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Carbon-Based Composites for Supercapacitor

Mohmmad Khalid, Prerna Bhardwaj and Hamilton Varela

Abstract

Supercapacitor is an emerging technology that promises to play an advance role in new generation electronic devices and systems. Carbon (activated carbon, graphene and carbon nanotube) have attracted tremendous attention for their potential applications in supercapacitor technologies due to their excellent mechanical strength, good electrical conductivity, high electron mobilities, excellent chemical stability in acidic and basic medium, good thermal stability in wide range of temperature, various morphological structures, and large specific surface area. This chapter aims to assess the current status of carbon nanomaterials and their composites for supercapacitor application by discussing the literature in this field and presenting a perspective for future research in supercapacitor technologies.

Keywords: carbon nanomaterial, mesoporous carbon, graphene, carbon nanotube, composite, supercapacitor

1. Introduction

The ever-growing need for energy because of continuous depletion of fossil fuels and associated increasing air pollution, has caused the urge of developing sustainable and clean energy sources. Renewable energy sources like solar and wind energy systems are intermittent in nature and do not show potential impact unless the effective energy storage system is connected. Though, traditional batteries are used to store the electricity produced by renewable sources, their toxic components and high cost have precluded them from wide adoption in modern technologies. The traditional capacitors which are made of two metal plates separated by dielectric materials show very little tendency to store energy as the batteries store. One of the latest energy storage systems is supercapacitor. It is an emerging technology that promises to play pivotal role in laying out the roadmap of energy storage system for future. Supercapacitor technology provides a bridge between traditional capacitors and batteries, where supercapacitors could store greater amount of energy than the conventional capacitor and are able to deliver more power than existing batteries. Energy in supercapacitors is directly related to the capacitance of the electrode, which can be boosted by developing highly porous carbon or by introducing pseudocapacitive materials into the carbon network. By this way, the energy storage capability of the supercapacitor electrodes can be increased at much high level than traditional capacitors. Besides having high power capability than batteries, their charge storing and charge releasing mechanism is efficiently reversible, so they are extremely promising candidates with long charge/discharge life. However, their energy storing capacity is still far behind

than the traditional batteries [1–5]. Therefore, there is a huge interest in increasing the energy density of supercapacitors. Almost all worldwide supercapacitor companies such as NESSCAP, Panasonic, AVX Maxwell and NEC use activated carbon as active material for the construction of commercial supercapacitors. However, progress in the development of other allotropes of carbon like graphene, carbon nanotube and other materials such as metal oxides and conducting polymers are continuing at a steady rate in supercapacitor applications. In order to boost the performance of supercapacitor, introduction of the pseudocapacitance in double-layer capacitive electrode seems to be a prevalent target amongst the current research and offers a good chance of developing the next generation high performance supercapacitor. The construction of a supercapacitor is slightly different from that of traditional capacitor, where electrolyte is the conductive connection between two electrodes unlike conventional capacitors [6]. These electrodes are polarized by applying suitable potential in the same way that batteries are polarized. The polarity of the supercapacitor electrodes is controlled by designing the supercapacitor assembly in the form of asymmetrical or symmetrical systems. Asymmetric supercapacitors, where positive and negative electrodes are different from each other, while, in case of symmetric supercapacitor both electrodes are consisted with the same materials in identical shape and size of the electrodes. The voltage of the supercapacitor devices in asymmetrical manner enhances by taking the advantage of the potential ends of two different electrodes. If the both electrode are same as in case of symmetrical supercapacitor design, the total value of capacitance is roughly half that of one electrode. On the basis of charge storage mechanism of the electrodes, supercapacitor can be divided into three types (**Figure 1**): (1) electrical double layer capacitors (EDLCs)—generally high surface area carbon materials and its derivatives are used for making electrodes, where ions are adsorbed on the surface of electrodes in the form of electric double layers (Helmholtz layer), one electrode collects positive ions and other is mirrored with opposite negative ions,

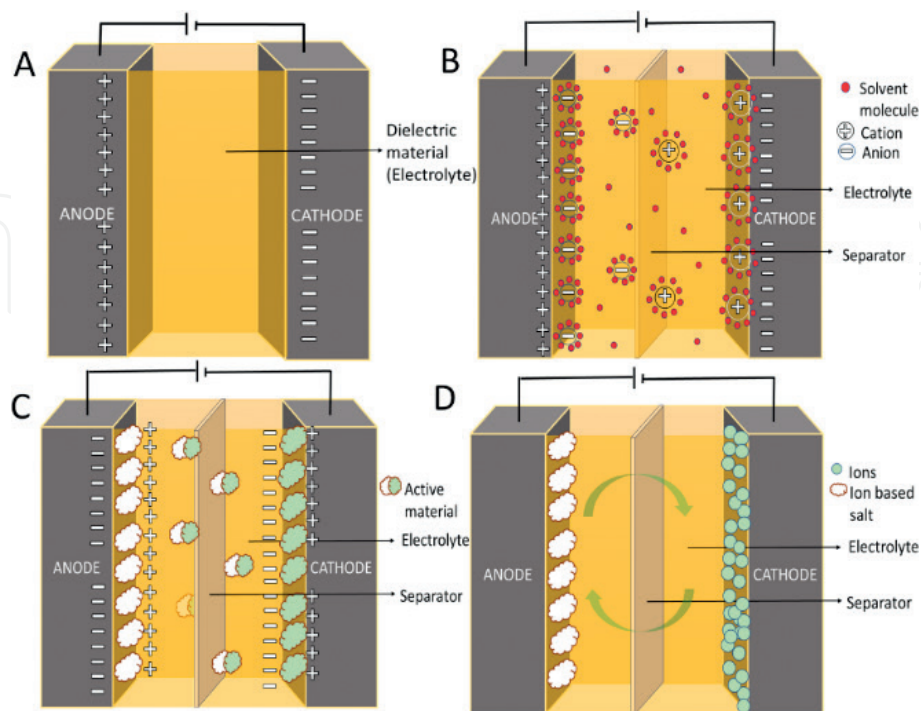


Figure 1. Schematic representation of (A) traditional capacitor, (B) electrical double layer capacitor, (C) pseudocapacitor and (D) hybrid supercapacitor [7].

therefore the total capacitance value of a double layer capacitor is the result of two capacitors connected in series, (2) pseudocapacitors—metal oxides and conducting polymers are used for fabrication of the electrodes, where redox (Faradaic) reactions occurs at the interface of electrode surface and electrolyte, It should also be noted that the suitable potential should be selected for the pseudocapacitive electrode materials, beyond the suitable potential window electrode will be degraded, and (3) hybrid supercapacitor—where electrodes are constructed using the significant features of both EDLC and pseudocapacitors, the most promising outputs seem to lie in the use of hybrid supercapacitors, which consists of carbon material and metal oxides/conducting polymer [8]. **Figure 1** demonstrates the schematic illustration of traditional capacitor, EDLC, pseudocapacitor and hybrid supercapacitor.

The fundamental equation (Eq. (1)) governing the capacitance of a traditional capacitor also stands for supercapacitors.

$$\text{Capacitance, } C = \epsilon_0 \epsilon_r A_e / d \quad (1)$$

Where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity, A_e is the surface area of the electrodes and d is the distance between them [9]. Hence, if we could increase the area of electrodes and decrease the distance between them then the capacitance will be improved.

Therefore, in order to choose an electrode material for a supercapacitor [10, 11] the following factors should be taken into account, i.e.,

- The specific surface area of the electrodes.
- Pore size distribution.
- The conductivity of the electrodes.
- The resistance to any oxidation/reduction on the surface of the electrode.
- Electrochemical stability of the electrolyte in the operating voltage.
- Resistance of the electrolyte towards electrode.
- Wettability of the electrolyte on the electrode.

In this chapter, we will focus on the advancement in research concerning use of carbon nanomaterials in developing supercapacitors.

2. Carbon nanomaterials

Carbon is one of the most abundant materials in nature. Thus, it is thought to be an economical choice for employing in energy conversion and storage technologies. Owing to the excellent mechanical strength, good electrical conductivity, high electron mobility, high chemical stability, large surface area and high tunable properties make carbon materials an ideal candidate for energy storage systems. Some of the common carbon materials which fulfill majority of the desired properties to act as an effective and efficient electrode for supercapacitors are—activated carbon, graphene and carbon nanotubes (CNTs).

2.1 Activated carbon

The basic properties of activated carbon (AC), i.e., low cost, high electrical stability and large surface area makes them most common materials used in commercial supercapacitors. ACs are generally produced by physical (thermal) and/or chemical activation of raw materials with high carbon content like coal, wood, etc. The physical activation is carried out by heating the raw material in absence of atmospheric air at very high temperatures, usually in the range 700–1200°C. The chemical activation process requires heating of carbon resource at a lower temperature of 400–700°C in presence of an activating agent such as zinc chloride, phosphoric acid, sodium hydroxide and others [12]. These two processes results in activated carbon with a high surface area (3000 m²/g) but with a pore size distribution in a wide range of macro-pores, mesopores and micropores (>50–2 nm) [13, 14]. The micropores are in general considered to be inaccessible for electrolyte ions thus not capable of supporting an electrical double layer. The mesopores have maximum contribution towards capacitance in an electrical double layer capacitor followed by micropores [15–17]. As discussed above, EDLC and pseudocapacitance both are surface phenomena, thereby, activated carbon with high surface area are perfect candidates for application as electrode material [12]. However, the experimental value of capacitance for activated carbon-based supercapacitor were found to be in the range 1–10 μF/cm² which is lower than the theoretical calculations [18]. This has been explained in detail by Kierzek et al. [19] and found that the surface area of the electrode material is not the only factor that determines performance of the electrode. There are other parameters which need to be considered for calculating capacitance for instance; shape, structure and size distribution of the pores along with the electrical conductivity and wettability of electrode in the particular electrolyte [12]. This gave birth to a new concept, i.e., use of mesoporous carbon (pore size 2–50 nm) for supercapacitor applications, which contributes in easy ion-transport over the conventional activated carbon and hence, demonstrates high power capability [20]. Fernández et al. [21] synthesized mesoporous carbon by carbonizing a mixture of poly(vinyl alcohol) and inorganic salt and showed a specific capacitance of about 180 F/g in aqueous H₂SO₄ electrolyte. The performance of mesoporous carbons can be further enhanced by controlled introduction of micropores. Xia et al. [22] showed that a specific balance between mesopores to micropores ratio can tune the specific capacitance to 223 F/g in 6 M KOH electrolyte at 2 mV/s scan rate with 73% retention cyclability. This improved capacitance has been attributed to the presence of hierarchical porous structure of the electrode material that consists interconnected micropores and mesopores, having the high surface area of 2749 m²/g, and large pore volume of 2.09 cm³/g. The interconnected porous structure facilitates the easy movement of ions. The performance of mesoporous carbon can also be improved by its functionalization. The functionalized mesoporous carbon can then act as an efficient pseudocapacitor electrode in addition to EDLC. Different functional groups like –OH, –COOH or –C=O can be easily introduced by activating the mesoporous carbon using strong acids like nitric acid, sulfuric acid or ammonium persulfate. For example, Jia et al. [23] pyrolyzed the mixture of milk powder and sodium hydroxide without any substrate resulting in the formation of N-doped mesoporous carbon which showed a high capacitance of 396.5 F/g at 0.2 A/g in the electrolyte solution of H₂SO₄ along with high stability in their capacitance value (95.9% capacitance retention after 2000 cycles at 50 mV/s). Ren et al. [24] have also observed that the capacitance of mesoporous carbon increased from 117 to 295 F/g (10 mV/s scan rate) after its treatment with nitric acid. **Table 1** summarize some carbon-based electrical double layer supercapacitors.

Electrode	Electrolyte (M)	Specific capacitance (F/g)	Current density	Retention capacity	Refs.
Layered NOMC	H ₂ SO ₄ (0.5)	810	1.0 A/g	50,000 cycles between 0 and 1.2 V	[25]
	Li ₂ SO ₄ (2.0)	710	1.0 A/g		
Ordered NOMC	H ₂ SO ₄	262	0.5A/g		[26]
	KOH	227			
hierarchically porous NOMC	H ₂ SO ₄ (0.5)	537	0.5A/g	10,000	[27]
NOMC from phenol-urea-formaldehyde	Ionic Liquid	225	0.5 A/g	1000	[28]
NOMC from aqueous assembly	Ionic liquid	186	0.25 A/g	—	[29]
N-doped micro-mesoporous carbon	KOH (6.0)	226	1.0 A/g	2000	[30]
NOMC		288	0.1 A/g	25,000	[31]

*NOMC, nitrogen-doped mesoporous carbon.

Table 1.

Summarizes some of the studies carried out by different research groups on capacitance values of N-doped mesoporous carbon materials.

Incorporation of heteroatoms such as nitrogen, boron, phosphorous, and sulfur (N, B, P, and S) into the carbon network by replacing some carbon atoms offers a significant change in the electronic, electrical, and surface charges properties of the carbon materials. Doping of heteroatom in carbon materials can be done either by in situ preparation of carbon or through post-treatment by heteroatom containing precursor. In particular, nitrogen doping has gained more attention in supercapacitor, because nitrogen doping not only improves the electrical conductivity and wettability but also contribute additional pseudocapacitance by enhancing the surface polarity and electron donor affinity of carbon. According to the studies made by Wang et al. [31], nitrogen doping facilitates the formation of well-defined mesopores and resulted improved electrochemical performance. Lin et al. [25] developed N-doped mesoporous few-layer carbon with a large surface area of 1900 m²/g for supercapacitor. It was reported that the as-developed few layer carbon showed highest ever specific capacitance of 810 F/g in three-electrode cell and 710 F/g in full cell at 1 A/g in 0.5 M H₂SO₄ and 2 M Li₂SO₄ electrolytes. The full cell device showed high stability with 50,000 repeating cycles between 0 to 1.2 V, and demonstrated highest specific energy of 23.0 W h/kg while maintaining the specific power density of 18.5 kW/kg in 2 M Li₂SO₄ electrolyte. However, the exact mechanism has not yet been confirmed but it is evident that the pyrrolic N, pyridinic N or quaternary N plays a crucial role in determining the ion flow towards the electrode, hence, influencing the capacitance of the electrode [32]. Nitrogen and phosphorus dual doped mesoporous carbon was also prepared, which reveals a high specific capacitance of 220 F/g at a current density of 1 A/g with excellent rate capability of 91% in a 6 M KOH aqueous electrolyte [33]. This value of capacitance was found lower than nitrogen and sulfur or nitrogen and oxygen dual doped mesoporous carbon synthesized using polyhedral oligosilsesquioxanes, which showed almost rectangular cyclic voltammogram curve in wide potential window from -2 to +2 V in ionic liquid electrolyte. These electrode materials showed a gravimetric and volumetric specific capacitance of 163 F/g and 106 F cm⁻³ at a current density of 0.25 A/g [34].

Another form of activated mesoporous carbon is the carbon nanofibers. The ease of preparation and highly mesoporous structure of these fibers exhibited excellent electrode material for electrochemical double layer capacitors [35]. Xu et al. [36] prepared polyacrylonitrile fibers followed by NaOH activation, and observed high specific capacitance of 371 F/g in the aqueous KOH (6 M), 213 F/g in non-aqueous LiClO₄ (1 M) and 188 F/g in ionic liquid electrolyte solutions. Mesoporous carbons have also been extensively studied in the form of composites with other active materials, including conductive polymers (polyaniline [37], poly3-hexylthiophene) and metal oxides (Manganese oxide MnO₂ [38, 39], Ruthenium oxide RuO₂ [11]). In particular, pristine conducting polymers with their excellent electrochemical properties have displayed capacitance 10–100 times higher than EDLCs but they suffer from some limitations like poor stability and short lifetime. Thus, combining the properties of conducting polymers with mesoporous carbon can result in an electrode material with optimum properties. For instance, chemical polymerization of polyaniline onto an ordered bi-modal-mesoporous carbon resulted in the formation of PANI nanowires growing out of mesoporous carbon substrate has been reported by Yan et al. [40]. The subsequent composite exhibited a specific capacitance of 517 F/g in 1 M H₂SO₄ electrolyte with 91.5% retention rate after 1000 cycles. Chen et al. have presented a facile synthesis of highly porous N-doped carbon nanofibers coated with polypyrrole by carbonization which showed a specific capacitance of 202 F/g in aqueous KOH (6 M) electrolyte at a current density of 1 A/g. It exhibited maximum power density of 90 kW/kg while maintaining high capacitance retention and cyclability. This kind of N-doped carbon nanofiber-based composites exemplifies unconventional and practically potential candidates for a competent electrode material for supercapacitors [41].

2.2 Graphene

Since the discovery of graphene by Novoselov and Geim in 2004, the research on this flattish material has received enormous attention. This flat sheet is a one-atom-thick layer of sp²-bonded, 2D honeycomb lattice of carbon with a fully conjugated structure of alternating C—C and C=C bonds. Its unique physico-chemical properties make this material a promising candidate for a large variety of applications. However, the use of graphene for most of the electronic applications often requires precise functionalization of individual graphene sheets into various device elements at molecular level. Therefore, surface functionalization of graphene sheets is essential, and researchers have devised various covalent and noncovalent chemistries for making graphene materials with the bulk and surface properties needed for many potential applications including energy conversion and storage. Its high mechanical strength, excellent electrical and thermal conductivity and large theoretical surface area (2600 m²/g) make this material particularly interesting for energy-storing devices. The other forms of carbon allotropes like Fullerene (0-D), carbon nanotubes (1-D) and graphite (3-D), all resemble the graphene hexagonal ring structure of graphene with different orientations in space, and each of these structures represent a unique property of its own [42]. Graphene, despite having exclusive physical and chemical properties and high theoretical surface area, it is not free from some drawbacks. The major drawback is of its sheet to sheet restacking (due to strong π - π interactions between its layers), which reduces the effective surface area rendering it nonfunctional for its application as multidimensional flexible electrode material. In order to overcome these shortcomings, constructive experiments have been made to fabricate nanoporous graphene by intercalation of other nanoparticles in graphene layers. Efforts are also being made to utilize the surface defects of crystal lattice structure of host material originated during

chemical synthesis for immobilization of electrolyte ions. In general, graphene activation can be achieved by methods like; introducing spacers between its layers, exfoliation method, templating technique or forming hydrogel by reducing graphene oxide. Thus, for application purposes graphene is not used as pristine but it has to be employed as reduced graphene oxide or activated graphene or doped graphene or graphene/metal oxide composites or graphene/polymer composites [43]. For instance, Zhang et al. [44] pioneered a new carbon material by chemical modification of one-atom thick layer of graphene (specific surface area $705 \text{ m}^2/\text{g}$), which demonstrated high specific capacitance values of 135 F/g in aqueous electrolyte and 99 F/g in organic electrolyte. In addition, it showed good retention ability over a wide range of voltage scan rates. Another group led by Vivekchand et al. [45] have reported the synthesis of graphene using thermal exfoliation of graphitic oxide at very high temperature of 1050°C . The product obtained had a high surface area of $925 \text{ m}^2/\text{g}$ and specific capacitance is 117 F/g in aqueous H_2SO_4 electrolyte. On the other hand, functionalization of graphene can also be achieved by controlled thermal exfoliation at low temperatures [46] without compromising its capacitance performance. Chemical functionalization of graphene oxide platelets grown on an intrinsically flexible, highly porous and ordered carbon films by nitrogen doping [47] has shown to enhance its electrical as well as supercapacitive properties. All the above-mentioned activation methods have led to the production of materials with high capacitance but for real-life practical application of these materials, another important factor to be considered is energy density. The commercially available batteries have higher energy density than supercapacitors. This means that supercapacitors can provide a very high energy pulse when required but can store less energy per unit weight, as compared to batteries. Liu et al. [48] have demonstrated the synthesis of 1-layer graphene in a curved form which restricted the face to face restacking of its sheets, hence, utilizing maximum possible electrode surface. This resulted in supercapacitor electrode material with very high specific energy density of 86 and 136 Wh/kg at room temperature and 80°C respectively at 1 A/g current density. Xu et al. [49] have also described the development of sponge-like graphene nanostructures that showed high energy density of 48 kW/kg . A new approach to efficiently exploit the surface of each layer of graphene structure is by employing the “in-plane” strategy in place of stacking [50]. In case of conventional (stacked) assembly, the entire electrochemical (specific) surface area cannot be used as some of the regions are unapproachable to the electrolyte ions (**Figure 2a**). Whereas the new structural design assists the percolation of electrolyte ions between graphene layers to reach the current collector. Consequently, facilitating the maximum usage of available specific surface area [50]. This type of in-plane 2D graphene supercapacitor has shown a maximum specific capacitance value of 250 F/g at current density 176 mA/g with good retention rate for 1500 cycles.

2.2.1 Graphene/metal-oxide composites

Variety of metal-oxides such as RuO_2 , MnO_2 , NiO , Fe_3O_4 , ZnO , TiO_2 , etc. have been explored for possible electrode material in supercapacitors. These so called active material, when added in an appropriate quantity to the graphene structure can result in excellent electrode material. The addition of metal oxide nanoparticle acts as nanospacers between the graphene layers to prevent its restacking. On the other hand, the flexible space between the 2-D graphene sheets provides a smooth horizontal way for the mobility of electrolyte ions improving its energy storing capacity. Lu et al. [51] have described the supercapacitor behavior of graphene-ZnO and graphene-SnO₂ composite materials. They found that electrochemical performance of graphene-ZnO composite was improved to a great extent in terms of capacitance

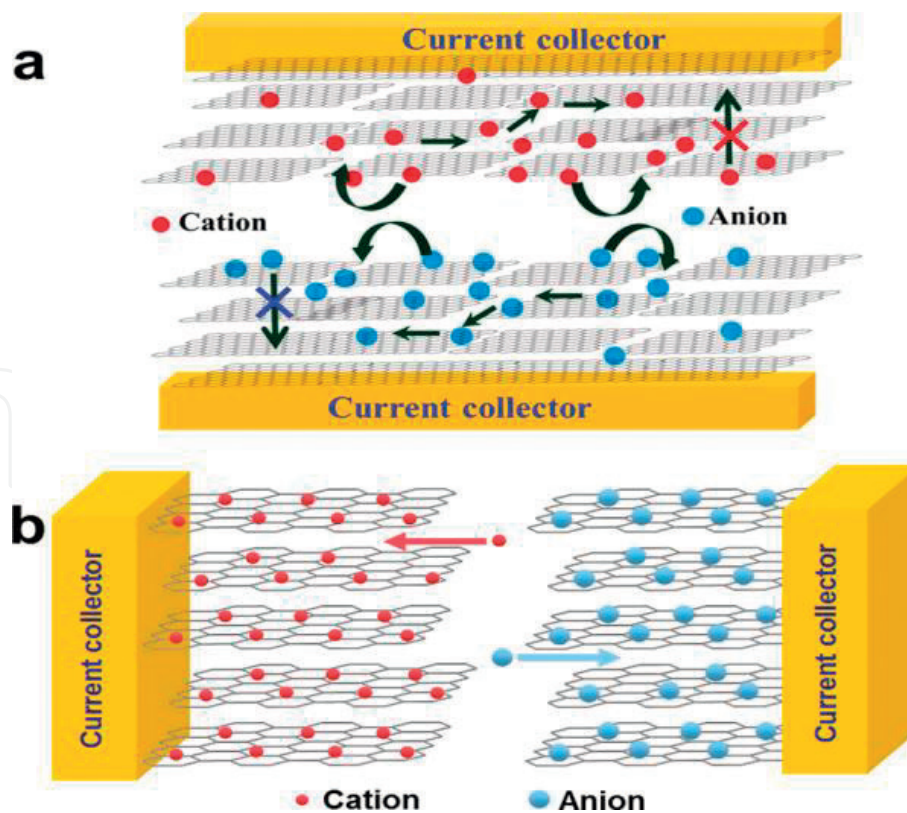


Figure 2. Schematic depiction of the (a) stacked geometry where all graphene layers are parallel to the current collectors, (b) operating principle in case of the in-plane supercapacitor device utilized for the performance evaluation of graphene as electrodes. Reproduced with permission from Ref. [50]. Copyright (2011) to American Chemical Society.

value and reversibility when compared to pristine ZnO or SnO₂ or graphene. Its specific capacitance was 61 F/g and energy density of 4.8 Wh/kg, which was also greater than that of graphene-SnO₂ samples. Graphene-MnO₂ composite with high MnO₂ content (78 wt.%) demonstrates a specific capacitance of 310 F/g at a scan rate of 2 mV/s. The authors claim that hybridization of graphene and MnO₂ caused increase in specific surface area resulting in higher conductivity and eventually high-performance rate [52]. Apart from conventional symmetric supercapacitors (using same material for both electrodes), a number of studies have been carried out to exploit the potential of asymmetric supercapacitors (using different material for each electrode) based on metal oxide/graphene composites [53]. The objective for fabrication of asymmetric supercapacitors is to obtain a higher energy density. The most vital step in its assembly is the choice of two such electrodes, which have same working potential range and sufficient wettability in the same electrolyte. The use of asymmetric model for supercapacitor allows the extension of operating potential window along with the improved capacitance performance rate. For example, Cao et al. [54] have established that an asymmetric supercapacitor developed using MnO₂ nanoparticles as anode and graphene as cathode exhibits a specific capacitance of 37 F/g and could operate up to voltage range of 2.0 V with 96% capacitance retention for 500 cycles. It displayed much higher energy density of 25.2 Wh/kg and power density of 100 W/kg when compared to 4.9 Wh/kg (MnO₂/MnO₂) and 3.6 Wh/kg (graphene/graphene) based symmetric supercapacitors.

2.2.2 Graphene/conducting polymer composites

The composites made from graphene and electrically conductive polymers [polyaniline, polythiophene, polypyrrole, poly(3,4-ethylenedioxythiophene)] have

attracted great deal of attention. The flexible and conductive nature of conductive polymers when combined with the intrinsic layered structure of graphene results in a material with potential for electrode application in supercapacitors. The increasing need for lightweight, flexible and smaller size supercapacitors in future electronics world has stimulated the interest in such graphene/polymer composite electrodes. These composites have improved mechanical strength and conductivity as compared to each material individually. They have been successfully implied in other applications like solar cells, fuel cells, transparent electrodes, etc.

The synthesis of graphene/polymer composite is facile and cost effective. Anodic in-situ polymerization of aniline on the graphene layered structure has been reported by Wang et al. [55]. The product formed was flexible, self-standing, strong and electrochemically stable. It showed a high electrochemical capacitance of 233 F/g at 2 mV/s scan rate with good stability for 2000 reversible cycles. The 2D structure of graphene can also be used to grow 1D nanorods of conductive polymer [56]. This represents an opportunity to utilize the maximum available surface area, hence, enhancing the energy storing capacity of the electrode. For example, graphene/polyaniline nanorod composite showed very high specific capacitance of 555 F/g in 1 M H₂SO₄ electrolyte with cyclic stability of 2000 cycles [57]. Some graphene and conducting polymer based composites have been listed in the **Table 2**. It is evident from the capacitance values in the table: that compositing conducting polymer with graphene convalesces its capacitance performance rate. However, this process may also lead to increase in the π - π stacking of graphene layer which in turn lowers the specific surface area of electrode. Therefore, there is a need to develop techniques for constructing 3-D structures of polymer matrix and introducing 1-D layer of graphene into it to avoid layer restacking.

2.3 Carbon nanotubes

Carbon nanotubes (CNTs) are quasi 1D nanomaterial formed by rolling one or more sheets of graphene concentrically. They have a unique cylindrical structure

Electrode material	Electrolyte (M)	Capacitance (F/g)	Current density	Retention cycle	Refs.
Graphene/Ppy	LiClO ₄ (0.1)	1510	—	—	[58]
GNS/PANI	H ₂ SO ₄ (1)	1130	—	1000	[59]
Graphene/PANI	H ₂ SO ₄ (1)	1126	—	1000	[60]
rGO/PANI	H ₂ SO ₄ (0.5)	970	2.5 A/g	1700	[61]
PANI/Graphene	HClO ₄ (1)	878	1.0 A/g	1000	[62]
GO/PANI	H ₂ SO ₄ (1)	746	0.2 A/g	500	[63]
Graphene/PANI	H ₂ SO ₄ (1)	640	0.1 A/g	1000	[64]
Graphene/PANI	H ₂ SO ₄ (2)	526	0.2 A/g	—	[65]
G-doped PANI	H ₂ SO ₄ (1)	531	0.2 A/g	—	[66]
GO-Ppy	H ₂ SO ₄ (1)	510	0.3 A/g	—	[67]
Graphene/PANI	H ₂ SO ₄ (2)	480	0.1 A/g	1000	[68]
Graphene/ Ppy	H ₂ SO ₄ (1)	420	0.5 A/g	200	[69]
Graphene/PEDOT	H ₂ SO ₄ (2)	342	0.02 A/g	—	[70]

Table 2.
 Some graphene and conducting polymer based composites and their capacitances.

with few micrometer length and diameter in the range of nanometers. CNTs are typically classified as single-walled (SW), double-walled (DW), or multi-wall (MW), corresponding to the number of graphene layers forming CNTs. The very first CNT was formally reported in 1991 by Iijima, when he closely observed the structure of carbon-soot obtained by an arc-discharge method using TEM technology [71, 72]. Since then, both SWCNTs and MWCNTs have been extensively studied for their numerous possible applications. The presence of hexagonal lattice structure of graphene with sp^2 bonded carbon atoms in CNTs contributes to its excellent properties like electrical and thermal conductivity, high mechanical strength, optimum chemical stability and low mass per unit volume [73]. In terms of tensile strength, CNTs are hundred times tougher than steel. They have Young's modulus of about 1.2 TPa (1 TPa for SWCNTs and 1.28 TPa for MWCNTs) and can withstand large strains before mechanical failure. The electrical conductivity of CNTs depends on their structure, i.e., MWCNTs with concentric tubular structure having inter-layer distance of about 0.34 nm shows metallic conductivity. Whereas, the SWCNTs have shown both metallic or semiconducting behavior depending on their chirality and diameter size. CNTs have been successfully synthesized and employed in various application namely chemical sensors, field emission sources, nanotweezer, scanning microscope probe tip, electro-mechanical actuators, etc. CNTs have a large crosswise dimension (<1, 1–2, 2–5, 5–10, and >10 μm), high specific surface area (SWCNT > 1600 m^2/g , MWCNT > 430 m^2/g), and excellent carrier mobility for both ions and holes (15,000 cm^2/Vs) and are being widely used as the active electrode in supercapacitors [74]. This can be attributed to the fact that CNTs have high aspect ratio so they tend to get entangled and form a porous structure with nanotube network skeleton. It also creates a mesoporous open central canal in case of MWCNTs. This provides an easy pathway for the electrolyte ions to move freely between electrode/electrolyte during charge and discharge cycles. In order to minimize the size of supercapacitor-based power cell for its real-world application, it is important to work towards high power density electrodes. Niu et al. [75] have fabricated a supercapacitor based on MWCNTs, which showed a capacitance value of 102 F/g, high power density >8 kW/kg and an energy density of ~1 Wh/kg in H_2SO_4 electrolyte. They also showed that such electrode material did not require any binder and was self-sufficient. A supercapacitor based on SWCNT electrode as reported by An et al. [76] showed comparatively higher specific capacitance value of 180 F/g in KOH (7.5 M) electrolyte solution with power density of 20 kW/kg and energy density in the range 7–6.5 Wh/kg. Similar to other carbon materials, CNTs are also being more commonly used as its composite. CNT/conductive polymer composite have attained a lot of attention in terms of its capacitive applications as it combines high pseudocapacitance of conductive polymers with excellent mechanical properties of CNTs. They can be synthesized chemically or electrochemically. The electrochemical method involves either deposition of polymer on a CNT electrode, or co-deposition of polymer and CNT on electrode. The composites formed by electrochemical co-deposition are found to be most homogeneous. They show enhanced electron delocalization due to the presence of conjugated carbon chain and an unusual interaction between the polymer and CNTs. As a result, they exhibit excellent electrochemical charge storage properties and fast charge/discharge switching, making them promising electrode materials for high power supercapacitors.

2.4 Hybrid carbon materials

More recently, several attempts have been made to merge the unique properties of several carbon-based nanomaterials to form a hybrid material. For instance, Li

et al. [77] have reported synthesis of a flexible, light weight and self-standing film by combining activated carbon, CNT and reduced graphene oxide. The hybrid film is prepared by weaving 3D porous framework using CNTs and graphene that was further used to accommodate activated carbon particles using their intrinsic van der Waals force. In such a material, each component has an important role to play like carbon particles block the restacking of graphene structure and the CNTs improve electronic conductivity. The AC/CNT/rGO electrode thus formed showed a specific capacitance of 101 F/g in organic electrolyte at 0.2 A/g current density with a maximum energy density of 30 Wh/kg. Supercapacitors, are generally known to work only in a narrow temperature range. However, a flexible hybrid film consisting of CNTs and rGO has been reported to be able to operate between the temperature range -40 and 200°C . The electrode material exhibited a maximum area specific capacitance of 330 mF/cm^2 with energy density of 1.7 mWh/cm^3 and 90% retention even after 100,000 cycles [78]. More interestingly, CNTs were intercalated between graphene sheets to retain high specific surface area by minimizing its aggregation [79], where π - π interaction between graphene sheets and CNTs also improve the electrical conductivity and mechanical strength. Similarly, Yu and Dai produced hybrid films of CNT and graphene interconnected network with well-defined nanoporous structure [80], which exhibited a specific capacitance of 120 F/g in 1 M H_2SO_4 electrolyte and an almost rectangular cyclic voltammogram even at high scan rate of 1 V/s. Yu et al. developed a continued CNT and graphene hybrid fiber with well-defined mesoporous structure [81], which showed specific surface area as high as $396\text{ m}^2/\text{g}$ with an electrical conductivity of 102 S/cm. The corresponding fiber-shaped supercapacitor demonstrate a volumetric specific capacitance of 305 F/cm^3 at 26.7 mA/cm^3 current density and a volumetric energy density of 6.3 mWh/cm^3 , which is comparable to the energy density of a 4 V-0.5 mAh thin-film lithium ion battery.

3. Summary and perspective

Carbon has already made a revolution in the world. Now its surface engineering with variety of functional materials and nanoporous structure are the fascinating parts of the research. In the light of the aforementioned studies, a broad range of carbon nanomaterials with various dimensions and unique morphological structure designs have been made and successfully implemented in energy storage device fabrication technologies. The incorporation of heteroatoms into the carbon network provides a new class of carbon materials with unique properties unmatched with parental carbon materials. Compositing carbon nanomaterials with metal oxides/ conducting polymers having pseudocapacitance increases energy density largely but compromise with rate capability and cycling life. In this chapter, we have thoroughly conferred the recent progress of carbon nanomaterials based supercapacitors. The potential of carbon nanomaterials and its composites for supercapacitors is in resolving the foreseen of clean energy mitigation. Various materials, methods and technologies have been employed in finding a solution for an energy storing device with high capacitance along with high energy/power density. No doubt, carbon materials are potential candidates for supercapacitor electrode materials but they need a supporting active material to enhance their performance. Nevertheless, increase in specific capacitance value, power density and energy density in certain cases gives a hope that if the research continues in right direction then one-day carbon material based supercapacitor can bring a new revolution in the electronic world. We are confident that the information presented in this chapter would definitely help in the research and development of carbon nanomaterials based supercapacitors.

Acknowledgements

Authors would like to place on record thanks to the São Paulo Research Foundation (FAPESP) for financial support under ongoing projects of Grant No. 2017/00433-5 and Grant No. 2013/16930-7.

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