

RESEARCH PAPER

Graphene-based Supercapacitors and their Future

Sneha R Prasad, Shivangi Srivastava, Rupali Nagar, and Neeru Bhagat*

Department of Electronics and Telecommunications Engineering, Symbiosis Institute of Technology, Symbiosis International (Deemed University) Lavale, Pune, India

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ABSTRACT

With the increasing use of electronics in everyday life, safe and effective energy storage devices have become a necessity. Methods to implement maximum possible charge storage along with compact size, economic feasibility, faster charging and discharging rates are few goals currently being chased by the research community. Supercapacitors can be a revolutionary technology in this regard and contribute to sustainable development in the energy sector. Novel methods of electrode material synthesis and design that are economically feasible, environmentally friendly and exhibit better charge storage capabilities are needed for developing next generation supercapacitors. The journey of graphene-based supercapacitors from 2006 has been quite interesting. However, with graphene and other carbon-based materials, new developments are required to meet the high-power density requirements. This paper discusses the design of future supercapacitor electrodes based on ordered mesoporous carbon structures. The ordered nature of mesoporous network would ensure better electrode electrolyte interaction and faster charge movement resulting in better charging rates. Such supercapacitors are expected to outperform even the best contemporary supercapacitors of today.

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INTRODUCTION

Supercapacitors are widely known as Energy Storage Systems capable of delivering instant high power. These are also known as Ultracapacitors as they can store significantly greater energy within the same volume as compared to a rechargeable battery and provide very fast charge-discharge rates. They can handle high values of current without causing supercapacitor cell degeneration or thermal runaway and thus can provide a safe alternative to batteries. The main distinction between supercapacitors versus rechargeable batteries is that the technique for charge storage in a battery is chemical, whereas in supercapacitors

it is physical in nature. Some advantages of supercapacitors over batteries are their relatively simpler charging circuit, higher overall safety, very high charge-discharge rate that is 100-50% in 30-40 days, and effectively unlimited number of charge-discharge cycles. They are also smaller in size and more environmentally friendly. The challenge in the wide-scale commercialization of supercapacitor technology is boosting their charge storage and delivery capabilities to match with lithium-ion or nickel-metal batteries. The above properties of supercapacitors make them the ideal choice in applications like inverter, wearable gadgets, electronic watches, and batteries of

* Corresponding Author Email: neeru.bhagat@sitpune.edu.in



electric cars where high specific power is required.

Supercapacitors are built like a parallel plate capacitor. These comprise of a separator sandwiched between either two identical (symmetric) or different (asymmetric) electrodes. The electrodes are soaked in a suitable electrolyte to ensure easy charge transfer. The performance of supercapacitors is measured in terms of energy density or specific energy, charge density, charging/discharging rates, etc. Energy density of supercapacitors refers to the amount of energy per unit of volume that can be obtained from charged supercapacitors. The unit of measurement of energy density is Wh/kg (gravimetric) or Wh/L (volumetric). Energy density is directly proportional to the duration of electrical power supplied for the same mass (volume) of the electrode material. Typical values of specific energy for a capacitor are < 0.1 Wh/kg whereas that of supercapacitors lies between 1 - 10 Wh/kg [1]. Supercapacitors are high-energy alternatives to regular capacitors and thus suitable for applications that require a sudden burst of power. However, they still cannot store large amounts of charge for a long time as needed for regenerative braking of electric vehicles [2]. Thus, supercapacitors occupy a position between capacitors and batteries in terms of functionality, combining the electrochemical aspects of both devices.

CONSTRUCTION AND MECHANISM OF A CONVENTIONAL SUPERCAPACITOR

Supercapacitors function via different energy storage mechanisms. The first is the Electrical Double Layer Capacitance (EDLC) [3]. The electrodes of a supercapacitor are held at a certain operating voltage. This voltage creates an electric field between the electrodes and accelerates ions through the supercapacitor. Ions in the supercapacitor electrolyte move towards the electrode with opposite polarity and get physically adsorbed on reaching the electrode. This interface thus has an electrode of certain polarity and some adsorbed ions of opposite polarity forming a layer of charge. Effectively, the interface can be regarded as two layers of charges with opposite polarities thus giving rise to the model of a parallel plate capacitor whose two plates are held at opposite polarities. Hence the name "double layer". The capacitance of a parallel plate capacitor varies inversely with the inter-plate region. Since the separation between electrode surface and

oppositely charged adsorbed ions is typically a few nm, these serve to enhance the capacitance to a large extent. It is noteworthy that this type of interaction is purely electrostatic in nature and no transfer of charge to- or from- the electrode to the electrolyte takes place. Now, if a redox species is present at the electrode-electrolyte surface, then an actual transfer of charges can take place across the double layer. This second mechanism is predominant in polymer or metal oxide-based electrodes. Here, charge transfer in addition to double layer formation is responsible for charge storage. Next, if the ions can diffuse through the electrode materials and intercalate/de-intercalate between the electrode layers, this constitutes the third mechanism of charge storage and is seen in pseudocapacitors. This process is similar to that of lithium-ion batteries and supports the electrochemical storage of electricity in electrochemical capacitor and is termed as pseudocapacitance. Due to the absence of redox reactions in the EDLC charge transfer process, such supercapacitors exhibit very fast response to change in potential (in comparison to slower faradaic reactions in pseudocapacitors) but they suffer from lower energy density since most of the charged ions are present only on the surface of the electrodes [4].

Another factor influencing the supercapacitor performance is the electrolyte selection. An aqueous electrolyte is usually used for ceramic separators and organic for paper and polymer-based separators. The electrolytes must be highly concentrated to provide a conductive medium for proper charge transfer. The standard concentration for these is approx. 0.2 molar [5]. Some commonly used organic electrolyte solvents include acetonitrile (ACN) in liquid form and propylene-carbonate (PC).

The salts used along with these solvents are tetraethylphosphonium tetrafluoroborate and triethylmethylammonium tetrafluoroborate [6]. Ionic liquids and gel-based electrolytes are considered ideal for supercapacitors due to their electrochemically and thermally stable properties. They are not volatile, do not catch fire easily and provide a cell voltage of 4.5 to 6 V in comparison to aqueous solvents that are limited to 1 V. But on comparing organic and ionic electrolytes, ionic liquids show a much lower conductivity of less than 10 mS/cm while organic liquids reach 1 S/cm. This limitation of ionic electrolytes can be overcome

by pairing the electrolyte with a well selected electrode material which aids charge transfer and results in high charge-discharge rates. Choosing the right electrode material is thus crucial for harnessing the full potential of supercapacitors. Thus, advances in materials science must continue to produce newer materials, better electrolytes, improving performance of existing materials, easing synthesis procedures, and improving electrode design. Fig. 1 shows a representative diagram of cross section of supercapacitors consisting of a separator sandwiched between porous electrodes soaked in electrolyte. There are current collectors on both sides forming a bridge to the supercapacitor leads. This kind of arrangement is very common in the supercapacitors used nowadays.

EMERGENCE OF GRAPHENE USE IN SUPERCAPACITORS

Pre-graphene era

Several materials have been tested as supercapacitor electrodes. Carbon and carbon derivatives such as activated carbon [7], carbons that are derived from common carbides [8] and carbon nanotubes (CNTs) [9] have been the most popular materials used throughout history. There are several formations of mesoporous carbons such as nanosheets, tubes and fibres that allow to fine tune properties of supercapacitors by varying their preparation methods and physical structure. Maksoud et al. discussed the innovative method of manufacturing 3-D porous carbon nanosheets in large scale through use of tree bark that displayed good capacitance of around 340 F/g [10]. The method while being non-toxic demonstrated an innovative way to

prepare carbon and carbon-based materials for use in supercapacitor electrodes [11]. Other electrode materials, including metal oxides [12] and polymers [13], have also gained popularity. Materials such as Ru (ruthenium) depositions on carbon aerogels and oxidized glassy carbon sheets have also been investigated [14,15]. Studies were also conducted on alternative materials such as polythiophene, polyparaffluorophenylthiophene [16] and different variations of carbon and metal oxide-based nanomaterials which have made notable improvements in measured values of total energy density and specific capacitance. In 2000, Frackowiak utilized multiwalled carbon nanotubes synthesised by decomposition of acetylene and chemical vapour deposition of propylene [17]. These performed well; specific capacitance varied from 4 to 135 F/g, apart from a gradual decrease in pseudocapacitance with use in comparison to previous efforts. Performance improvements achieved by use of CNTs encouraged use of graphene which was soon to be discovered.

Structure and properties of Graphene

Graphene shows special properties mainly due to inherent defects in low purity samples. Graphene has been synthesised via both top-down and bottom-up approaches. Top-down approach involves distributing a single stack of carbon and applying chemical, thermal or physical methods to generate single layer graphene sheet. In bottom-up approach, the honeycomb structure of graphene layer is built atom by atom [18]. Some ways to synthesise graphene include mechanical exfoliation [19,20], chemical vapour deposition [21] and chemical exfoliation [22,23,24]. Graphene displays good flexibility and tensile strength as

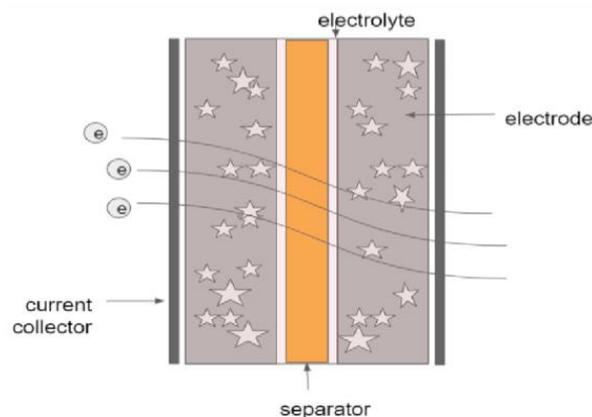


Fig. 1. Representative diagram of cross-section of a supercapacitor

it can stretch up to 120% of its original length. It has excellent electrical and thermal conductivity and can allow up to 98% of light transmission. It is lightweight and strong and thus used for several day-to-day applications such as solar cells. It is a highly stable substance due to strong C-C atomic bonding in its plane. Since there is no gap between the conduction band and valence band, it has very high electron mobility up to $15,000 \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$ [25,26,27]. Some drawbacks of graphene are that it is usually expensive to manufacture layers of uniform thickness. It is also hydrophobic and thus unsuitable for use in certain applications.

The graphene era

In the last decade, new discoveries made with reference to mesoporous carbons and graphene led to significant improvements in several characteristics of supercapacitors and rapid developments in the fields of automotive, medical, and wearable technology. Since its discovery in 2004 by Novoselov [28] who described it as a mono-crystalline graphitic film, graphene has been applied in multiple fields in the electronics industry. This network of carbon atoms organized in a thin layer resembling a honeycomb-like structure along the 2-D plane is a good conductor of heat and electricity. Thus, it is used for several applications in nanoelectronic devices [29]. Graphene's use in supercapacitors is driven by its unique and desirable properties. Of the various allotropes of carbon, graphene has high effective surface area, good chemical stability, high mechanical strength, serves as an excellent canvas to decorate transition metal oxides, conducting polymers, and elements like boron (electron withdrawing) and nitrogen (electron donating) which can attract or contribute to the graphene plane's pi-electronic charge density. Graphene and its innate defects play a vital role in charge storage mechanisms by providing the best combination of high electrochemical surface area, porosity, tunable electron densities etc. Though the nanostructured graphene and its pores can store charge via the double layer mechanism, graphene composites can have different charge storage mechanisms. Graphene composites with transition metal oxides or conducting polymers can allow faradic charge transfer along with double layer formation at electrode-electrolyte interface. The popularity of graphene in the field of supercapacitors is due its huge potential to form

composites and function via more than one type of charge storage mechanism. Structural flexibility of graphene sheets, conductivity and good mechanical strength are desirable attributes for forming graphene-polymer blends with potential application in wearable technology. This paper first discusses the evolution of materials based on graphene over the years and its function when used in supercapacitor electrodes to provide a concise summary of how supercapacitor technology has evolved as research progressed. Then, the future of graphene-based supercapacitors in terms of electrode design is discussed.

Jang et al. in 2006 started the first research on future development of energy storage devices. They noted that supercapacitors function on surface ion absorption and redox reactions [30]. The authors used nanostructured graphene electrodes that allowed easy passage of electrolyte through them. The abundance of Li^+ ions at the anode and in the electrolyte ensured availability of ion movement across the electrode. This coupled with large surface area of electrode materials aided in better contact of the ions with graphene electrodes and were the primary reasons for the drastic increase in energy density. They also focused on the architecture of lithium-ion exchange cells and found that when these cells were combined, they produced 30 times better results than symmetric supercapacitors that are used conventionally. The team proved this by calculating the energy density as 160 Wh/kg of the lithium-ion cell [30]. In 2008, Rao and co-workers investigated three different methods of preparation of graphene and applied these as electrode materials. The methods of preparation included thermal exfoliation of graphite oxide [31], heating nano diamond in helium atmosphere and thus producing graphene and finally by using camphor and nickel nanoparticles [32]. These methods led to formation of graphene, but the structure and defects therein were different. They proved that the characteristics of supercapacitor electrodes formed by different graphene forms were directly in relation to graphene quality and number of layers. The team reported specific capacitance of 117 F/g by using thermally exfoliated graphene. By using ionic liquid, a specific capacitance of 75 F/g and energy density of 31.9 Wh/kg was achieved [33]. This research paved the path for researchers to explore different methods to synthesize graphene with different properties.

In 2010 Liu et al. discovered that one of supercapacitors' key limitations was their poor energy density (5-10 Wh/g). This is very low as compared to lead acid, Ni-MH, or lithium-ion cells, and hence they theorized that a supercapacitor combining the qualities of both batteries and capacitors would be ideal. So far for an electrical double layer (EDL) capacitor, an activated carbon electrode having a large surface area was the preferred choice. On the other hand, pseudocapacitors used materials such as polyaniline (PANI) [34]. A conductive polymer-graphene redox pair yielded energy density of 39 Wh/kg using a conductive polymer-graphene redox pair's pseudo capacitance method [35]. However, this proved unsuitable for applications that required rapid charging and draining. Thus, application of ionic liquids was proposed to overcome this drawback. Liu used mesoporous curved graphene sheet electrodes with ionic liquid EMIMBF₄ (1-ethyl-3-methylimidazolium tetrafluoroborate) that yielded an energy density of 90 Wh/kg at room temperature which was comparable to a Ni metal hydride battery. At a current density of 1 A/g and a potential of 4 V, the observed specific capacitance ranged between 100 and 250 F/g [36].

The era of graphene and its composites

In 2012, Strong and group recognized the need for an electrochemical capacitor that has both a high density in energy and increased rate of discharge. The researchers aimed to modify the process of graphene synthesis. The maximum specific capacitance observed in single layer graphene till date was well below the theoretical calculated value of 550 F/g [37]. The authors developed a method to synthesize solid state graphene from Graphene Oxide (GO) using irradiation by an Infrared laser and the resultant graphene was termed as Laser Scribed Graphene (LSG). The resulting films showed a conductivity of 1738 S/m which was significantly more than any carbon-based film and allowed the devices to be very thin. Some advantages of LSG electrodes were presence of open pores, a large and accessible specific surface area of the LSG (1520 m²/g) and the simultaneous reduction and exfoliation using laser that prevents agglomeration of graphene. These devices were very thin (< 100 micrometer) and could be used in micro device applications having both stacked as well as spirally wound structures. To estimate the performance of these LSG samples

the cyclic voltammetry (CV) and galvanostatic charge discharge (CC) methods were used. The capacitors exhibited a specific capacity of around 265 F/g with a maximum current density of 1000 A/g. Similarly, some other studies have shown use of chemically modified graphene in ultracapacitors for displaying a specific capacitance of up to 135 F/g in aqueous solutions [38]. Dong et al. produced a 3-D graphene and cobalt oxide for application in supercapacitor electrodes the same year [39]. Some of the underlying issues observed by them were the abundance of inherent defects during the synthesis of graphene oxide compromising the intrinsically increased surface contact area of graphene. Also, high conductivity value of graphene was reduced due to contact resistance. They utilized chemical vapor deposition to create 3-D graphene/Co₃O₄ nanowire foams to solve these challenges for achieving a 768 F/g at 10 A/g to 456 F/g at 30 A/g of specific capacitance which was more than graphene with MnO₂ [40], NiO [41] or PANI [42] electrodes that were reported previously. Over time 3-D graphene has been developed in several domains based on bottom-up approaches such as CVD and self-assembly of graphene oxide [43,44]. A 3-D structure that was mechanically strong and had good electrical conductivity along with good thermal stability was reported by Shi, Xu, Sheng and Li [45]. The material employed was a self-assembled graphene hydrogel (SGH) with a large specific capacitance equal to 155 F/g. It was made by hydrothermally reducing GO sheets in a single step [45]. In the year 2012, Yang et al. developed a 3-D macro-porous chemically modified graphene (CMG) film using polystyrene colloid by an embossing technique [46]. The porous e-CMG films laid the groundwork to form a combination with pseudocapacitive oxides such as MnO₂, boosting cross-surface electron movement. A notable achievement was that these films reached a value of 389 F/g at 1 A/g and maintained 97.7% retention of initial specific capacitance at a high rate of 35 A/g.

In 2013, a composite of GO and single walled nanotubes (SWNTs) was discovered to have a significant energy density of 63 Wh/kg as well as a specific capacitance of approximately 201 F/g [47]. It was further demonstrated that a colloidal suspension of GO [48,49] and SWNT reduced by hydrazine through a co-reduction process resulted in a 3-D hybrid structure. This improved the uniformity and carbon nanotube electrochemical

performance. The graphene supercapacitor that was obtained showed a significant specific capacitance (261 F/g; single electrode) as well as energy density (123 Wh/kg; two-electrode configuration). These electrodes were reported to have extensive uses in the realm of energy storage, including hybrid automobiles [50].

The above studies clearly indicate that the methods of preparation of materials, their surface areas, pore sizes, conductive fillers and chemical properties of composites directly influence the performance of supercapacitors, specific capacitance values, energy density, charge-discharge rates, etc. These aspects combined with the design of electrodes, choice of electrolytes, and innovating structure of nanomaterials for better interaction between electrode materials and electrolytes can help develop better performing supercapacitors.

Asymmetric supercapacitors

This section discusses the different approaches adopted by researchers to improve supercapacitor performance. Cao et al. investigated symmetric and asymmetric supercapacitors, in 2013 [49]. They developed high voltage asymmetric supercapacitors using manganese oxide (MnO_4) at the cathode and graphene at the anode. This manganese oxide was obtained from the reduction of KMnO_4 in dimethylformamide (DMF) where they could witness the crystallization process and the amorphous structure of the MnO_4 nanoparticles [51]. The graphene electrode in this asymmetric cell exhibited capacitance of 37 F/g, an energy density of 25.2 Wh/g and a power density of 100 W/kg [52]. In 2014, Wu et al. were able to prepare a new kind of 3-D ultra-thin graphene NiO hybrid using a nano-casting process and chemical bath deposition of NiO [53]. This method allowed thinner active material that helped the charged particles to travel easily, along with the capacitive characteristics of NiO. Since the material was devoid of binder material, the specific capacitance for this hybrid was 425 F/g at a current density of 2 A/g while demonstrating strong electrode/electrolyte contact. Developments made in the asymmetric supercapacitor area by Couly et al. in 2017 resulted in much better performance [54]. Their approach involved the use of micro-sized and flexible asymmetric supercapacitors. It was observed that MXene, which is a metal carbide in 2-D, in PVA (poly vinyl alcohol) gel showed

swelling of layers and re-stacking of MXene flakes [55] resulting in an asymmetric design which improved electro-chemical performance and other relevant characteristics of the electrode. Thus, they obtained 8.6 Wh/cm³ of volumetric energy density and 0.2 W/cm³ of power density [56]. The same year, Moysowicz et al. studied graphene production for electrodes used in supercapacitors using hydrothermal treatment. The porous structure of GO was observed using electrochemical measurement and low porosity of rGO was noticed. van der Waals interaction caused re-stacking during hydrothermal conditions [57,58]. The group also observed that low current density (0.2 A/g) resulted in maximum specific capacitance of 262 F/g. At high current density (20 A/g), capacitive performance of 198 F/g was recorded. Thus, they proved that hydrothermal processes can be used to develop high performance graphene-supercapacitor electrodes with better rate capability [59].

THE PRESENT-DAY SUPERCAPACITORS -

Recent developments in wearable technology have given rise to a need for high power flexible micro supercapacitors [60]. Since these electrodes are susceptible to deterioration over time and with regular use, new techniques of micro-fabrication are needed [61]. Electrodes free of polymer binders, separators and conductive additives have improved utilization ratio and volumetric capacitance of superconductor devices and have also simplified the process of fabrication considerably [62,63,64]. He et al. presented an electrochemical exfoliation technique for production of porous 3-D graphene surface in 2018. This was then used to fabricate thin paper-like electrodes of thickness approx. 80 μm using electrolyte infusion [65]. H_3PO_4 (phosphoric acid)/PVA was casted on exfoliated graphene and graphite foil. This could be easily cut into required sizes and was mechanically robust enough to be used in wearable devices. A volumetric capacitance of approximately 3.4 F/cm³ was achieved at an applied current density of 5 A/cm³ and showed a cyclic performance of 20000 charge-discharge cycles, prompting further research in wearable device technology. Fig. 2 shows the improvement in supercapacitor performance from 2008 to 2021. This improvement has been due to development of better synthesis methods, newer materials and better electrode designs and thus indicates that

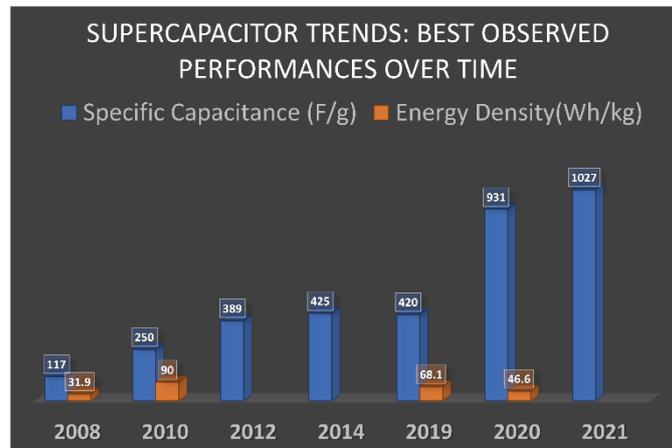


Fig. 2. Progress of supercapacitors over the years measured via specific capacity and energy density [23], [26], [36], [43], [57], [58], [69] and [106].

supercapacitors can be potential contributors in the journey towards sustainable development.

The trends of energy density and power density over a period of three decades for a battery and a supercapacitor have been discussed by Zhao et al. [66]. They found that while batteries showed an improvement of about 3 times in terms of their energy densities, supercapacitors showed about 20 times increase. Further, supercapacitors showed an increase of about 25 times in their power density values over a period of 1990-2020. The batteries chosen for research were Li-ion batteries while supercapacitors included carbon based EDLC, pseudo-capacitors, hybrid capacitors and more.

Development of sustainable and environmentally friendly technology has always been a challenge. To tackle the problem of waste management, in 2019 Elessawy et al. used polyethylene terephthalate (PET) bottles and urea waste to produce nitrogen for doping in GO films [67]. This nitrogen fixation improved charge propagation and ion diffusion and provided 405 F/g value of specific capacitance at 1 A/g and 68.1 Wh/kg value of energy density. Further, several attempts have been made to increase the area of contact surface of graphene as reported-by Shi et al. in the year 2020 [68]. Modern Hummer's method was used to produce GO followed by graphene-based nanocarbon (GNPC). This material coupled with an organic electrolyte where at 1 A/g, the specific capacitance is 420 F/g, that is very close to the ideal value. They achieved a power density of 304 W/kg, which was ten times higher

than devices available in the commercial market. In 2021, Chakrabarty and group used quantum dots along with graphene [69]. In this study CeO₂ quantum dots of size 5 nm were deposited on an rGO film giving a specific capacitance of 135 F/g. Further, the group created four samples ranging from CRGO1 to CRGO4, where the samples had different weights of GO as 10, 25, 50 and 100 mg respectively. They observed that the sample with 50 mg of GO (CRGO3) showed significant specific capacitance of value 1027 F/g at 1 A/g.

In a recent study, Karthikeyan and co-workers discuss a hybrid method of energy storage that combines the positive aspects of both conventional batteries as well as supercapacitors [70]. The environmentally non-friendly, corrosive and flammable nature of conventional batteries along with uncontrolled heating are some of the undesirable battery attributes. Supercapacitors prove to be cleaner, cheap and safer alternatives as they store charge by different methods like surface redox reactions and/or ionic diffusion followed by intercalation. Combining different charge storage methods along with careful selection of electrode materials helps to increase the overall charge storage capacity of supercapacitors. One such method discussed is the Lithium-ion hybrid capacitor which is also termed as 'Ultrabattery' which is a combination of EDLC and lead acid battery. The future of energy storage is thus rapidly evolving by combining the short charging time of supercapacitors and the high energy density and long cycle life of batteries.

Matthew and Balachandran's work reported

structural deformations in graphene and their effects on its electrochemical properties [71]. The deformations were categorized as those that had either 2-D or 3-D spread. While ripples and wrinkles formed in the 2-D plane, 3-D deformations were called crumples. The ripples refer to the curvature in the graphene sheets, wrinkles refer to the folds/ edges of the sheet combined sometimes with curvature of sheets while crumples are deformation that combine curvature, folds and pockets created by folding of the graphene sheet giving it a three-dimensional characteristic. These different defects exhibit different electrochemical properties as charge density varies due to dangling bonds at edges and near folds. This affects the way ions interact with the electrode material. Crumpled graphene is found to be the best choice for electrode material since it displayed the best overall topography as well as pore size; 2-25 nm, throughout the surface. The larger surface area provided an increase in average specific capacitance up to 329 F/g. Further, crumples helped in mitigating stacking of graphene sheets by acting as spacers. Restacking in graphene is a common problem and undesirable as the high surface area attribute is lost due to restacking. Thus, crumpled graphene provides a larger surface area for in-plane porous structure leading to high capacitance [72]. An aerosol spray of graphene oxide solution was subjected to thermal reduction, which when combined with a suitable medium generated a high yield of crumpled graphene. Xu et al. (2020) reported a single step method for pyrolysis of phenanthroline and melamine in an argon atmosphere to produce nitrogen rich crumpled graphene [73]. This form of graphene is highly useful in supercapacitors and can be improved by using Pt, Ag, metal oxides and phosphides. Due to the high theoretical specific capacitance of manganese oxide, a hybrid with crumpled graphene is a good choice for electrode material. A Ni₂P hybrid was observed to have capacitance as high as 1912 F/g [74]. Matthew explained that to achieve the optimum value of capacitance, a balance between porosity and density of the electrode material must be met. In this regard, crumpled graphene performed significantly better than graphene sheets and reduced graphene oxides.

In 2021, Hajare and team focused on improving the supercapacitor performance by the addition of carbon electrodes [75]. The

synthesis of carbon electrode composites led to use of various other strategies like heteroatom doping, coupling of nanocarbon along with carbon substrate and analysing the architecture of the pore size. With these strategies, the team intended to improve the performance of carbon electrode composite. Few of the latest synthetic strategies included synthesis of sulphur doped rGO and GO/polythiophene done through in-situ polymerization [76]. Similarly, synthesis of carbon aerogel can be done in an environmentally friendly way with the use of biomass as a precursor [77]. The paper showed that the method produces CA-PANI composites when polyaniline was added. Askari et al. have shown that MoS₂/CoS₂/rGO electrode display more stability even after 5000 cycles [78]. 2-D materials are also explored and presented positively for energy storage devices as their structure unifies the large surface area, and spacings that can favour charge/ion intercalation [79].

Carbon nanotubes, particularly, multi walled carbon nanotubes (MWCNT) have also been explored when interacting with PANI and TiO₂ along with H₂SO₄ and aniline sulphate (AS) at room temperature. This results in a 3-D nano composite which yields a value of 270 F/g and shows excellent cyclic stability. The highest specific capacitance was observed at 525 F/g at scan rate of 1 mV/s [80]. Carbon composites like GO, rGO and incompletely reduced graphene oxide are also discussed. Some new materials outlined are PANI electrodeposited onto carbon material (C) and functionalized carbon fabric (FC) to acquire PANI/C and PANI/FC. This is done through the process electro-co-polymerization of an aniline and metanilic acid and it yields a specific capacitance of 408 F/g [81]. Carbon aerogels, carbon cloth and carbon sphere were also studied, and it was observed that the porous nature of carbon aerogels allows for excellent electrical applications [82]. Composites synthesized from carbon spheres through the process of centrifugation were also observed to have high electrical conductivity [83]. It was noted that the capacitive retention was around 95.02% in case of S-doped reduced graphene oxide/carbon nanotubes/polyaniline (S-rGO/CNTs/PANI). The working electrode type when properly selected, provided a good electrode–electrolyte match that is essential for higher capacitance.

The other approach that resulted in better performing supercapacitors is doping. Malik et

al. discussed two kinds of doping materials for graphene oxide, namely metal and non-metal composites [84]. Metal doping was done with materials like tungsten, lanthanum, bismuth and ruthenium. Tungsten oxide is structured to have a high active surface, avoids agglomeration, and creates more space for rapid reactions [85,86]. Lanthanum oxide displayed very good electrochemical stability with an energy retention rate of around 0.6. It reduced innate defects in rGO and thus lead to reduced internal resistance [87]. MnO is an ecologically harmless and cheaper alternative to ruthenium and studies have been done to observe the performance of nanostructured MnO [88]. In case of non-metal doping, nitrogen has been the choice material as it provides a highly interconnected 3-D structure with good pore distribution. It encourages high permeation of the electrolyte and low internal resistance [89]. Nitrogen, sulfur, boron and -Ga-As are a few other kinds of materials used for non-metal doping. Sulphur based composites are a good way to draw up to 203.2 F/g in case of supercapacitors [90]. Some other ways are polymer based composites and polyaniline (PANI). Graphene-PANI hybrid papers have been reported using polymerization methods. These are biocompatible and provide better electrochemical performance as discussed by Yan et al. [91]. This paper also outlines Graphene-Ppy nanofiber films and their ability for enhanced absorption of electrolyte particles [92]. Modified graphene such as 2-D thin films enable maximum usage of available surface area and Laser scribed graphene solves the problem of slow rate capability frequently experienced by supercapacitors. 2-D sandwiched nanocomposites have materials such as ferrous oxide which shortens the diffusion path for ions and allows for short charging period [93]. 3-D graphene has also been an upcoming area of research owing to their good thermal and chemical stability [94]. Reduced graphene oxide along with silver nanorods demonstrated a specific capacitance of 550 F/g [95]. Some other ways rGO can be used is with MnO₂, nickel cobalt layer, PANI and so forth.

Yibowei and team reported polymer composites for improved performance of electrodes for supercapacitors. The most common zero-dimensional materials are fullerene and carbon quantum dots that can be used as fillers [96] but showed very less solubility that resulted

in lump formation. This was resolved by physical and chemical modification of fullerene by using polymers such as polyethylene glycol (PEG), polystyrene (PS) and polyethylene (PE) in doping the fullerene [97]. While the incorporation of C-dots in nanocomposites increased the ionic motion and electron transport in supercapacitors due to its graphite structure [98,99]. When these carbon quantum dots were incorporated with Ti and polypyrrole, it showed immense change in capacitance, conductivity and resistance of charge transfer lowered by 58%. Further, with 1-D carbon like carbon nanotube incorporated with polymer matrices was used to enhance the specific capacitance, energy, and power density, especially as electrode materials [100]. For 2-D carbon, graphene was taken along with fluoropolymers (polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE)) as composites were prepared by in situ polymerization, solution mixing, electrochemical polymerization, and hydrothermal polymerization [101,102]. They proved that these nanocomposite polymer film in a three-electrode system showed a specific capacitance of 556 F/g compared to all the two-dimension ones. Due to increased demand for flexible super capacitors, CNTs and its derivative have shown massive potential in their applications [103,104]. Carbon aerogels are 3-D carbon because of their mesoporous structure and low density they are used as electrodes. The supercapacitor capacitance with activated carbon depends on its pore distribution since they have increased conductivity and surface area. Activated carbon polypyrrole composite was created using tubular polypyrrole and it showed high capacitance as compared to normal activated carbon [105]. Akhtar et al. demonstrated an electrochemical supercapacitor based on graphene and polypyrrole composite that exhibited 931 F/g specific capacitance [106]. The better ion movement through the electrode was understood to be the reason for better charge storage. While graphene sheets provided the necessary large surface area, polypyrrole enabled to store charge via polarons mediation. Polarons can be regarded as electron-phonon pair that induce movement of electrons with the help of lattice vibrations. The resulting supercapacitor demonstrated energy density of 46.6 Wh/kg and showed that conjugated polymer layers intercalated with graphene can be used for boosting supercapacitor performance.

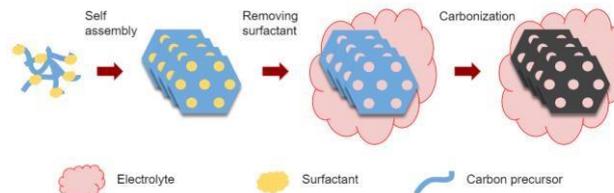


Fig. 3. Synthesis of stacked and ordered, self-assembly based hierarchical mesoporous carbon [91].

THE FUTURE OF SUPERCAPACITORS

Supercapacitors' future depends on the progress in generating new materials or increasing the performance of existing materials. Besides the conventional ways of doping, using composites or hybrid materials, approaches which have made a significant progress in increasing the capacitance are now discussed.

Materials which not only have large surface areas but also have unhindered accessibility, three-dimensional architectures synthesized with the help of spacers like nanotubes, nanowires, quantum dots, nanoparticles, innate defects such as those in graphene sheets, hydrogel porosity, conducting polymers, etc. structures that result in a better contact of electrode-electrolyte and materials that are light weight are required. Thus, innovations in synthesis techniques need to be made to craft materials with suitable morphologies and desirable properties. In this regard, soft templating method can be a good choice. The method of Amphiphilic Surfactant Templating is built upon research carried out by Meng [107]. In this work, the supercapacitor is designed by introducing stacked and ordered mesoporous hierarchical carbons (S-OMCs) in the electrode. The design is proposed as shown in Fig. 3. OMCs have an integral pore network which is ordered and thus can provide unhindered access to the electrode inner layers thereby increasing adding the pseudocapacitive nature. The presence of mesopores ensures an increased electrolyte-electrode interfacial area thereby contributing to more active adsorption sites. A direct contact of the electrode and the electrolyte can thus be maintained. Ordered pores in addition help in seamless movement of ions or electrons to and from the electrodes to the electrolyte thereby reducing the resistance encountered in other electrode designs. The stacking of ordered mesoporous templates can be implemented by using conducting filler material like functionalized

graphene, functionalized fullerenes or quantum dots. The porosity of carbon material, say few-layered graphene, can additionally be used as layers for intercalation of metal oxide nanoparticles or conductive polymers to achieve high mechanical and electrical stability. Since OMC can also have polymer substrates, it is possible to generate flexible supercapacitors for use in wearable and foldable devices. The use of chemical doping such as boron and nitrogen have shown a steep rise in the total specific capacitance of OMCs as well [108]. The ability to increase charge transfer and holding capacity with the help of pores arranged in a crystal lattice like structure, gives OMCs a considerable advantage over other materials. This new architecture of materials thus has potential to be thoroughly investigated by researchers in coming years. Fig. 3 shows the process of soft template-based synthesis of stacked mesoporous carbon. In this method, copolymer surfactant micelles and a carbon precursor are made to interact with each other to form mesopores of order 3-7 nm. The micelles self-assemble to form a soft template and the presence of weak forces causes the polycondensation of precursor on the template. The resulting mesoporous template can be stacked together to form a porous 3-D structure. A suitable electrolyte or binder material can be filled between the spaces. Later the soft template is removed, and carbonization of the precursor is carried out. The authors propose this method for producing 3-D stacked and ordered mesoporous hierarchical carbon in bulk. It is simple to implement and causes lesser wastage of material. Further research and experimentation can be carried out on this method of synthesis.

CONCLUSION

Through the years graphene has proved to be the preferred choice for supercapacitors because of its increased conductivity, excellent mechanical strength, and high surface area of contact.

Several different materials have been explored including 3-D graphene as well as graphene oxide films, nanographene hybrids with metal oxides, polymers, and different combinations of electrolytes. Out of these, recent works demonstrating hybrid materials and 3-D hydro and aerogel structures have shown promising results regarding specific and volumetric capacitance. The best specific capacitance obtained so far is 697 F/g with graphene-quantum dots and 931 F/g with graphene-polymer composite [69, 106]. Further research and improvement in the following areas needs to be actively pursued to fully harness the benefits of graphene as an electrode material:

- Novel environmentally friendly methods of synthesis of graphene-based materials should be considered. Developing sustainable and low-cost methods of largescale manufacturing of graphene, graphene oxides and hybrid materials is needed to meet the requirements of the growing electronics industry.

- More research needs to be done on micro and flexible capacitors to achieve minimum thickness and size as well as good capacitance for powerful wearable electronics, micro drones, medical and robotics applications.

- The overall energy density and charge storage capacity of supercapacitors must be further improved by use of nanohybrid materials. Devices that can function at voltages of 3-4 V and beyond need to be effectively developed and made available for commercial use as replacements for Lithium based cells. This will enable faster charging and discharging for several functions such as regenerative braking in electric vehicles and may also nullify the need for heavy metal-based batteries in future.

- Further interest needs to be directed toward exploring use of quantum dots and ways to increase interconnections and surface area in 3-D ordered mesoporous graphene structures can be developed.

- The proposed stacked and ordered hierarchical mesoporous carbon structures as new electrode design can achieve higher capacitance values.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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