Review article

A brief review on supercapacitor energy storage devices and utilization of natural carbon resources as their electrode materials

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GRAPHICAL ABSTRACT
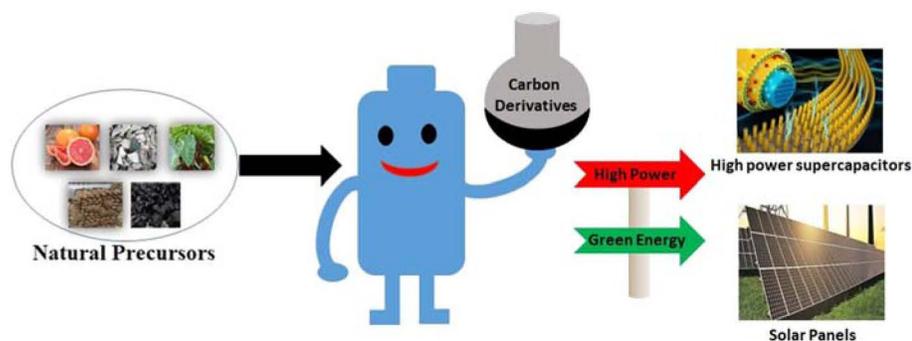
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ABSTRACT

Affordable and clean energy is one of the major sustainable development goals that can transform our world. Currently, researchers are focusing on cheap carbon electrode materials to develop energy storage devices, including high energy density supercapacitors and Li-ion batteries. In this review article, the prime focus has been given on different types of natural carbon sources used for synthesis of graphene and carbon products/ derivatives towards the fabrication of supercapacitors with high electrochemical performance. The review also contains the recent status of the synthetic methods of such type of materials and their subsequent application as electrodes in supercapacitors along with the technological aspects of the supercapacitors made out of those natural resources. The main outlook of the review article is to understand the importance of these natural resources for using as precursors in large-scale synthesis of various carbon products/derivatives in an economic way. This is the first review article describing all possible directions related to such typical natural resources and application of their carbon derivatives/products for better electrochemical properties. The article will be very

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helpful for future research work in the field of carbon electrode materials derived from coal, graphite, and biomass and their gainful utilization in supercapacitor energy storage devices.

1. Introduction

The need for the new material gives birth to new technology. However, economic viability for any new technology is the prime requirement for its sustainability. The graphene and natural carbon derivative in the form of oxides (Graphene oxide-GO), dots (Graphene quantum dots-GQD), and tubes (Carbon nanotubes-CNT) is an output of the same need. In view of the development of future technologies, the present world requires enormous amount of carbon nanomaterials with promising and excellent chemical, physical, mechanical, and thermal properties [1–3]. The year 1991 is known for the invention of graphene, a sp^2 hybridized material with extraordinary properties, which opened a wide opportunity for researchers and industries towards the development of various applications such as batteries, fuel cells, and electronics devices [4–7]. Graphene is also known for its large conjugated structure, which signifies the delocalization effects of π-electrons. This effect makes a graphene a zero-band gap material and restricts its usage in optronics applications [8,9]. There are several graphene derivatives varied in the structural and chemical manner from each other. To enhance the properties of these derivatives is an important aspect for its usage in various applications which can be done by intercalating derivatives with the polymer matrix.

Here, the focus is mainly on the carbon materials derived from natural carbon precursors, graphene oxide (GO), and the reduced form of graphene oxide (rGO) which are common and most important derivatives of graphene. Graphene is known for its electrical conductivity, whereas GO behaves most probably as an insulator. In general, the oxidation process leads towards the loss of conductivity. The fundamental properties of GO depend on the degree of oxidation. The conductivity of graphene derivatives mainly relies on the oxide network of the precursor. The conversion from conducting to insulating properties is due to the disruption of sp^2 bonding [10–12]. There are several approaches has been developed for synthesizing graphene derivatives, but production at low cost and high yield is still the biggest challenge. Thus, the precursor materials such as graphite, coal, coke, anthracite, and biomass are very important towards the large-scale production of graphene derivatives for high-end applications. Every precursor has different structure and basic properties, for example, graphite is a hexagonal structured carbon form with sp^2 orbital planes with each layer is separated by 0.34 nm [13]. There are different ranks of coal (anthracite, bituminous, lignite) also used for the synthesis of graphene derivatives [14,15]. The precursor in the form of coal is also known as three-dimensional cross-linked heterogeneous carbon materials. The different ranks of coal vary from each other, for example ca.70%, 75%,

85%, and 94% of carbon concentration present in lignite, sub-bituminous, bituminous, and anthracite respectively [16–19]. There have been many studies on the synthesis of graphene derivatives by using graphite and coal. For example, Pandey et al. [20] used graphite for the synthesis of reduced graphene oxide (rGO). Similarly, the synthesis of graphene oxide [21,22], carbon nanomaterials [23,24], and carbon nanotubes [25–27] was studied by several researchers using coal as a precursor.

In this review, the compatibility of other active and inactive component of supercapacitors with the activated carbon derived from biomass and natural sources will also be optimized. Also, various components of the activated carbon-based electric double layer capacitance (EDLC) and their type will be reviewed and the novel state-of-art methods of developing superior electrolyte, current collector, separator, and binder which exhibit superior electrochemical performance will be discussed. Many reports on various types of porous carbon obtained from different sources have been found which are chemically activated and used as electrode materials in supercapacitor [28,29]. In this regard, naturally available biomass can be very useful as source material for the synthesis of porous carbon. Porous carbon prepared from these materials has an upper hand over the others in terms of sustainability as they are obtained in an environmentally friendly way from renewable waste biomass as well as natural sources [30]. Also, because of the *in situ* nano-adsorbent formations in the biomass-derived activated carbon in a very cost-efficient and easy, the results are quite fulfilling. However, most of the reports available in the literature for porous carbon are focused on the electro-catalytic and pollutant removal applications [31,32]. There are very few reports on developing of porous carbon materials from waste biomass and other natural sources to be used in EDLC. In this review, the emphasis is also given on activated carbon obtained from biomass. A lot of biomass materials have been used as precursors for obtaining the carbon powder which includes animal bones, dead leaves, coconut husk, chicken eggshell membranes, cow-dung, food waste, etc. [33]. The biomass material sources can be broadly summarized in five significant categories i.e. plant-derived, food-derived, microorganism-derived, animal-derived, and lastly carbon materials derived from natural sources such as coal.

The various reactions that take place in the carbonization stage and the subsequent oxidation of the biochar could eventually transform the initial structure and chemical composition of the final carbon-derived material. The high yield of carbon from biochar, doping, and heteroatom greatly depends on the composition of elements as well as the chemical constitution of the biomass precursors. Biochar contains high amount of silica, inorganic mineral compounds, and/or thermally

Table 1
Few of the activated carbon obtained from different biomass and their important parameters and application.

Biomass precursors	Parameters	Applications	Refs.
Production of activated carbons from agricultural residues	Surface areas, ranging between 250 and 2410 m^2/g and pore volumes of 0.022 and 91.4 cm^3/g	Most effective in removing the metals copper (Cu^{2+}), lead (Pb^{2+}) and zinc (Zn^{2+}), from drinking water	[34]
Lignocellulosic biomass	Surface area of 1247 m^2/g and micropore volume of 0.51 cm^3/g	Applications of biomass-based carbon molecular sieves (CMSs) in gas separation	[35]
Algal biomass	21% O_2/CO_2 atmosphere is at least effective to reduce NO emission from most algal biomass combustion compared to air-based atmosphere	Control of NO_x emissions from direct combustion or co-firing of algal biomass for energy utilization	[36]
Micractiniumreisseri grown in wastewater	Biomass productivity (0.076 g L^{-1} d^{-1}) and lipid productivity (0.014 g L^{-1} d^{-1})	Improved fatty acid profile in the biomass and biodiesel quality-related parameters	[37]
Rice straw	Surface area of 1007 m^2/g, maximum capacitance 332F/g	High energy symmetric supercapacitor in aqueous and non-aqueous electrolytes	[38]
Agar	Superior specific surface area 1672 m^2/g, total pore volume 0.81c.m^3/g, maximum specific capacity 226F/g	Production of commercial activated carbon with high porosity for supercapacitors	[39]

unstable organic impurities. High-temperature treatment followed by acid/base washing removes these non-carbon compounds, creating abundant micropores and mesopores [30]. Therefore, it is pivotal to explore and grasp various characteristics associated with carbon-material precursors such as whether they contain inherent oxygen or nitrogen functional groups, micro or mesoporous networks, and also whether they possess higher yield of carbon which will magnify its application in environment as well as in energy domain [39,40]. The activated carbon obtained from different biomass and their important results and application are shown in Table 1. Mishra et al. [41] has discussed the modification of carbon cloth which is composed of woven carbon fibers into flexible supercapacitors by oxidation, doping, and by growth of different nanostructures.

However, recently researchers started working in the field of composites and blends by cross-linking graphene derivatives with various conjugate and non-conjugate polymers [42,43]. The polymer cross-linking improves the properties of graphene derivative materials and, finally, provides the best overall performance of the device. Polymers are the chain of monomers mainly known for their excellent properties (thermal, mechanical, electrical, etc.) [44–46]. Each property of the polymers is correlated with each other. The intermolecular arrangement and disturbance mostly based on the thermal properties of the polymer. However, charge transport mechanisms, ionic mobility, and hopping phenomenon are described by electrical properties of the polymer. Composite materials studies are mainly obtained by combination of different materials with best properties. Specifically, polymer matrix composites include desirable thermal, mechanical, and electrical properties with excellent efficiency [47]. These enhanced and modified properties make the polymeric composite uniquely suitable for a broad range of applications: energy [48], automotive industry, surface coating and aerospace industry, and electronics and communication engineering [49–51]. Recently, researchers have prepared composites by intercalating/cross-linking polymers with different graphene/carbon derivatives with the aim to enhance further surface properties. The potential response of these composite materials was mainly studied by using different compositions of the materials. The process of preparing carbon/graphene derivatives composites is similar to other nanocomposites. However, the composites in the film form can be considered as one of the better and important challenges towards existing industrial materials [52]. Composites are more preferable than blends because they help to preserve the individual properties of polymer and filler [53,54]. The macro-range properties of polymer nanocomposites completely depend on the interfacial compatibility and intercalation between the graphene/carbon derivatives and nano-filler polarity and phase match [55]. The properties of nanocomposites also depend on the distribution and dispersion of nanofiller which is of different shape and size. By considering different factors of synthesis such as different techniques, temperature, time of mixing, etc., can lead to achieve best properties of graphene-derivatives-based composites [56–58]. There are several significant approaches are made such as the use of single and multiple polymeric matrices and work towards the modification of surface properties of graphene derivatives which are sufficiently versatile to get the best compatible nano-composites [59–61]. The dispersion of conjugated and non-conjugated or polar and non-polar polymers with different range of graphene/carbon derivatives can also affect the resultant properties of the composites. However, the functional group or the chemical structure of the graphene derivatives also plays a vital role for the final properties of nano-composites. Although there are a large number of research papers and reviews in the field of polymer nano-composites approached, this review article also leads towards the importance of precursors, synthesis process, properties and applications. This article incorporates the broad survey in the direction of latest work done on preparation of graphene derivatives and supercapacitor application [62–65]. Moreover, this article also presented the counterpart of nanocomposites that are elaborated by means of different carbon derivatives, polymers, and inorganic nanomaterial for various applications [66–68]. The summary of nanocomposites applications by using different graphene derivatives is shown in Fig. 1.

The technological advancements of modern society and the escalating global economy have caused a huge demand for energy-storage devices. As the reserves of fossil fuels are exhaustible and considering the hazardous impacts on environment and climate due to greenhouse gases, it is a necessity for us to switch from fossil fuel to renewable energy sources for sustainable development. The well-known renewable sources cannot be used for commercial and residential purpose as disruptions in supply can cause large loss [69]. So, with the holistic approach of clean energy arises the need to explore new storage and conversion technologies. In this regard, electrochemical energy storage has been regarded as the most promising among various renewable energy storage technologies due to high efficiency, versatility, and flexibility

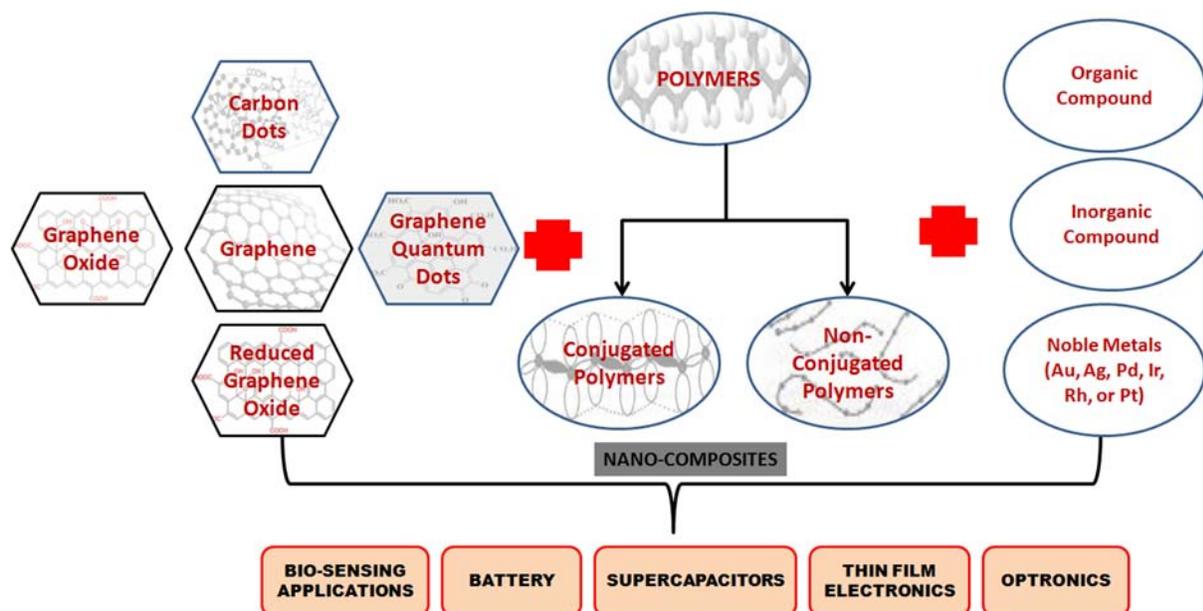In recent years, several new electrochemical energy storage systems

Fig. 1. Summary of the applications of polymer-nanocomposites derived from different graphene derivatives.

such as secondary metal-ion batteries, redox-flow batteries, and electrochemical supercapacitors have drawn the attention of researchers [70–72]. Theoretically the electrochemical energy storage and release is achieved by charge and discharge of electrons and electrolyte ions at the electrode–electrolyte interface. Batteries and electrochemical capacitors are two kinds of typical electrochemical energy storage devices, both of which store electricity in electrochemical processes although through two different mechanisms [73]. Li-ion batteries (LIBs) have become the most important hot research topic of interest as far as the renewable process of energy is concerned. The research on LIBs is mostly based on the anodic and cathodic materials showing significant capacity for the subsequent cycles [74,75]. In batteries, a reversible faradaic redox reaction takes place in both cathode and anode during charge–discharge process. This faradaic nature of charge storage leads to high capacity and energy density in LIBs, but due to its slow nature, they are often handicapped by low power density and poor cycle life. On the other hand, supercapacitors operate through adsorbing/desorbing charged ions from the electrolyte on the highly porous surface of the electrode depending on potential difference [74]. As a result, supercapacitors possess high power density (10^3–10^4 W kg^{-1}), which means that they can deliver high amount of electrical energy much faster rate than Li-ion batteries, which is one of the prime requirement in next generation of electric vehicles and other high-energy-consuming electronic gadgets. In addition to this, supercapacitor possess long cycle life ($> 10^6$ cycles), low maintenance cost, and better safety compared to batteries, which make supercapacitors very promising as renewable energy storage technology. Electrochemical supercapacitors have found applications in the backup (consumer electronics, digital cameras, computers, uninterruptible power supplies (UPS), inverters, security installations, drills, and telecommunication), and regenerative braking. They can also be used as an energy storage system for grid substations and are also being implemented as primary or secondary power source for electric vehicle, hybrid electric vehicle, bus, trams, and trains [76–78].

The capacitance of the supercapacitor decreases and the equivalent series resistance (ESR) increases when the supercapacitor is subjected to prolonged cycling. Also, the performance of supercapacitors deteriorates at high temperature and voltage. The electrolyte and electrode interface also contributes significantly to the degradation of the supercapacitor. Degradation depends a lot on the functional groups attached to the carbon surface, electrode polarity, moisture content, as well as the composition of the electrolyte. The stability of the current collectors and polymer binder also plays a crucial role in the long-term performance of the supercapacitor. So, all these factors must be taken into consideration for construction of supercapacitors [79]. Therefore, all the recent research and developments in the field of electrochemical

supercapacitor are directed towards: i) Increasing the energy density without compromising with the high power density; ii) increasing the specific capacitance of the electrode by the development of new electrode material having high surface area; iii) reducing the cost of supercapacitor by constructing electrodes from natural sources; 4) widening the cell voltage by using or developing new suitable electrolytes; and iv) developing compatible combinations of electrolyte and electrode material which can achieve a wide range of operating voltage and temperature with high capacitance and reduced self-discharge rate [80]. One of the routes to increase the energy density of supercapacitors so that it can match the current rechargeable batteries is to increase the specific surface area of the carbon electrode. In this review, we will focus on the synthetic route of different graphene-/carbon-derivative-based electrode materials. This is because they inherently contain high carbon content and interconnected porous network. The precursors such as coal and coke are also abundant and cheap, thus can be carbonized and activated using various methods to obtain required electrode materials. In this review, the compatibility of other active and inactive components of the supercapacitors with the activated carbon derived from biomass and natural sources will be optimized. Also, the review on the various components and types of the activated carbon-based EDLC is made with reference to the novel state-of-art methods of developing superior electrolytes, current collectors, separators, and binders leading to superior electrochemical performance.

The main function of a supercapacitor is to store energy by the distribution of the charged ions of the electrolyte on the surface of the electrodes [81,82], as depicted in Fig. 2. Firstly, reversible electrostatic accumulation of ions at the electrical double layer on the surface of porous electrode called electrical double layer capacitor (EDLC). Carbon materials with high surface area fall into this category. Secondly, the reversible redox reaction of surface functional moieties with electrolyte ions comprises the category of pseudocapacitors. Conducting polymers, a few oxide compounds of transition metals such as Ruthenium and Manganese, and hetero-atom doped carbon materials comprise pseudocapacitive energy storage. Traditionally, pseudocapacitors have much higher specific capacitance than EDLC, but their capacity retention ability at high current density as well as long-time operation is poor due to slow and degenerative redox process. Hybrid capacitor, a third kind of supercapacitors, is basically a combination of non-faradaic EDLC-type electrode at one end and a faradaic battery-type electrode at the other end. The faradaic battery-type electrode is comprised of transition metal oxide, sulfides, phosphides, etc. In the literature, the battery-type electrodes are often wrongly merged with pseudocapacitive electrodes, although their charge storage mechanism is significantly different from each other [83–85]. Pseudocapacitive charge storage involves highly reversible surface redox process without
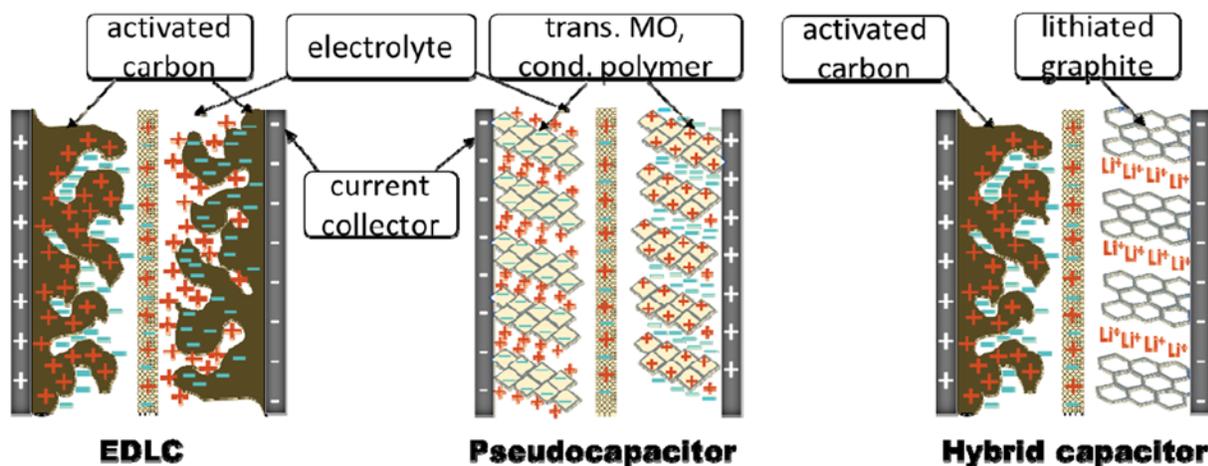

Fig. 2. Schematic diagram of different types of supercapacitors.

any phase transformation. On the other hand, battery-type electrodes store charge through reversible faradaic process, where phase transformation occurs between charged and discharged electrodes.

2. Synthesis of graphene derivatives from coal/graphite

2.1. Importance of precursors

Precursors always play an important role in the synthesis of graphene derivatives. The size, shape, and yield of the final product depend on the structure and properties of the precursor. The chemical structure and functional groups present in the precursor always support to produce the final and best graphene derivatives. In past, graphite was a major precursor to synthesize and obtain the graphene derivatives. However, in last few years' researchers have started working on a broad range of precursors from organic, inorganic, to natural sources like coal and biomass to synthesize graphene/carbon derivatives [82,85–87].

2.1.1. Graphite as a precursor

The synthesis of graphene derivatives from graphite is a trend followed by researchers since past decades. Graphite can also be called a multilayer structured graphene. Graphite as a precursor also got attention due to its unique chemical structure and behaviour. The graphite itself is capable of acting as an oxidizing and reducing agent. Another important reason to use graphite as a precursor is its intercalating capability of chemical bonds over the basal plans [88]. When any molecule intercalates between other two molecules, such process is known as intercalation. The uniqueness of graphite is that each layer can either accept or donate electrons to other intercalated molecules without any loss of carbon atoms. This intercalation process helps to vary the interlayer spacing between layers, which decreases the strength of the material. This entire process, known as the exfoliation process, led the researchers to obtain single-layer graphene sheets or graphene derivatives from graphite precursor [89,90]. Chemical exfoliation process requires a strong oxidizing agent which helps to

convert graphite to the oxidized form of graphite, well known as graphite oxide (GO). This introduction of oxidizing agent produces oxygen-attached graphene layers, which mainly increase the interlayer spacing between layers. The choice of the oxidizing agent and exfoliation method depends on the required graphene derivative. The addition of an oxidizing agent also creates different functional groups such as carboxyl and carbonyl groups over the basal planes or at the edges of the sheets. Basic chemical structure of graphite and different graphene derivatives structure produces after the exfoliation process is depicted in Fig. 3.

2.1.2. Coal as a precursor

In the present scenario, coal is the most abundant and affordable material used worldwide as a source of energy. However, coal can be regarded as carbonaceous material with complex chemical structure, and the exfoliated form of coal contain 10^{-10} to 10^{-9} m sized crystalline forms of carbon atoms cross-linked with defects [15]. Coal is an important source to synthesise different graphene or carbon derivatives and has found a wide range of applications in a multidisciplinary field [91,92]. The heterogeneous chemistry of coal depends on its different chemical constituents particularly on nature of carbon and minerals [93]. Coal basically has a short-range graphitic-like structure [94]. The crystalline structure of coal is the intermediate structure of carbon between an amorphous and graphitic state which is known as the turbostratic structure [94]. However, the amorphous form of coal represents non-aromatic carbon structure due to the significant amount of defective structured material. In comparison to graphite structure having a minimum of 70 layers of aromatic carbon, coal has only 3–4 layers. This structure of coal makes it more feasible for the synthesis of graphene derivatives.

2.2. Methods for synthesis graphene derivatives

2.2.1. Chemical exfoliation method

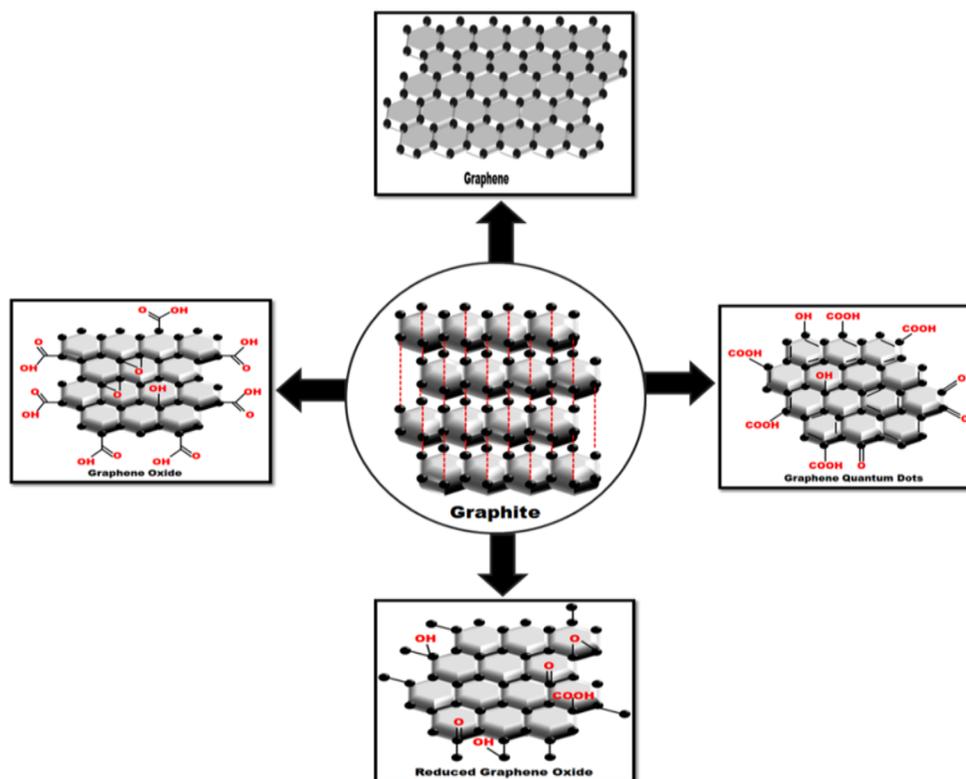Top-down and bottom-up are well-known synthetic methods to

Fig. 3. Chemical structures of different graphene derivatives obtained after chemical exfoliation of graphite.

obtain graphene derivatives from different precursors [95]. Graphene derivatives are mainly obtained from a carbon material or precursor by chemical exfoliation, hydrothermal, ultrasonication, and several other types of methods [96]. All the above-mentioned synthetic process comes under the top-down approach. However, the controlled synthesis is an example of a bottom-up method which is complicated and certainly needs many steps. In the present review article, in general, we are discussing the widely used synthetic methods.

The chemical exfoliation or oxidation method is one of the important methods to synthesize graphene derivative from carbon sources. Due to the use of strong acids for cutting carbon sheets, this is known as chemical exfoliation or oxidation-cleavage method. The main objective of this method is to break C–C or C = C by using sulphuric acid, nitric acid, or any other oxidizing agent. In the study of Yingpeng et al. [97], graphene oxide (GO) was prepared by using coal as a precursor by chemical exfoliation method. The synthesized GO solution was fabricated on a quartz surface and graphene sheets were obtained after thermal treatment. The produced graphene was also claimed to be highly conducting in electrical application. Due to doping of N-atoms on the graphene lattice, the final product also called n-type graphene.

Kumaresan et al. [98] reported the synthesis of graphene oxide (GO) and reduced graphene oxide (rGO) by using graphite as a precursor. The produced GO from graphite was annealed at 400 °C in muffle furnace to obtain reduced graphene oxide (rGO). The objective of the study was to prepare CoAl-LDHs and rGO nanocomposites. The study claims that a high amount of rGO present in nanocomposite contributes towards the low evolution performance rate of H_2 under the visible spectrum [99]. This is because rGO decreases the light absorption ability due to catalytic activity at the surface. The d-spacing of prepared rGO was 0.367 nm indicating π–π stacking of a small number of rGO nano-sheets containing a lesser number of structural defects.

Ghosh et al. [100] reported on the synthesis of reduced graphene oxide by using well-known Hummers and Offemen method [101]. The procedure was carried out by using graphite powder added in 23 ml of concentrated H_2SO_4 under an ice-bath condition to control the

suspension temperature. At that same cooling temperature, $NaNO_3$ was added slowly in the above solution. Then, the $KMnO_4$ was added gradually to the above solution. A colour change from back to dark green can be observed. After that, the solution was kept in an oil bath at 110 °C for 12 h for exfoliation and cutting of graphitic sheets. A dark brown colour solution will be obtained. Further, for terminating the chemical process hydrogen peroxide (H_2O_2) was added in the solution. The above solution was centrifuged to separate the large and small particles. The above residue and filtrate part was kept for dialysis for 2 weeks. The collected solution was dried and the GO powder was finally obtained. The complete procedure is shown in Fig. 4. The as-prepared GO shows the presence of different functional group which interrupts in graphene layer stacking. However, rGO, a reduced form of GO which has eliminated lots of functional groups, helping to stack graphene layer, and multilayer rGO was obtained. The synthesized rGO sheet represents a large surface area which is more clotted and interconnected itself. The synthesized GO is believed to advance the development of memory device applications.

Other than graphene or GO, some more graphene derivatives, such as graphene quantum dots, carbon dots, carbon nanotubes, etc. also play an important role in advancement in supercapacitor technology. The synthesis of carbon dots with excellent fluorescent properties can be obtained via chemical oxidation cutting technique by using H_2SO_4 and HNO_3 at high temperature [102,103]. In 2019, Mayank et al. [102] reported the synthesis of carbon dots using anthracite as a precursor by chemical exfoliation method. The synthesis process used anthracite containing 80–90% carbon.

2.2.2. Green synthesis

The chemical exfoliation method is widely used for synthesis of graphene derivatives despite that it has some well-known disadvantages. Due to the usage of a large number of chemicals, it is highly hazardous and toxic as well as costly. The best way to solve the problem is to approach the green synthesis by using different plant extracts [104,105]. The main objective of green synthesis is to reduce the cost
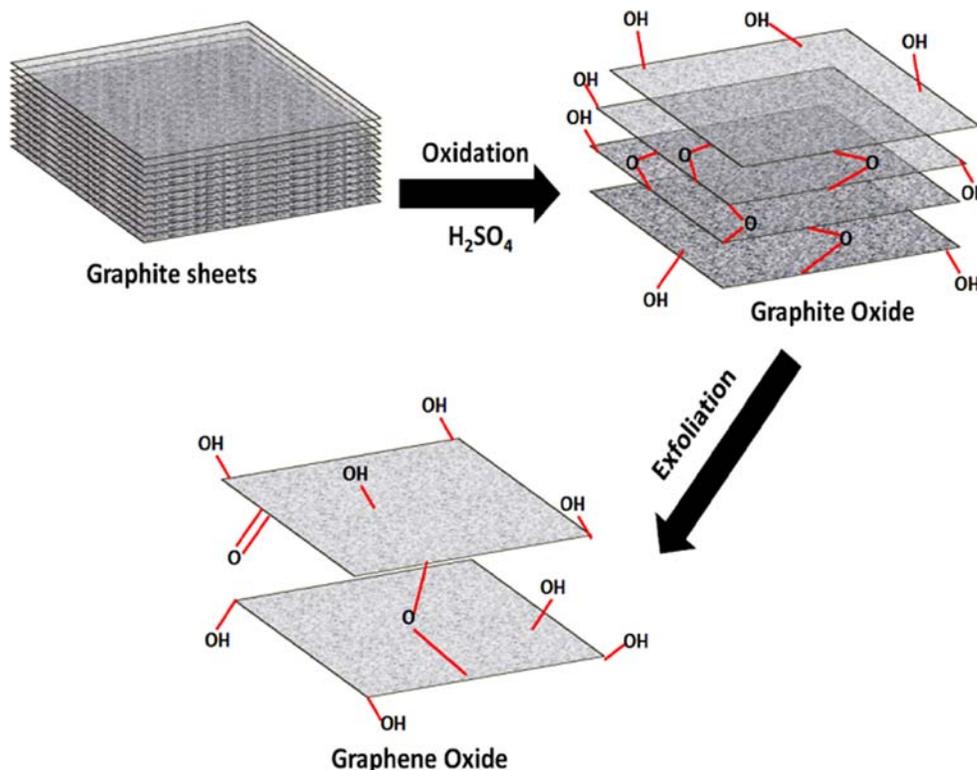

Fig. 4. Schematic representation of the formation of graphene sheets by using Hummers and Offemen method.
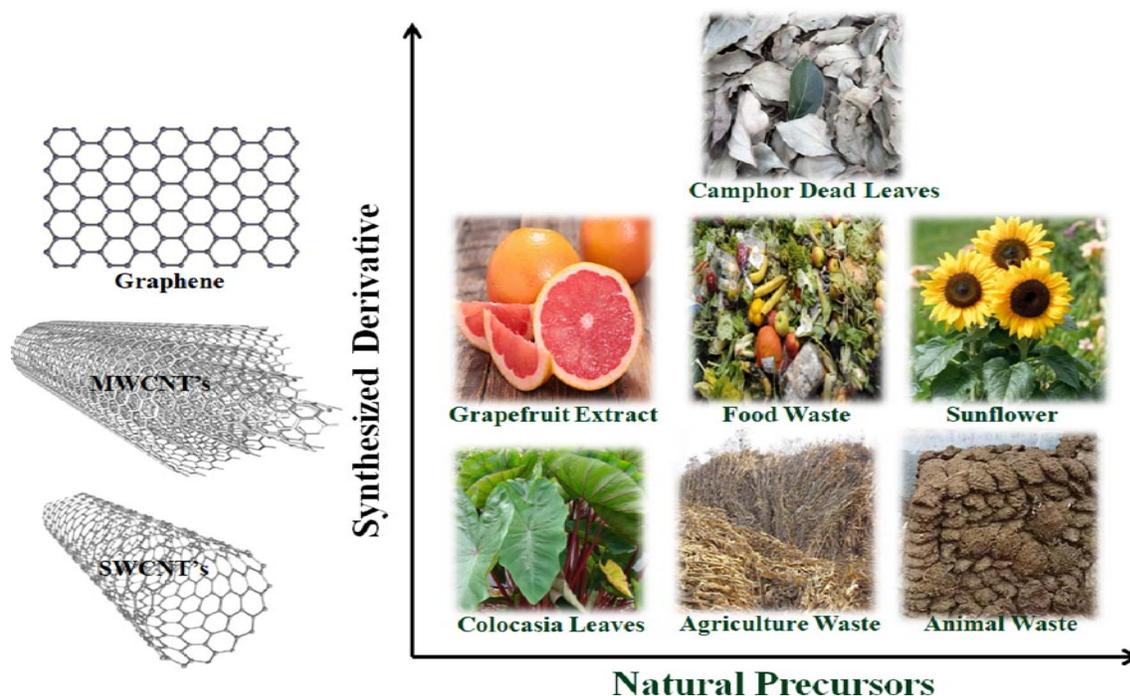
Fig. 5. Different natural precursors use to synthesis carbon and graphene derivatives.

and the toxicity of the process. The approach towards the green method of research is to utilize several plant extracts such as colocasia [106], agriculture waste [107], grapefruit extract [108], etc., as summarized in Fig. 5. Gourav et al. [109], approached a green synthetic route by using Aloe-vera leaves for the production of reduced graphene oxide (rGO). They successfully achieved the 73% of reduction efficiency just by using 7.3 g of leaf extract. They also found that the use of plant extract as a reducing agent decreases the interfacial resistance of the synthesized rGO. Due to that, the rGO exhibited good conductivity with high current density in comparison to GO. The proposed green synthesis method also demonstrates the function of sugar and anthraquinones which play a vital role in reduction of GO. The overall research work done on green synthesis claims that the produced rGO shows remarkable dye adsorption property. The synthesis believed to be useful for sustainable electronics and sensor device applications. Fathy et al. [110] synthesised single-layer graphene oxide using oil palm leaf extract through a green synthesis route. They also used pretreated rice straw for the delignification process [111,112]. The XRD results confirmed the formation of single-layer GO with large interlayer spacing. The results obtained from TEM and EDX confirmed the regular sheet-type structure in the presence of minerals as impurities. They claimed that their method is an environmentally feasible and low-cost approach to obtain GO and can be modified to get bulk production of GO. Pei et al. [113] reported the synthesis of GO sheets by using water electrolytic oxidation of graphitic sheets through green synthesis method. They claimed that the intercalation of graphitic sheets efficiently prevents the anodic reaction which includes electrocatalytic reaction of water at higher voltage. This process can be used to speed up the oxidation of graphene, which is faster than the usual methods. The synthesized GO obtained from the above process represents similar characteristics in view of chemical and structure to those synthesized from well-known chemical exfoliation method (e.g Hummers method) [114]. Some research also claimed that the GO can be synthesized by using a green and electrochemical process by using nanosheet graphene as a precursor [115]. The green synthesis process is most suitable to get graphene with minimal defects or contamination. However, the defects can be removed by electrochemical reduction at 100–400 °C. The green and electrochemical methods are one of the well-suited methods to synthesis graphene in bulk which can be used for the preparation of electrodes for sensors and electrocatalysis applications.

In present scenario, carbon nano-derivatives grab the attention of researchers for the development of storage, environmental, and energy applications. Therefore, researchers are more concentrating towards the green and environmentally friendly synthetic methods. This helps to reduce the usage of toxic chemicals and greenhouse gases. Last ten years are known as progressive years concerning for the synthesis of one dimensional, two-dimensional carbon, and graphene derivatives by using natural and waste materials as precursors. The research work done on the green synthesis method claimed that the process helps to produce a high and better quality of carbon and graphene derivatives in bulk quantity [116]. The approach towards the green synthetic method opens the door to explore several more possible properties of carbon and graphene derivatives. There are several hydrocarbons used for the synthesis of graphene and carbon derivatives which are costly and hard to avail. Therefore, the natural precursors which are renewable, low cost, and easily available are the best source of hydrocarbons. As natural precursors are easily available, it can be a major source for industrial scale and bulk production of graphene and carbon derivatives. The conversion of natural waste to graphene and carbon derivatives could be an effective approach towards the development of energy storage and nano-electronics device applications. Liu et al. [117], produced rGO by green synthesis method for the supercapacitor electrode materials. The synthesized rGO showed excellent physical properties, large surface area and also expose the highly reduced form. The electrochemical performance as an electrode material represents the excellent and high specific capacitance (341F/g and cyclic stability until 5000 cycles). The researcher overall claimed that the green synthetic process reveals certain excellent properties of rGO for the fabrication of supercapacitor applications.

2.2.3. Activated carbon from biomass

The conversion of raw materials i.e. biomass into carbon requires two necessary steps: i) carbonization (hydrothermal carbonization and pyrolysis), ii) activation (physical and chemical activation). Carbonization is a conversion process of biomass into carbon through heat treatment method. This ultimately increases the carbon content of

substance by reducing volatile matter content. It facilitates the process of activation by developing an initial pore structure and also by increasing the strength of the material. Adjusting carbonization conditions in order to obtain an optimum product is an important step. It has been observed that increasing temperature of carbonization causes an increase in the reaction rate but it also reduces the amount of pore volume available. This reduction in pore volume mainly occurs due to the condensation of the biomass material. Once the temperature is increased, the mechanical strength of the material also increases due to the condensation process. Therefore, temperature selection in carbonization plays a crucial role in obtaining the desired product.

The general difference between two main processes of carbonization, i.e. pyrolysis and hydrothermal carbonisation, is as follows:

- The pyrolysis process is done in presence of a very limited amount of oxygen or in an environment of inert atmosphere at a specific temperature, while
- Hydrothermal carbonisation converts biomass into carbon material by the thermo-chemical process under a specified pressure (25 atm.) and also a relatively low-temperature (120 °C–250 °C). Hence, water can stay as it is in liquid form with or without the catalyst. Hydrothermal carbonisation uses water in supercritical or subcritical circumstances. Therefore, the dehydration takes place effectively and the precursors can be hydrolysed into hydrochar which will contain oxygen functional groups. Other functional groups can also be doped into hydrochars using suitable additive of precursors [118–120].

There are certain significant advantages of pyrolysis process over hydrothermal carbonization which sets the pyrolysis process as the most commonly used process. Firstly, the pyrolysis process does not need an oxygen environment; subsequently, air emissions are curtailed to a great extent, making it ecologically viable as well as non-threatening to humans [120]. Secondly, pyrolysis is a fast process which does not involve any kind of solvents, so it can be done within seconds [121]. Thirdly, the plants used for pyrolysis have an easier and quicker installation process. Lastly, pyrolysis is solvent-free process so there is no restriction in terms of temperature and pressure. Therefore, pyrolysis can serve as an efficient method of converting biomass precursors into carbonized materials.

Chemical or physical activation is often necessary for the development of a network of pores in carbon materials. The activation process is basically oxidation of the carbonised product in order to create some micropores of width lesser than 2 nm. This serves a crucial role for adsorption of electrolyte ion. Physical activation consists of carbonizing the carbon material in a totally inert atmosphere for removal of the non-carbon elements. Then, the activation process is carried out with the help of appropriate gaseous precursors such as steam, CO_2, or O_2 to oxidize for development of porosity. Physical activation is carried out at temperatures ranging between 600 and 1200 °C. In case of chemical activation, the carbon materials are mixed with active agents such as KOH, H_3PO_4, $ZnCl_2$, etc., which are then carbonized at temperatures ranging between 400 and 900 °C. The activated porous carbon obtained from the chemical activation has a high surface area of 2000 $m^2 \, g^{-1}$, large pore volume comprised of micropores, and also a few small mesopores. Among these two activation methods, chemical activation is the most common activation method as it has certain advantages over physical activation process such as the relatively lower temperature of activation. The most common activation method used for the preparation of activated carbon is chemical activation as it has comparatively low temperature and other excellent properties. There are a few disadvantages of chemical activation process such as chemical agents which may cause corrosion and also it requires a washing process for the removal of chemical precursors. But the advantages outweigh few of the disadvantages.

3. Supercapacitor applications

The basic operating principle of an electrochemical supercapacitor and a conventional capacitor is same. Therefore, to grasp the working of supercapacitors we need to delve a bit into the working mechanism of the conventional capacitor. A conventional capacitor is an energy storage device which stores electrical energy by means of polarization. A capacitor comprises of two metallic sheets or electrodes separated by a dielectric. On the application of voltage/ potential difference across electrodes, opposite charges are accumulated on two plates. The electrode remains charged after the removal of potential difference and only gets discharged when both electrodes are brought into contact.
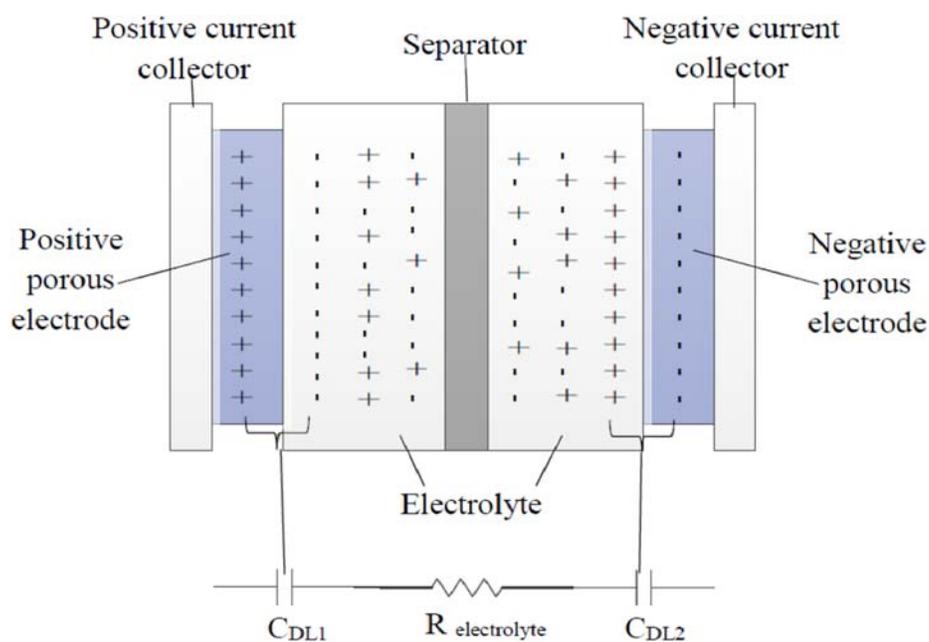

Fig. 6. Illustration of an open circuit charged electrical double-layer capacitor or supercapacitors, where C_{DL1} and C_{DL2} denote the double-layer capacitance at the junction between the electrode surface and electrolyte solution [125].

Separation of unlike charges by the dielectric creates electric field and, thereby, facilitates storage of charge.

3.1. Theoretical concept of supercapacitors

Some of the basic mathematical equations and terms governing conventional capacitors also govern the operation of supercapacitors. Those mathematical equations and factors on which supercapacitor performance depends are elaborated below:

3.1.1. Capacitance (C)

Capacitance (C) of a conventional capacitor is an amount of charge Q stored to the voltage (V) applied between the two counter plates/electrodes of the capacitor:

Also,

$$C = \frac{Q}{v} \tag{1}$$

Also,

$$C = (\varepsilon_0 \varepsilon_r) \frac{A}{d} \tag{2}$$

where, C = Capacitance of conventional capacitor (Farad, F), ε_o = Permittivity of vacuum-free space (8.854×10^{-12} F/m), ε_r = Relative permittivity of the dielectric between the two electrodes, A = Surface Area of the electrodes facing each other (m^2), d = Distance between the two counter electrodes (m) [122].

From the above equations, we can see that the capacitance of a conventional capacitor is directly proportional to the permittivity of the dielectric and surface area and it is inversely proportional to the distance between the electrodes. Therefore, in supercapacitors, electrode materials like activated carbon having a high surface area of over 1000 m^2/g are used. The surface area of the electrode is directly proportional to the capacitance value. So, electrode material plays a vital role in obtaining high capacitance [123,124]. Therefore, from Eq. (2) of conventional capacitors, we can evaluate the capacitance value of the supercapacitors or EDLC.

In case of EDLCs, "d" in Eq. (2) represents the separation between the Outer Helmholtz plane (OHP) and charged surface of electrode and ε_r is the relative permittivity of the medium between them. As this distance is very small and porous electrodes have larger surface areas, both of these factors are important and contribute to obtaining very high capacitance. In case of EDLC, two capacitors are formed at each electrode. When the capacitor is charged, two electric double layers (EDL) are formed at each electrode, as shown in Fig. 6. The capacitances for two individual capacitors of the EDLC are denoted by C_{DL1} and C_{DL2}. Both capacitors are in series and, therefore, the equivalent capacitance of the EDLC is given by:

$$C_{eq} = \frac{C_{DL1} * C_{DL2}}{C_{DL1} + C_{DL2}} \tag{3}$$

The supercapacitor shown in Fig. 6 represents symmetric supercapacitors. The electrodes material, composition, and dimensions are identical. The equivalent capacitance will be exactly half of one of the electrode capacitance. If the supercapacitors are asymmetrical, then the smaller capacitance will limit the total capacitance [126].

3.1.2. Calculation methods

An ideal symmetric EDLC cell consists of two identical electrodes of same mass, and the charge storage is completed through the formation of double layer. The energy storage mechanism in such system is purely electrostatic and the current is independent of the voltage. The cell capacitance of such EDLC is calculated using the following equation:

$$C_{cell} = \int \left(\frac{i.\, dt}{\Delta V} \right) = \frac{i.\Delta t}{\Delta V} \tag{4}$$

As the voltage is directly proportional to time, such an EDLC system is identified by linear charge–discharge profiles with nearly 100% coulombic efficiency. Therefore, the capacitance of this system can be calculated by using the discharge profile of galvanostatic charge–discharge testing and expressed in terms of F. In order to compare capacitance values from different experiment, it is necessary to normalise the F value in terms of electrode mass or area. For this, cell capacitance is divided by total mass, area, or volume of the two electrodes, which gives rise to specific cell capacitance (Csp, cell) and expressed in terms of F.g^{-1}, F.cm^{-2}, or F.cm^{-3}. These three specific capacitance terms are also known as gravimetric, areal, and volumetric capacitance, respectively. The specific capacitance of a single electrode in symmetric EDLC cell (Csp, el) can be calculated by multiplication of Csp of the cell with a factor of 4.

In case of pseudocapacitor and hybrid capacitor systems, the galvanostatic charge–discharge profiles obtained during electrochemical testing are mostly non-linear, which means that the charge storage is not independent of voltage. This is because the charge storage in such system involves faradaic redox process on the electrode surface (Pseudocapacitive), or on the whole electrode (battery-like). Therefore, in these systems the capacitance is not an appropriate term to quantify the charge storage. Instead, charge or discharge specific capacity (Q) is more appropriate in these two systems, which is simple multiplication of current applied and time of charge or discharge and expressed in terms of mA.h.g^{-1}

The electrical energy (E) stored in ideal symmetric EDLC can be calculated from the charge–discharge measurement using the following equation:

$$E = \frac{1}{2} C.\, V_{max}^2 \tag{5}$$

where, Vmax is maximum voltage value in the discharge profile of after the ohmic drop. In case of non-linear charge discharge profiles for pseudocapacitor or hybrid capacitor system, the discharge energy could be calculated by integrating the area under the discharge curve (or charge energy from charge curve):

$$E = I.\, \int_{t(V_{max})}^{t(V_{min})} V(t).\, dt \tag{6}$$

The energy values obtained from different cells is calculated in terms of electrode mass or volume, and expressed as specific energy or energy density with the unit of W.h.kg^{-1} or W.h.l^{-1}, respectively. So, the stored energy in capacitor is directly proportional to the capacitance and square of the applied voltage. Hence, increase in capacitance can directly increase the energy density of supercapacitors. Also, the increase in breakdown voltage limit will help to achieve high energy densities. Increase in surface area of the electrode can also help to achieve capacitance contributing the increase in energy density [123–127]. The power density of supercapacitors depends on the energy delivered per unit time. The equation for the maximum power of a capacitor calculated at a particular equivalent series resistance (ESR) is given by:

$$P_{max} = \frac{V^2}{4 * ESR} \tag{7}$$

The above equation shows that the series resistance is inversely proportional to the power density. So, in order to increase the power densities, limiting of the series resistance to a much lower value is required. High power density can be achieved by matching the load and ESR. Conventional capacitors possess significantly high power densities, but considerably lower energy densities in comparison to electrochemical batteries and fuel cells. This implies that the energy storage capacity of a battery is more than a conventional capacitor but has comparatively low power density. However, capacitors can hold much lower energy per unit mass or volume. Therefore, capacitors can generate enormous power by releasing stored electrical energy quickly and,
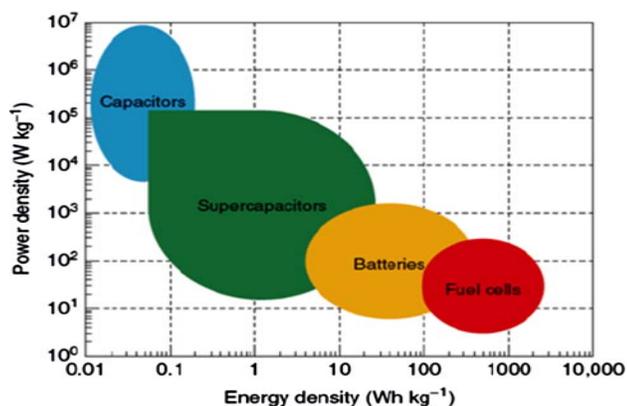
Fig. 7. Ragone plot comparing various energy storage and conversion devices [121].

hence, they have high power densities. Fig. 7 shows a "Ragone plot" which is plotted to represent the specific energy density and specific power density of various energy storage and conversion devices along x-axis and y-axis, respectively. From the plot, it can be observed that the supercapacitor lies in between conventional capacitors and batteries. So, in future, supercapacitor technology can help to bridge the gap between capacitor and battery. Even though very high capacitance supercapacitors have been developed, still they are far behind in matching the energy densities of mid- to high-end batteries and fuel cells.

3.1.3. Equivalent series resistance (ESR)

According to theory, the circuit of a capacitor is considered as a device which is integrated with two components of capacitance that have equivalent series resistance and equivalent parallel resistance [121,128]. Irrespective of the material used for electrode or type of capacitor, the equivalent series resistance (ESR) is always present in a capacitor. The key factors which contribute to ESR, are: resistances of the current collector, electrolyte medium, and electrode surface which is usually linear ohmic. But the main origin of ESR is not from these linear ohmic parts, but from the boundary region resistance of Schottky barrier. This barrier is obtained due to interface of the electrode surface and the electrolyte medium. The ESR is directly proportional to the thickness of the diffusion layer. Hence, with an increase in the thickness of the diffusion layer, the ESR also increases, and the capacitance decreases. It has been observed that the thickness of the diffusion layer can be altered by changing the potential difference, temperature, mechanical pressure, and concentration of electrolyte. The relationships of these four parameters with ESR are discussed below:

i. Relationship between ESR and voltage: When we increase the applied voltage on the diffusion layer, the layer is expected to get reduced in terms of thickness which will consequently decrease the ESR and, hence, capacitance will be increased.

ii. Relationship between ESR and temperature: Increase in temperature causes an increased thermal motion of ions which, in turn, causes elevation of ESR, thereby, a reduction in capacitance.

iii. Relationship between ESR and mechanical pressure: In application of mechanical pressure, the capacitance and performance of supercapacitors are enhanced as ESR gets significantly reduced.

iv. Relationship between ESR and electrolyte concentration: Boosting or enhancing the concentration of electrolyte causes the diffusion layer to become thin, which causes a rise in capacitance as ESR will be reduced.

ESR causes degradation in the efficiency of supercapacitors with the following two aspects: (a) charging and discharging power: the charging and discharging time constant is $\tau = RC$, τ increases with the increase in ESR which, in turn, lowers the capacitor power. Therefore, ESR plays a crucial role in power density. (b) ESR is in series, so it shares the voltage with capacitance component while charging. Therefore, if the ESR is quite large it will take a bigger share of the applied voltage, lowering the energy density. So, ESR plays a vital role in determining the energy density in case of supercapacitors.

3.1.4. Cycle life and charge–discharge rate

Supercapacitors stability also greatly depends on factors such as cycle life. Theoretically, supercapacitors are expected to work without ageing the infinite duration of time because the main components of supercapacitors like activated carbon electrode and electrolyte medium are electrochemically inert. In practice, it has been observed that the supercapacitor features substantially deteriorate with time. This deterioration takes place while in use, mainly due to the total capacitance decrease and ESR increase. Even though not infinite, a supercapacitor's life cycle is much longer as compared to other available energy storage devices [129]. The cycle life of Li-ion battery is reported to be 400–1200 load cycles while supercapacitors are reported to have 500,000 life cycles [130]. There is no chemical or constitutional change related to non-Faradic processes due to absence of involvement of charge transfer between the electrode material and electrolyte medium. Supercapacitor ageing mainly depends on the rate of evaporation of liquid electrolyte in the course of time but the supercapacitors which consist of the polymer electrodes are an exception [129]. This evaporation is mainly dependent on two factors: i) temperature and ii) operating voltage. Another factor which affects the ageing or degradation of the supercapacitor is root mean square (RMS) current. So, in analyzing the estimated lifetime of supercapacitors, RMS current, along with voltage and temperature, must be taken into consideration for a more realistic deduction.

Supercapacitors are used for energy storage over a wide range of time ranging from few seconds to numerous days. For ascertaining the energy storage time of a supercapacitor, one of the main decisive factors is its self-discharge rate. When supercapacitor is disconnected from external load or the circuit which was charging, its voltage slowly reduces to a lower value. This spontaneous drop in voltage is called self-discharge. From Eq. (4), it can be determined that the reduction in self-discharge also reduces the energy density of the supercapacitor. This will be a severe limitation in fixed energy density applications for a long duration of time. On the other hand, a chemical cell has much slower self-discharge rate and the longevity of self-life is several months. From the time of inception of the idea of supercapacitors, it has been observed that supercapacitors self-discharge rates are much higher than chemical cells. Therefore, by considering the developmental works achieved until now, studies are still not in a state to commercialize supercapacitors in a charged state [131,132]. Researchers have given immense attention to improve the energy and power density of electrochemical supercapacitors but the developmental work and research undertaken to understand the mechanism of self-discharge in electrochemical supercapacitor has been relatively less. Few of the pathways of voltage degradation due to self-discharge mechanism are: i) electrolyte decomposition, ii) impurities, iii) internal ohmic leakage, and iv) charge redistribution. Also, short-term history, such as duration of charge/discharge before the circuit, has a huge impact on self-discharge.

A prototype of charge redistribution occurring on the surface of porous electrodes, e.g. an activated carbon electrode, as distinguished by different time constants has been described in many papers. So, this can be considered to be an important aspect which has an impact on self-discharge rate [133]. Self-discharge consists of two distinguished phases, one is the rapid diffusion phase and another is steady decaying of the voltage phase. As a direct consequence of the redistribution of concentration gradients, the supercapacitor dissipates energy at a very fast rate in the diffusion phase. However, elimination of this phase is possible by extending the charging process or by application of small

current. If the current is large, it will create an uneven distribution of ions as the reaction rate and the rate of transfer of ions across the electrolyte medium will be mismatched.

3.2. Components of supercapacitor

3.2.1. Electrolyte

Electrolytes or solution of electrolytes play an important role in the formation of an electrical double layer in EDLC. They contribute to the occurrence of redox reactions in pseudocapacitors for storage of charge, but they also affect the overall performance of the supercapacitor to a great extent. The electrolyte provides ionic conductivity as well as facilitating charge transfer medium between both electrodes [134,135]. Good stability through a wide potential window is one of the important characteristics of good electrolyte. The working electrode voltage of an electrochemical supercapacitor depends on the wide potential range of electrolytes [136,137]. Some of the other characteristics that attribute to a good electrolyte are low ESR (equivalent series resistance), higher ion concentration, electrochemical stability, smaller size of the ions, less toxic, and commercially viability. A few important factors that must be taken into consideration while preparation of electrolyte are the proper choice of solvent, electrolyte interaction with the electrode, ions, and solvent interaction as they affect the self-discharge rate as well as the cycle life of electrochemical supercapacitor. All these properties must be optimized to prepare superior quality electrolyte. The electrolytes are broadly classified into liquid electrolyte, solid-state electrolyte, and redox-active electrolyte.

The energy density of a supercapacitor is directly proportional to the square of the voltage window width and the capacitance. So, the energy density can be increased if we increase the range of the operating potential window (V) or if we increase the specific capacitance of the electrode. As per our best literature survey, the highest specific capacitance in aqueous electrolyte is reported till date is of 800 Fg^{-1} in H_2SO_4 [134]. Xuehang et al. [137] reported the potential window of aqueous electrolyte is 1.0–1.3 V (electrolysis of water occurs at 1.23 V) whereas organic electrolyte has a voltage window range of 2.5–2.7 V. Cheng et al. [121] used ionic liquids as an electrolyte, resulting in a potential window ranging from 3.5 to 4 V. So, operating a supercapacitor beyond the above-mentioned operating voltage of the electrolyte will significantly shorten the cycle life of the supercapacitor [79]. To achieve similar energy density of a superior electrochemical supercapacitor, we need specific capacitance of about 1000 Fg^{-1}, 128 Fg^{-1}, and 65 Fg^{-1} in aqueous, organic, and ionic electrolytes, respectively. The specific capacitance is directly proportional to the surface area of the electrodes. The surface area cannot be increased to infinity and, even if we increase the surface area of the electrodes to some extent, this will cause a simultaneous reduction in the density of the electrodes, ultimately decreasing the volumetric capacitance. Therefore, we can increase the energy density mainly by increasing the voltage window width of the electrolyte. Thus, the developmental works regarding increasing in the potential window width can be achieved via two pathways. First path is a usage of non-aqueous electrolyte which is mainly salt dissolved in some organic solvent; but these electrolytes possess some threats as their vapour pressures are high and they are also highly flammable.

Even after remarkable upgradation in the electrode material, virtually all the latest commercial electrochemical supercapacitors using non-aqueous electrolyte mostly employ organic electrolyte with cell voltages ranging from 2.5 to 2.8 V. These electrochemical supercapacitors either use propylene carbonate (PC) or acetonitrile (ACN) as solvent and tetraethylammoniumtetrafluoroborate (TEABF4) as the salt. Both these electrolytes are characterized by low resistive losses and significantly high conductivities (> 50 mS/cm for ACN and > 10 for PC). EDLC that require high voltage electrolyte usually employs carbonates, sulfones, and adiponitrile as organic solvents. Lately, ionic liquids have grabbed the attention of the researchers and many

electrolyte research works have been reviewed on ionic liquids [138]. They have a larger potential window (3.5–4.0 V) and relatively lower vapour pressure as compared to organic solvents. Therefore, even with lower specific capacitances, we can achieve higher energy density with ionic liquids. The ionic liquids can also be easily customized so that they acquire some other essential properties. Ionic liquids are on great demand due to non volatility, high ionic conductivity and high thermal stability [139]. While developing electrolytes for high voltages, we must consider all factors and control any kind of side reactions that may emerge during developing. But these organic, as well as ionic electrolytes have some disadvantages such as not being economically viable, complicated handling procedures, prone to electrolyte leakage, and high inflammablity. On the other hand, aqueous electrolytes have the advantage of eco-friendly, less expensive, simple preparation methods, and they also possess good ionic conductivity as well as transportation of proton, which are essential factors for obtaining low ESR. So in spite of having lower working voltage than the organic electrolyte, aqueous electrolyte ions can transport at a much faster rate. The researcher also reported that activated carbon electrode showed excellent electrochemical performance in 6 M KOH electrolyte as compared to 6.0 M LiCl and 1.0 M Na_2SO_4 electrolytes [140]. The activated carbon electrodes at 0.5 Ag^{-1} displayed the highest specific capacitance of 124 Fg^{-1} in 6 M KOH. Also, the cyclic efficiency (almost 100%) and current densities are highest in 6 M KOH than the other two electrolytes. The ESR, reported to be only 0.66 Ω, is quite small in case of 6 M KOH. Therefore, based on these results, it is concluded that ideal concentration of aqueous electrolyte for activated carbon-based supercapacitor is 6. KOH. Also, neutral aqueous electrolytes of lithium sulphate salt (Li_2SO_4) serves as a promising electrolyte for eco-friendly EDLC [141]. Therefore, researchers are searching for novel ways to increase the operating voltage of aqueous electrolyte so that they can increase the overall energy density of the supercapacitors in a less expensive way.

Solid polymer electrolytes (SPE) have been in the limelight as they are multifunctional electrolytes with strong ionic conductivity and mechanical properties. For energy storage application, an SPE is developed by combining a sturdy cross-linked epoxy-based matrix with fast-diffusion lithium salt/ ionic liquid electrolyte by using a one-pot curing process. The most commonly used SPE's are poly(acrylonitrile) (PAN) or poly(ethylene oxide) (PEO) because of their propensity for cation solution. PEO has an ether oxygen group and PAN has a cyano group along with a cation which separates the electrolytic cation/anion as charge carriers. Kwon et al. [142] successfully developed epoxy-based cross-linked SPE by plasticizing lithium salt, ionic liquid, and inorganic slurry of Al_2O_3 prepared in single-pot. They reported that when these SPEs are used with activated carbon electrodes, they displayed supercapacitor performance and showed comparatively high power density and energy density (9.3 kW at 44 W h/kg and 75 W h/kg at 382 W/kg). In order to manufacture advanced solid-state supercapacitors, researchers are trying to immobilize ionic liquids within the inorganic compound (silica) and organic materials (copolymer/ polymer) frameworks without any compromise to the ionic liquid's properties.

3.2.2. Binders

The fabrication of electrodes in case of EDLC is usually done by printing or brushing a layer of slurry or paste on a substrate. The substrate is current collector and the slurry or paste is casted on the substrate as a mixture which is prepared by mixing electrode materials (carbon or/and graphene derivatives), binders, and conductive additives by ultrasonic/mechanical stirring. The binder is an inactive component of the supercapacitor which is used in the electrode paste to bind the conductive additives and electrode material together, as shown in Fig. 8. The binder also plays a role of cohering agent by binding the slurry to the substrate (current collector). Hence, during the operation of the electrodes, the activated materials (graphene or carbon derivatives) do not fall off in electrolyte solution. The binders or the cohesive
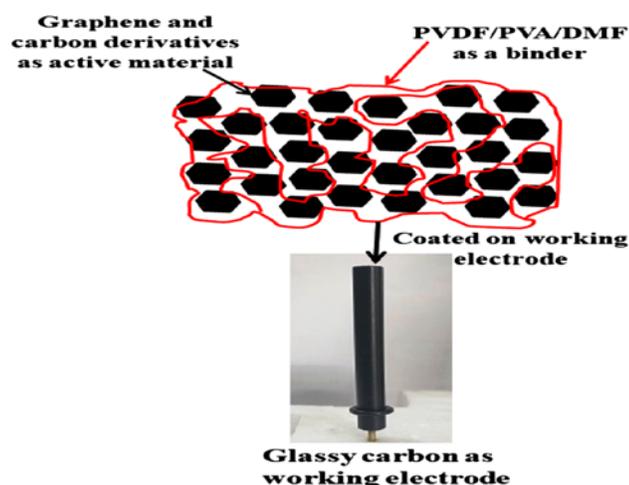
Fig. 8. Schematic diagram of binder binding the active material coated on working electrode.

agents cover the activated material surface, leading to covering of the pores of the activated material, in turn affecting the electrochemical performance of the supercapacitor [143]. Some of the important factors that must be taken into consideration in preparation of supercapacitor binder having high energy density are: i) the conducting additive must be spread uniformly during electrode fabrication so that a uniform conductive network is formed, ii) there must be good electrical connection between the conductive additives and the activated materials, facilitating the transport of electrons and diffusion of ion and also reducing the resistivity, iii) during charging and discharging of the supercapacitor the binder should not fall off, iv) the binder must be compatible with the supercapacitor electrolyte, and v) high adhesive properties [144]. Therefore, it is crucial to examine the above-mentioned properties of the binders and also the content of the binder in the electrode paste so that we can select a suitable binder which does not hinder the electrochemical performance of supercapacitor.

One of the most common and state-of-art binders which have been extensively used in the fabrication of EDLC is the fluorinated thermoplastic binders, such as polyvinylidene difluoride (PVdF) and polytetrafluoroethylene (PTFE). Another commercially used binder is polyvinyl alcohol (PVA). Also, there has been a report of another binder PVdF-hexafluoropropylene (PVdF-HFP) which is derivative of PVdF binder. Another one, Nafion is derived from PTFE. The main advantage of these binders is that they are compatible with all sorts of liquid electrolyte (aqueous, organic, and ionic) used in EDLC. These binders are also suitable for the fabrication of composite electrode [145]. Some report also described the specific capacitances at scan rate of 20 mV s^{-1} of the three electrodes fabricated using activated carbon with three different types of binders [136].

Natural cellulose, obtained from naturally occurring materials like cotton, wood, etc., for the production of paper, cellophane, tissue paper, etc., is a cheap, abundant, and renewable option for the binder. Also, very low average production costs make natural cellulose quite attractive as a binder. The main drawback of natural cellulose is its insolublility in water and most organic solvents, which make it difficult to be introduced in supercapacitors. Natural cellulose can be dissolved in a few ionic liquids such as 1-ethyl-3-methylimidazolium acetate (EMIM Ac). As EMIM Ac is economically viable and also it can be fully recycled, it is an alternative processing method which should be explored [146–148]. There have been report of polyvinyl butyral/ polyvinylpyrrolidone (PVB/PVP)-based electrodes, which have a higher specific surface area than PVDF-based electrodes [149]. So, factors like content of binder, compatibility with the electrode material, electrolyte, solvent, current collector, and cost should be taken into consideration while choosing a proper binder which will increase the adhesive

properties, conductivities, mechanical strength, and electrochemical stability.

3.2.3. Current collector

A current collector is nothing but a substrate or a working electrode on which the electrode materials are coated. The major roles played by the current collector in a supercapacitor are i) collection of electric current as well as facilitating conduction current from the electrode to the power sources or electrical equipment and ii) to provide mechanical support to the electrode. A current collector should possess minimum contact resistance with the activated carbon electrode. Significantly high electrical conductivity and the bonding with the electrode should be strong and stable in order to ensure superior electrochemical performance of ~~the~~ supercapacitor. Aluminium foil, copper foil, graphene foil, and nickel foil are mostly used as current collectors for supercapacitors [144,147,148,150].

Sumboja et al. [151] reported the modification of Al current collectors by using synthesized carbon nanofibers (CNF), significantly reducing the interface impedance between aluminium and the active materials. The supercapacitors having CNF-coated aluminium foil as current collector represented good efficiency, attributed to its exceptionally low internal resistance of 0.4 cm^2 which, in turn, caused an increase in power performance of the active material. Also, these supercapacitors reported excellent cycle stability until 10,000 cycles [150]. Sumboja et al. [151] prepared a current collector for supercapacitor which was nanoarchitectured with a nanowire array of indium tin oxide. They were directly grown to provide an efficient conductivity path. Few researchers also explained the edge of graphene-modified copper and aluminium current collectors respectively [152,153]. They reported that the copper and aluminium current collectors covered with graphene showed a reduction in charge-transfer resistance. Also, there was no corrosion in both the current collectors, thereby, improving cyclic stability and electrochemical performance of the supercapacitor. It opens research opportunities towards the improvement of current-collecting ability of modified collector. The research also suggested improvements in bonding between the active material and current collector. Hence, it can be used even during adverse working conditions such as alternating low and high temperature. This is also reported that after many cycles, an organic electrolyte-coated electrode forms a layer of active material which can be peeled off from the surface of electrode which decreases the electrochemical efficiency [143,144]. Therefore, to avoid such circumstances, some novel as well as scalable approach must be used to modify the aluminium current collectors.

Jiang et al. [152] also suggested the use of laser scanning for coating and to construct micro-nanostructures on the current collector (aluminium) surface. The supercapacitors using laser-aluminium current collector reported very high capacitance of 110 Fg^{-1} at 0.1 Ag^{-1}. However, a pristine aluminium current collector shows maximum capacitance of 20 Ag^{-1} which is at 21.3% retention even after 10,000 cycles. This is mainly because of the high specific area (6.469 m^2 g^{-1}), lower electrical resistance (0.33 Ω m^{-1}), and good interfacial bonding between the current collector and active materials. This approach can serve as a very effective method for modifying current collector's surface [144].

Wu et al. [154] combined a carbon fibre active layer to the aluminium current collector coated with an active layer, thus increasing the conductivity of the current collector. The carbon fibre active layer has 0.4 cm^3 g^{-1} mesoporous pore volume, which is quite large. This larger volume is attributed to the superior electrochemical performance of the supercapacitor. It shows a specific energy of 7 W h kg^{-1} and 18 W h kg^{-1} at −10 °C and 25 °C, respectively, when the specific power of the cell is 25 kW kg^{-1}.

Baskakov et al. [155] prepared supercapacitor current collectors by fused deposition using a composite of carbon nano-materials and polylactic acid. Nickel is another very popular current collector as it

exhibits stability in case of aqueous alkali and high mechanical strength possesses good conductivity and also has good adhesive properties [156]. Also, there are reports on nickel current collectors which have been modified by deposition of a few graphene layers via CVD (Chemical vapour deposition) [153]. These modified graphene-coated nickel current collectors possess high intrinsic specific surface area and also have good conductivity as the electrical contacts between the current collector and active materials are significantly improved, as shown in Fig. 9.

There is no supercapacitor in which the current collectors are made up of only carbon material (e.g. graphene). The conventional current collectors made of metals (Al, Cu, Ni, etc.) have the drawback of being heavy, increasing the overall weight of the supercapacitor. Thus, there is urgency to develop a new and improved current collector, which is quite subtle, and does not face any corrosiveness in presence of acid electrolyte and also modify the existing current collectors.

3.2.4. Separator

The separator plays an important role in supercapacitor energy storage devices, since it separate two oppositely charged electrodes and promote movement of ions through the pores. The separator will be wet with electrolyte, so the selection of separator has to be in accordance with the electrolyte used. Even though separator allows passage of ions, it is an isolator with no electrical conductivity. Polypropylene, NKK, Nomex, and Cellulose-like sheets are mostly used as separators. Whtatman filter papers and even Egg Shell membrane was also used due to their promising porosity [157]. Selection of suitable separator increases the capacitance and decreases the ESR, and hence improves the overall performance of supercapacitor.

3.3. Packaging of supercapacitor devices

While fabricating commercially, the designs that are used are of pouch cell, coin cell, and cylindrical cell. The coin cell design is depicted in Fig. 10a, in which circular electrodes are separated by separator assembled in metal casing where there is high pressure inside the cell. The cylindrical cell design is widely used in commercial supercapacitors in which electrode sheets are rolled with separator sheets as in Fig. 10b. These sheets are inserted into a cylindrical metal case. The connecting tabs are soldered to the electrode sheets followed by injection of electrolyte. The supercapacitors are sealed to ensure inert and moisture free atmosphere inside the supercapacitor devices as well as to prevent leakage. If the electrode and separator sheets are arranged in layer by layer manner, the design is known as pouch cell as in Fig. 10c. Pouch cell design utilizes space efficiently compared to the rest of designs. The supercapacitor assembly is done in polymer bags which are sealed properly.

In a nutshell, this review gives an outlook on the naturally occurring precursors including coal, graphite, and biomass used for synthesising carbon-based supercapacitor electrode materials, which are less expensive compared to graphene, carbon nanotube carbon aerogels etc. It provides the basics technical understanding of EDLC useful for the new researchers in the field of fabrication and testing of supercapacitor energy storage devices using such kind of natural carbon resources. The utilization of these abundant carbon resources in making supercapcitor electrode materials will ultimately reduces the cost of final product. However, such kind of carbon electrode materials warrant more improvement and optimization study for getting a suitable combination with electrolyte, binder, current collector, and separator along with the fabrication process to finally have a perfect and efficient supercapacitor.

4. Summary

Graphene-derivatives-based supercapacitors will be the next generation energy storage device because of their promising attributes. This review gives the detailed explanation and reports on the synthesis of carbon/graphene derivatives using different precursors and methods providing the advantages of activated carbon derived from natural precursors for EDLC/supercapacitor over other electrode materials such as metal oxides, CNTs, conducting polymers, and other composites. There are reports of several novel as well as conventional methods to achieve high energy density of supercapacitors. The compatibility of other inactive and active components with the activated carbon is observed to be having prominent role in fabrication of supercapacitor energy storage devices. The various properties and novel synthetic methods of electrolytes, binders, current collectors, separators, and additives have been widely explored which leads to the development of supercapacitor with excellent electrochemical properties. PTFE as well as other novel and eco-friendly binders are being explored to get certain
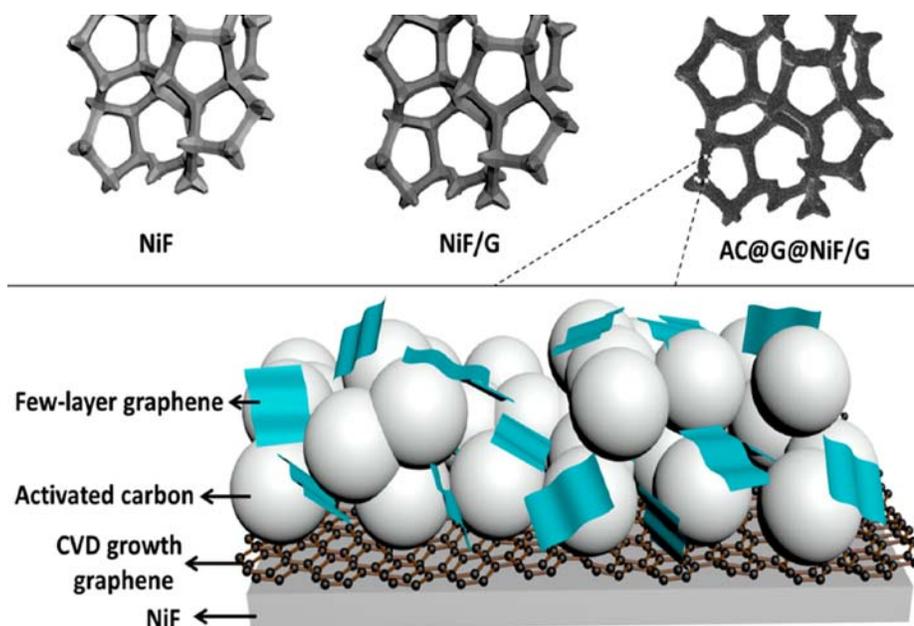

Fig. 9. The schematic diagram AC@G@NiF/G electrode which has activated carbon as active materials and the NiF current collector is modified with layers of graphene sheets [153].
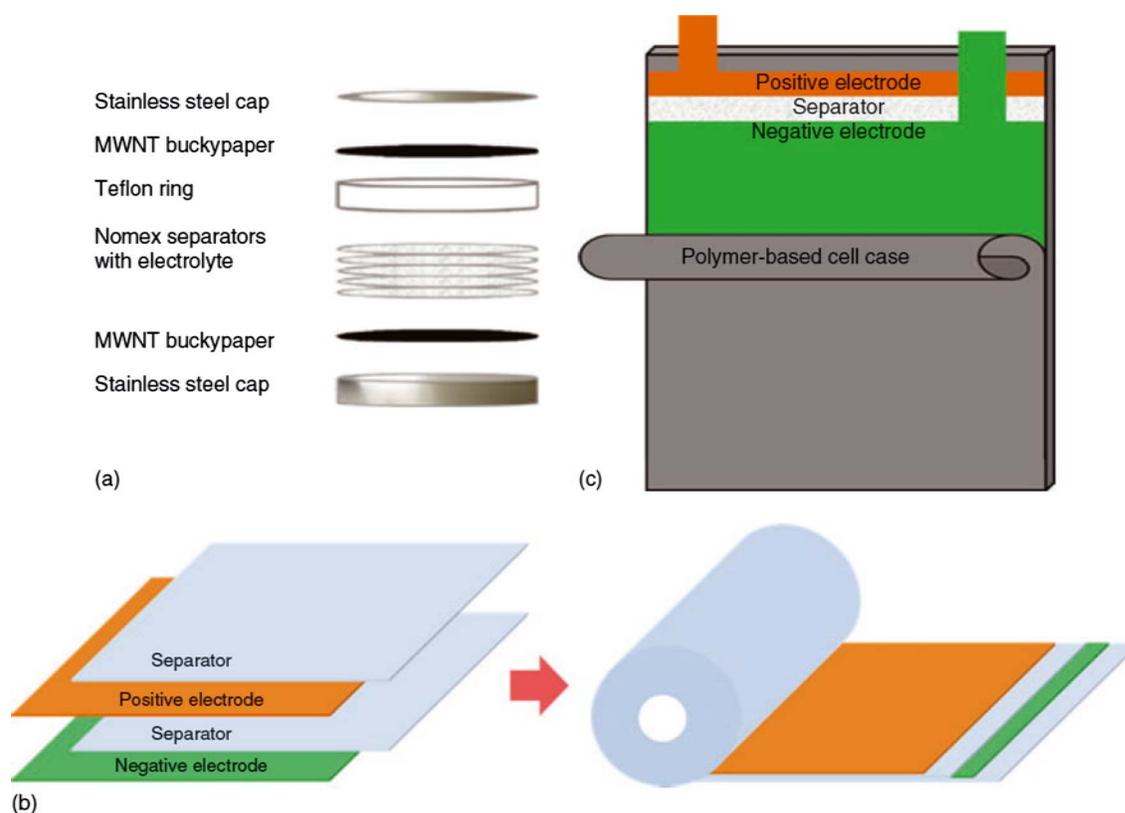
Fig. 10. The schematic diagram of (a) coin cell; (b) cylindrical cell; (c) pouch cell [126,158].

equivalent performance of the supercapacitor. From best of our literature survey, the best conductive additive is found to be carbon black. Very few reports are available on the separators used in supercapacitors and this inactive material must be emphasized as wettability of the separator plays a vital role in performance supercapacitor. Apart from the commercially available organic electrolyte, there are reports on ionic liquids tailored in novel ways for superior performance. Some of the key factors that must be considered before developing supercapacitor energy storage devices are: i) the storage mechanisms and other technological backgrounds must be studied in order to improve the chemical reactions occurring within the supercapacitor; ii) the precursors of carbon/graphene derivatives should be selected properly since the precursors containing high carbon content and inherent interconnected mesoporous and microporous network will serve as better electrode materials; and iii) special emphasis must be given to less-toxic and abundant materials, electrolyte, and binders for commercial application. All these factors and novel materials and methods must be researched in order to develop supercapacitors to meet the energy demand in the near future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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