible and highly conductive, take their top priority to be used as electrode material for flexible batteries [93].

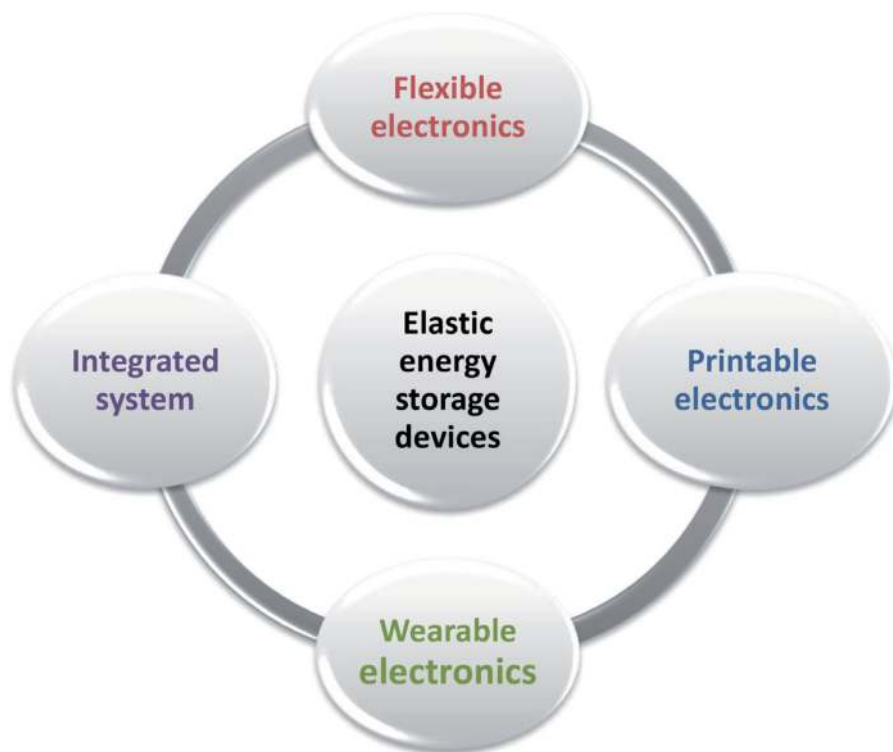


Figure 4.
Applications of flexible energy storage devices.

Ajayan et al. reported porous cellulose paper having CNTs embedded on it used as electrode. The paper was capable of bending, twisting and rolling to any degree [63]. Ren Jingn et al. used MWCNT/LiO₂ as electrodes to form a malleable wire-shaped Li-ion battery. The battery showed the power-density of 880 W/kg and energy-density of 27 Wh/kg. The prepared wire-shaped batteries were fabricated into low weight, flexible and malleable battery textile to check their application [94].

Fang et al. developed a lithium sulfur battery by twisting a fibrous cathode fabricated by aligned CNTs coated with sulfur and an anode of Li wire. The composite cathode displayed capacity of 1051 mAh/g versus sulfur which retained 600 mAh/g after 100 running cycles, showing good cycling performance [95].

7.2 Flexible supercapaitors

In the modern era, transportable electronic devices including mobiles, wearable electronics and light weight elastic electronic devices are of great demand. While talking about portable energy storage devices, one cannot ignore supercapacitors. Supercapacitors are having applications in every electronic device because of higher specific capacitance and power density [96–98]. Therefore, flexible supercapacitors are always preferred for elastic electronic devices. CNTs are proved to be excellent electrode material for flexible supercapacitors owing to their high aspect ratio, high conductance and porosity [99, 100].

Wang, Q. et al. reported synthesis of strong flexible CNT-MnO₂ nanosheets with excellent capacitance for flexible supercapacitor [101]. In another approach, reduced graphene-oxide and carbon nanotubes were developed as electrodes for flexible supercapacitors. The addition of CNTs provided a dense structure having mesopores in hybrid fiber. The electrode exhibits high tensile strength, high conductance and capacitance of 354.9 F/cm³ [102]. CuO/MWCNTs nanocomposites were synthesized which showed the specific-capacitance of 452.8 F/g and the scan rate of 10 mV/s [103].

Niu et al. prepared stretchable buckled SWCNT films combined with polydimethylsiloxane (PDMS) and used them as electrode fo flexible supercapacitor [104] it showed maximum flexibility and strechability.

8. Conclusion

CNTs are on the cutting edge of nano science research and finding enormous applications in energy storage devices. Excellent adsorption capabilities, high surface area, better electrical conductivity, high mechanical strength, corrosion resistance, high aspect ratio and good chemical and physical properties of CNTs have grabbed tremendous attention worldwide. Among energy storage devices, Li ion batteries, electric double layer capacitors and pseudocapacitors are more commonly used. In Li-ion batteries CNTs are use as cathodes as well as anodes. It is observed that as compared to conventional LIBs, the maximum energy storing capacity of CNTs based Li-ion batteries is 1000 mAh/g i.e. three times higher than conventional. In case of supercapacitors, CNTs based electrodes include bare CNTs, polymer/CNTs electrodes and metal oxide/CNTs electrodes. Carbon nanotubes based flexible electrodes have become popular due to their distinctive advantages such as less weight, flexibility and diversity of shapes etc. Flexible energy storage devices such as flexible lithium ion batteries and flexible super capacitors are used as wearable devices, soft electronic devices and roll up display. In order to achieve flexible energy storage devices, the main challenge of selecting appropriate material having high capacity and conductivity can be achieved by using carbon nanotubes.

Author details

Maria Tariq¹, Tajamal Hussain^{1*}, Adnan Mujahid¹, Mirza Nadeem Ahmad²,
Muhammad Imran Din¹, Azeem Intisar¹ and Muhammad Zahid³


1 Institute of Chemistry, University of the Punjab, Lahore, Pakistan

2 Department of Applied Chemistry, Govt College University Faisalabad, Pakistan

3 Department of Chemistry, Agriculture University of Faisalabad, Faisalabad,
Pakistan

*Address all correspondence to: tajamalhussain.chem@pu.edu.pk

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References

- [1] Liu, J., et al., *Advanced energy storage devices: basic principles, analytical methods, and rational materials design*. Advanced science, 2018. 5(1): p. 1700322.
- [2] Sumboja, A., et al., *Electrochemical energy storage devices for wearable technology: a rationale for materials selection and cell design*. Chemical Society Reviews, 2018. 47(15): p. 5919-5945.
- [3] Mehtab, T., et al., *Metal-organic frameworks for energy storage devices: batteries and supercapacitors*. Journal of Energy Storage, 2019. 21: p. 632-646.
- [4] Li, J., et al., *Studies on the cycle life of commercial lithium ion batteries during rapid charge-discharge cycling*. Journal of Power Sources, 2001. 102(1-2): p. 294-301.
- [5] Gogotsi, Y. and R.M. Penner, *Energy storage in nanomaterials—capacitive, pseudocapacitive, or battery-like?* 2018, ACS Publications.
- [6] Eftekhari, A., *Metrics for fast supercapacitors as energy storage devices*. 2018, ACS Publications.
- [7] Merlet, C., et al., *On the molecular origin of supercapacitance in nanoporous carbon electrodes*. Nature materials, 2012. 11(4): p. 306-310.
- [8] Boota, M., et al., *Organic-inorganic all-pseudocapacitive asymmetric energy storage devices*. Nano Energy, 2019. 65: p. 104022.
- [9] Miller, E.E., Y. Hua, and F.H. Tezel, *Materials for energy storage: Review of electrode materials and methods of increasing capacitance for supercapacitors*. Journal of Energy Storage, 2018. 20: p. 30-40.
- [10] Zhou, Y., et al., *Ultrahigh-Areal-Capacitance Flexible Supercapacitor Electrodes Enabled by Conformal P3MT on Horizontally Aligned Carbon-Nanotube Arrays*. Advanced Materials, 2019. 31(30): p. 1901916.
- [11] Allagui, A., et al., *Capacitive behavior and stored energy in supercapacitors at power line frequencies*. Journal of Power Sources, 2018. 390: p. 142-147.
- [12] Lu, Z., et al., *Superelastic hybrid CNT/graphene fibers for wearable energy storage*. Advanced Energy Materials, 2018. 8(8): p. 1702047.
- [13] Wen, L., F. Li, and H.M. Cheng, *Carbon nanotubes and graphene for flexible electrochemical energy storage: from materials to devices*. Advanced Materials, 2016. 28(22): p. 4306-4337.
- [14] De Volder, M.F., et al., *Carbon nanotubes: present and future commercial applications*. science, 2013. 339(6119): p. 535-539.
- [15] Soni, S.K., B. Thomas, and V.R. Kar, *A Comprehensive Review on CNTs and CNT-Reinforced Composites: Syntheses, Characteristics and Applications*. Materials Today Communications, 2020: p. 101546.
- [16] Jia, X. and F. Wei, *Advances in production and applications of carbon nanotubes*, in *Single-Walled Carbon Nanotubes*. 2019, Springer. p. 299-333.
- [17] Li, H., *Practical evaluation of Li-ion batteries*. Joule, 2019. 3(4): p. 911-914.
- [18] El Kharbachi, A., et al., *Exploits, advances and challenges benefiting beyond Li-ion battery technologies*. Journal of Alloys and Compounds, 2020. 817: p. 153261.
- [19] Liu, S., et al., *Deep-discharging li-ion battery state of charge estimation using a partial adaptive forgetting factors least*

- square method. IEEE Access, 2019. 7: p. 47339-47352.
- [20] He, Y., et al., *A new model for State-of-Charge (SOC) estimation for high-power Li-ion batteries*. Applied Energy, 2013. **101**: p. 808-814.
- [21] Lin, C., et al., *Li₄Ti₅O₁₂-based anode materials with low working potentials, high rate capabilities and high cyclability for high-power lithium-ion batteries: A synergistic effect of doping, incorporating a conductive phase and reducing the particle size*. Journal of Materials Chemistry A, 2014. **2**(26): p. 9982-9993.
- [22] Liu, J., *Addressing the grand challenges in energy storage*. Advanced Functional Materials, 2013. **23**(8): p. 924-928.
- [23] Liu, X.-M., et al., *Carbon nanotube (CNT)-based composites as electrode material for rechargeable Li-ion batteries: a review*. Composites Science and Technology, 2012. **72**(2): p. 121-144.
- [24] Chen, Y., et al., *Hollow carbon-nanotube/carbon-nanofiber hybrid anodes for Li-ion batteries*. Journal of the American Chemical Society, 2013. **135**(44): p. 16280-16283.
- [25] Chen, L., et al., *Porous graphitic carbon nanosheets as a high-rate anode material for lithium-ion batteries*. ACS applied materials & interfaces, 2013. **5**(19): p. 9537-9545.
- [26] Goriparti, S., et al., *Review on recent progress of nanostructured anode materials for Li-ion batteries*. Journal of power sources, 2014. **257**: p. 421-443.
- [27] Kang, C., et al., *3-dimensional carbon nanotube for Li-ion battery anode*. Journal of Power Sources, 2012. **219**: p. 364-370.
- [28] Kawasaki, S., et al., *Metallic and semiconducting single-walled carbon nanotubes as the anode material of Li ion secondary battery*. Materials Letters, 2008. **62**(17-18): p. 2917-2920.
- [29] Bhatt, M.D. and C. O'Dwyer, *Recent progress in theoretical and computational investigations of Li-ion battery materials and electrolytes*. Physical Chemistry Chemical Physics, 2015. **17**(7): p. 4799-4844.
- [30] Wang, X.X., et al., *Preparation of short carbon nanotubes and application as an electrode material in Li-ion batteries*. Advanced Functional Materials, 2007. **17**(17): p. 3613-3618.
- [31] Park, K., et al., *Electrochemical nature of the cathode interface for a solid-state lithium-ion battery: interface between LiCoO₂ and garnet-Li₇La₃Zr₂O₁₂*. Chemistry of Materials, 2016. **28**(21): p. 8051-8059.
- [32] Xiong, X., et al., *Role of V₂O₅ coating on LiNiO₂-based materials for lithium ion battery*. Journal of Power Sources, 2014. **245**: p. 183-193.
- [33] Yu, H. and H. Zhou, *High-energy cathode materials (Li₂MnO₃-LiMO₂) for lithium-ion batteries*. The journal of physical chemistry letters, 2013. **4**(8): p. 1268-1280.
- [34] Li, Q., et al., *Conjugated carbonyl polymer-based flexible cathode for superior lithium-organic batteries*. ACS applied materials & interfaces, 2019. **11**(32): p. 28801-28808.
- [35] Diao, G., et al., *Nickel and cobalt effect on properties of MWCNT-based anode for Li-ion batteries*. Applied Nanoscience, 2020: p. 1-7.
- [36] Sides, C.R., et al., *A high-rate, nanocomposite LiFePO₄/carbon cathode*. Electrochemical and Solid State Letters, 2005. **8**(9): p. A484.
- [37] Sarno, M., *Nanotechnology in energy storage: the supercapacitors*, in *Studies in*

Surface Science and Catalysis. 2019, Elsevier. p. 431-458.

[38] Li, J., *Review of electrochemical capacitors based on carbon nanotubes and graphene*. *Graphene*, 2012. **1**(01): p. 1.

[39] Kumar, S., et al., *Carbon nanotubes: A potential material for energy conversion and storage*. *Progress in energy and combustion science*, 2018. **64**: p. 219-253.

[40] Tashima, D., et al., *Space charge distributions of an electric double layer capacitor with carbon nanotubes electrode*. *Thin Solid Films*, 2007. **515**(9): p. 4234-4239.

[41] Hiraoka, T., et al., *Compact and Light Supercapacitor Electrodes from a Surface-Only Solid by Opened Carbon Nanotubes with 2 200 m² g⁻¹ Surface Area*. *Advanced Functional Materials*, 2010. **20**(3): p. 422-428.

[42] Sevilla, M., et al., *Surface modification of CNTs with N-doped carbon: an effective way of enhancing their performance in supercapacitors*. *ACS Sustainable Chemistry & Engineering*, 2014. **2**(4): p. 1049-1055.

[43] Magu, T.O., et al., *A review on conducting polymers-based composites for energy storage application*. *Journal of Chemical Reviews*, 2019. **1**(1, pp. 1-77.): p. 19-34.

[44] Dong, B., et al., *Preparation and electrochemical characterization of polyaniline/multi-walled carbon nanotubes composites for supercapacitor*. *Materials Science and Engineering: B*, 2007. **143**(1-3): p. 7-13.

[45] Yazdi, M.K., et al., *PANI-CNT nanocomposites*, in *Fundamentals and Emerging Applications of Polyaniline*. 2019, Elsevier. p. 143-163.

[46] An, K.H., et al., *High-capacitance supercapacitor using a nanocomposite*

electrode of single-walled carbon nanotube and polypyrrole. *Journal of the Electrochemical Society*, 2002. **149**(8): p. A1058.

[47] Bashir, F., et al., *Tailoring electrical and thermal properties of polymethyl methacrylate-carbon nanotubes composites through polyaniline and dodecyl benzene sulphonic acid impregnation*. *Polymer Composites*, 2018. **39**(S2): p. E1052-E1059.

[48] Hussain, T., et al., *Polyaniline/silver decorated-MWCNT composites with enhanced electrical and thermal properties*. *Polymer Composites*, 2018. **39**(S3): p. E1346-E1353.

[49] Wei, C., et al., *Polymer composites with functionalized carbon nanotube and graphene*, in *Polymer Composites with Functionalized Nanoparticles*. 2019, Elsevier. p. 211-248.

[50] Hussain, T., et al., *Polystyrene adsorbed multi-walled carbon nanotubes incorporated polymethylmethacrylate composites with modified percolation phenomena*. *MRS Advances*, 2018. **3**(1): p. 25-30.

[51] Zhi, M., et al., *Nanostructured carbon-metal oxide composite electrodes for supercapacitors: a review*. *Nanoscale*, 2013. **5**(1): p. 72-88.

[52] Lee, T.H., et al., *High energy density and enhanced stability of asymmetric supercapacitors with mesoporous MnO₂@CNT and nanodot MoO₃@CNT free-standing films*. *Energy Storage Materials*, 2018. **12**: p. 223-231.

[53] Wu, P., et al., *Synthesis and characterization of self-standing and highly flexible δ-MnO₂@CNTs/CNTs composite films for direct use of supercapacitor electrodes*. *ACS applied materials & interfaces*, 2016. **8**(36): p. 23721-23728.

[54] Yang, P., et al., *Low-cost high-performance solid-state asymmetric*

- supercapacitors based on MnO₂ nanowires and Fe₂O₃ nanotubes. *Nano letters*, 2014. **14**(2): p. 731-736.
- [55] Ramezani, M., M. Fathi, and F. Mahboubi, *Facile synthesis of ternary MnO₂/graphene nanosheets/carbon nanotubes composites with high rate capability for supercapacitor applications*. *Electrochimica Acta*, 2015. **174**: p. 345-355.
- [56] Huang, M., et al., *Layered manganese oxides-decorated and nickel foam-supported carbon nanotubes as advanced binder-free supercapacitor electrodes*. *Journal of Power Sources*, 2014. **269**: p. 760-767.
- [57] Zhou, R., et al., *High-performance supercapacitors using a nanoporous current collector made from super-aligned carbon nanotubes*. *Nanotechnology*, 2010. **21**(34): p. 345701.
- [58] Zhang, L., et al., *Flexible hybrid membranes with Ni (OH)₂ nanoplatelets vertically grown on electrospun carbon nanofibers for high-performance supercapacitors*. *ACS applied materials & interfaces*, 2015. **7**(40): p. 22669-22677.
- [59] Reddy, A.L.M., et al., *Multisegmented Au-MnO₂/carbon nanotube hybrid coaxial arrays for high-power supercapacitor applications*. *The Journal of Physical Chemistry C*, 2010. **114**(1): p. 658-663.
- [60] Gwon, H., et al., *Recent progress on flexible lithium rechargeable batteries*. *Energy & Environmental Science*, 2014. **7**(2): p. 538-551.
- [61] Xiao, X., et al., *Freestanding mesoporous VN/CNT hybrid electrodes for flexible all-solid-state supercapacitors*. *Advanced Materials*, 2013. **25**(36): p. 5091-5097.
- [62] Utsunomiya, T., et al., *Self-discharge behavior and its temperature dependence of carbon electrodes in lithium-ion batteries*. *Journal of Power Sources*, 2011. **196**(20): p. 8598-8603.
- [63] Pushparaj, V.L., et al., *Flexible energy storage devices based on nanocomposite paper*. *Proceedings of the National Academy of Sciences*, 2007. **104**(34): p. 13574-13577.
- [64] Hu, L., et al., *Highly conductive paper for energy-storage devices*. *Proceedings of the National Academy of Sciences*, 2009. **106**(51): p. 21490-21494.
- [65] Morris, R.S., et al., *High-energy, rechargeable Li-ion battery based on carbon nanotube technology*. *Journal of Power Sources*, 2004. **138**(1-2): p. 277-280.
- [66] Endo, M., et al., *'Buckypaper' from coaxial nanotubes*. *Nature*, 2005. **433**(7025): p. 476-476.
- [67] Niu, Z., et al., *Compact-designed supercapacitors using free-standing single-walled carbon nanotube films*. *Energy & Environmental Science*, 2011. **4**(4): p. 1440-1446.
- [68] Yao, B., et al., *Paper-based electrodes for flexible energy storage devices*. *Advanced Science*, 2017. **4**(7): p. 1700107.
- [69] Cheng, Y., et al., *Flexible and cross-linked N-doped carbon nanofiber network for high performance freestanding supercapacitor electrode*. *Nano energy*, 2015. **15**: p. 66-74.
- [70] Lee, S.W., et al., *Self-standing positive electrodes of oxidized few-walled carbon nanotubes for light-weight and high-power lithium batteries*. *Energy & Environmental Science*, 2012. **5**(1): p. 5437-5444.
- [71] Zhang, Y., et al., *High-performance lithium-air battery with a coaxial-fiber architecture*. *Angewandte Chemie International Edition*, 2016. **55**(14): p. 4487-4491.

- [72] Wang, B., et al., *Fabricating continuous supercapacitor fibers with high performances by integrating all building materials and steps into one process*. *Advanced Materials*, 2015. **27**(47): p. 7854-7860.
- [73] Pan, S., et al., *Wearable solar cells by stacking textile electrodes*. *Angewandte Chemie*, 2014. **126**(24): p. 6224-6228.
- [74] Chen, T., et al., *Nitrogen-Doped Carbon Nanotube Composite Fiber with a Core-Sheath Structure for Novel Electrodes*. *Advanced Materials*, 2011. **23**(40): p. 4620-4625.
- [75] Wang, J.-Z., et al., *Highly flexible and bendable free-standing thin film polymer for battery application*. *Materials Letters*, 2009. **63**(27): p. 2352-2354.
- [76] Wang, C., et al., *Functionalised polyterthiophenes as anode materials in polymer/polymer batteries*. *Synthetic metals*, 2010. **160**(1-2): p. 76-82.
- [77] Mihranyan, A., et al., *A novel high specific surface area conducting paper material composed of polypyrrole and Cladophora cellulose*. *The Journal of Physical Chemistry B*, 2008. **112**(39): p. 12249-12255.
- [78] Meng, C., C. Liu, and S. Fan, *Flexible carbon nanotube/polyaniline paper-like films and their enhanced electrochemical properties*. *Electrochemistry communications*, 2009. **11**(1): p. 186-189.
- [79] Xiao, Q. and X. Zhou, *The study of multiwalled carbon nanotube deposited with conducting polymer for supercapacitor*. *Electrochimica Acta*, 2003. **48**(5): p. 575-580.
- [80] Frackowiak, E., et al., *Supercapacitors based on conducting polymers/nanotubes composites*. *Journal of Power Sources*, 2006. **153**(2): p. 413-418.
- [81] Wang, J., et al., *Highly-flexible fibre battery incorporating polypyrrole cathode and carbon nanotubes anode*. *Journal of power sources*, 2006. **161**(2): p. 1458-1462.
- [82] Patil, D.S., et al., *Polyaniline based electrodes for electrochemical supercapacitor: Synergistic effect of silver, activated carbon and polyaniline*. *Journal of Electroanalytical Chemistry*, 2014. **724**: p. 21-28.
- [83] Zhou, C., et al., *Construction of high-capacitance 3D CoO@ polypyrrole nanowire array electrode for aqueous asymmetric supercapacitor*. *Nano letters*, 2013. **13**(5): p. 2078-2085.
- [84] Che, J., P. Chen, and M.B. Chan-Park, *High-strength carbon nanotube buckypaper composites as applied to free-standing electrodes for supercapacitors*. *Journal of Materials Chemistry A*, 2013. **1**(12): p. 4057-4066.
- [85] Gates, B.D., *Flexible electronics*. *Science*, 2009. **323**(5921): p. 1566-1567.
- [86] Bauer, S., *Flexible electronics: sophisticated skin*. *Nature materials*, 2013. **12**(10): p. 871-872.
- [87] Liu, J. and X.W. Liu, *Two-dimensional nanoarchitectures for lithium storage*. *Advanced materials*, 2012. **24**(30): p. 4097-4111.
- [88] Jabbour, L., et al., *Cellulose-based Li-ion batteries: a review*. *Cellulose*, 2013. **20**(4): p. 1523-1545.
- [89] Nyholm, L., et al., *Toward flexible polymer and paper-based energy storage devices*. *Advanced Materials*, 2011. **23**(33): p. 3751-3769.
- [90] Choi, K.H., et al., *Thin, deformable, and safety-reinforced plastic crystal polymer electrolytes for high-performance flexible lithium-ion batteries*. *Advanced Functional Materials*, 2014. **24**(1): p. 44-52.

- [91] Li, N., et al., *Flexible graphene-based lithium ion batteries with ultrafast charge and discharge rates*. Proceedings of the National Academy of Sciences, 2012. **109**(43): p. 17360-17365.
- [92] Zhu, H., et al., *Tin anode for sodium-ion batteries using natural wood fiber as a mechanical buffer and electrolyte reservoir*. Nano letters, 2013. **13**(7): p. 3093-3100.
- [93] Liu, L., W. Ma, and Z. Zhang, *Macroscopic carbon nanotube assemblies: preparation, properties, and potential applications*. Small, 2011. **7**(11): p. 1504-1520.
- [94] Ren, J., et al., *Elastic and wearable wire-shaped lithium-ion battery with high electrochemical performance*. Angewandte Chemie, 2014. **126**(30): p. 7998-8003.
- [95] Fang, X., et al., *A cable-shaped lithium sulfur battery*. Advanced materials, 2016. **28**(3): p. 491-496.
- [96] Lu, X., et al., *H-TiO₂@ MnO₂//H-TiO₂@ C core-shell nanowires for high performance and flexible asymmetric supercapacitors*. Advanced materials, 2013. **25**(2): p. 267-272.
- [97] Zhou, S., et al., *Cellulose Nanofiber@ Conductive Metal-Organic Frameworks for High-Performance Flexible Supercapacitors*. ACS nano, 2019. **13**(8): p. 9578-9586.
- [98] Han, Y. and L. Dai, *Conducting polymers for flexible supercapacitors*. Macromolecular Chemistry and Physics, 2019. **220**(3): p. 1800355.
- [99] Liu, L., Z. Niu, and J. Chen, *Flexible supercapacitors based on carbon nanotubes*. Chinese Chemical Letters, 2018. **29**(4): p. 571-581.
- [100] Zhu, S., J. Ni, and Y. Li, *Carbon nanotube-based electrodes for flexible supercapacitors*. NANO RESEARCH, 2020.
- [101] Wang, Q., et al., *Flexible supercapacitors based on carbon nanotube-MnO₂ nanocomposite film electrode*. Chemical Engineering Journal, 2019. **371**: p. 145-153.
- [102] Xu, T., et al., *Reduced graphene oxide/carbon nanotube hybrid fibers with narrowly distributed mesopores for flexible supercapacitors with high volumetric capacitances and satisfactory durability*. Carbon, 2019. **152**: p. 134-143.
- [103] Paulose, R. and M. Raja, *CuO nanoparticles/multi-walled carbon nanotubes (MWCNTs) nanocomposites for flexible supercapacitors*. Journal of nanoscience and nanotechnology, 2019. **19**(12): p. 8151-8156.
- [104] Niu, Z., et al., *Highly stretchable, integrated supercapacitors based on single-walled carbon nanotube films with continuous reticulate architecture*. Advanced Materials, 2013. **25**(7): p. 1058-1064.