Chapter 3
Components of Supercapacitor

The components and design of the supercapacitors are similar to the batteries. The components of a supercapacitor device consist of; (i) Electrode material, (ii) Electrolyte material, (iii) Current collector, (iv) Binder and (v) Separators (presented in Fig. 3.1). The electrode and electrolyte materials are regarded as the active component and others are the passive components of the supercapacitor. Normally, a supercapacitor consists of two current collectors/active electrode materials that are separated by a layer of electrolyte or separator.

Although, all the active and passive components have contributions to the storage performance of a supercapacitor, but the electrode material and electrolyte both play a major role.

3.1 Electrode Materials

The electrode materials have a major contribution towards the storage performance of a supercapacitor. Based on the electrode materials, the supercapacitors can be classified into three categories; electrochemical double layered capacitor (EDLC), pseudo capacitors and hybrid capacitors. The classification of the supercapacitors on the basis of electrode materials is illustrated in Fig. 3.2 (Hadjipaschalis et al. 2009). The carbon materials like activated carbon, carbon aerogels, carbon nano tubes (CNTs), graphene etc. show the EDLC behavior. These electrode materials are electrochemically inert and the charge storage takes place only due to the physical accumulation of the charges/ions on the electrode surface. On the other hand, the highly redox active transition metal oxides are under the pseudocapacitive category, where the charge storage takes place because of the physico-chemical adsorption (redox reaction) on the electrode surface (Sarangapani et al. 1996; Simon and Gogotsi 2008; Wang et al. 2009b; Babakhani and Ivey 2010a; Raccichini et al. 2015).

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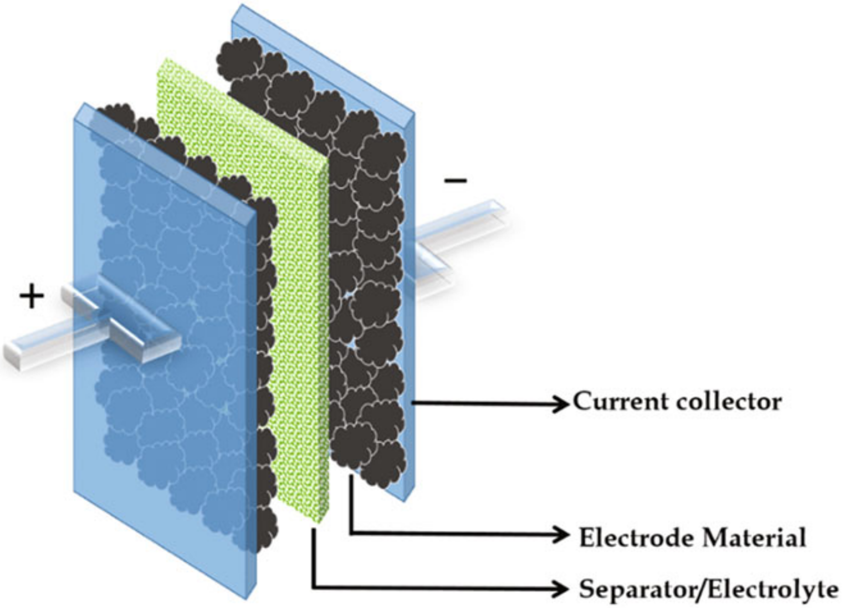

Fig. 3.1 Components of supercapacitor

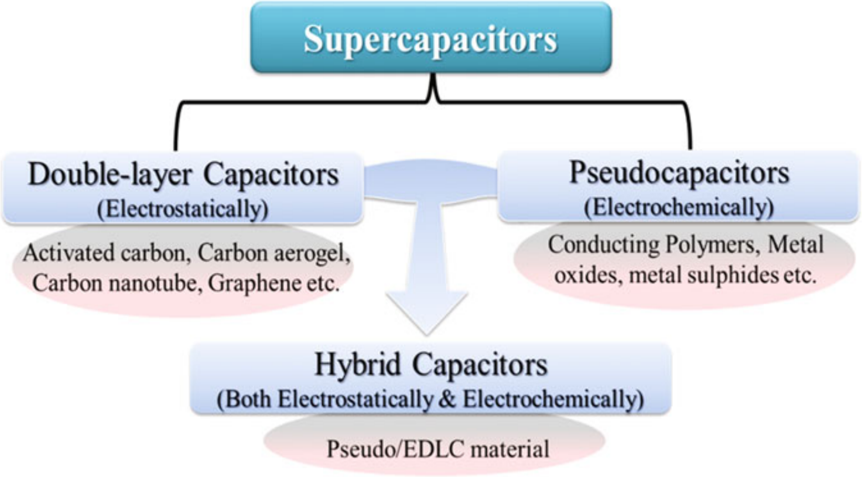

Fig. 3.2 Classification of supercapacitors based on the electrode material and the charge storage mechanism

3.1.1 Carbon Based Electrode Materials

Because of their chemical stability, exceptional electrical conductivity, large theoretical surface area, low manufacture and processing cost, environmental friendliness, high temperature tolerance; carbonaceous materials have gained undivided attention as the electrode material for fabrication of EDLC type supercapacitors (Eikerling et al. 2005; Zhang et al. 2009). The charge storage takes place only by the physical accumulation of charged ions at the electrode/electrolyte interface of the electrode material rather than in the bulk material. Therefore the capacitance performance strongly depends on the specific surface area and surface morphology of the electrode materials. The high surface area carbon materials primarily includes the carbon nanotubes, carbon nano fibers, carbon aerogels, template mediated porous carbon materials etc. (Qu and Shi 1998; Barisci et al. 2000; Endo et al. 2001; Shiraishi et al. 2002; Lee et al. 2006b; Morishita et al. 2006; Fang and Binder 2006; Xu et al. 2008). Many of the researcher have been demonstrated the charge storage performance of these carbon materials and observed the capacitance values of 75–175 F/g and 40–100 F/g in aqueous and organic electrolytes respectively (Burke 2000; Wang et al. 2012a). Generally, the materials having more surface area gives higher capacitance values, thus many methods like heat treatments, steam/alkaline activation, plasma surface treatments etc. have been employed to enhance the specific active surface area of the carbon materials (An et al. 2001; Frackowiak et al. 2002; Raymundo-Piñero et al. 2002, 2006). But in some of the instances, it has been found that the specific capacitance values are not directly proportional to specific surface area of the electrode materials. This is due to the restricted access of the electrolyte ions to all the micro pores in the electrode layer. However, no such concordant information is available on the consequence of optimum pore size of the carbon materials towards the supercapacitor performance. Some of the literatures demonstrated that the optimal pore size may be ~0.8–0.4 or ~0.7 nm for the organic and aqueous electrolytes respectively (Salitra et al. 2000; Raymundo-Piñero et al. 2006). Meanwhile, along with the surface area and pore size distribution, the surface functional group plays a vital role in the capacitance performance enhancement of carbon materials (Momma et al. 1996; Regisser et al. 1996; Béguin et al. 2005; Hulicova et al. 2005; Frackowiak 2007; Seredych et al. 2008). It has been revealed that the hetero atoms (N, S, O etc.) on the surface of carbon materials increase the adsorption of the electrolyte ions, increasing the hydrophilicity of the carbon materials (Fan et al. 2006; Leitner et al. 2006; Hulicova et al. 2006; Wang et al. 2012a). The wettability of the electrode surface accelerates the transportation of the electrolyte ions throughout the availed micro pores. Therefore, increased charge accumulation on the electrode surface takes place leading to increased specific capacitance values (Wang et al. 2012a). In addition to this, the oxygen containing functional groups on the carbon surface induce redox reactions contributing to 5–10% enhancement in total capacitance value (Salitra et al. 2000; Frackowiak et al. 2002). The higher surface area, porous structure and presence of hetero atoms and functional groups of the carbon material assist a lot to increase the specific capacitance performances. Unfortunately, the high contact resistance between the individual carbon particles increases the series resistance of the electrode, thus the electrochemical supercapacitor performance decreases (Zhang et al. 2009). Therefore the development of more conductive carbon materials for less series resistance is highly indispensable.

Graphene is a well-known 2D allotrope of carbon and is also the building unit of most of the other dimensionalities (Geim and Novoselov 2007). It can be wrapped up into 0-D bucky balls, rolled into 1-D nanotube or stacked into 3-D graphite as can be seen in Fig. 3.3. The high surface area, light weight, layered structure of graphene and presence of different redox sites on the reduced graphene oxide (rGO) surface makes graphene a suitable electrode material for the designing of energy storage devices (Li ion battery, supercapacitor etc.) (Raccichini et al. 2015). Also, because of the theoretically large surface area (2675 m^2/g) and higher intrinsic specific capacitance value (550 F/g), it has been chosen as the suitable material for electrochemical double layered capacitor (Ivanovskii 2012; Chen et al. 2013; Raccichini et al. 2015). The specific capacitance value of graphene based materials strongly depends upon the synthesis protocol adopted, procedures followed for designing of the electrode, choice of electrolyte etc. (Raccichini et al. 2015).

But the major disadvantage is that during the synthesis of graphene, restacking of the single sheets take place showing decreased value of the theoretical surface area (Raccichini et al. 2015). Moreover the hydrophobic nature restricts free access of the aqueous electrolyte ions all over the surface of graphene leading to lower experimental capacitance values. So, a method to develop hydrophilic graphene with more accessible surface area and less series resistance is highly required.

As discussed in the above sections, the EDLCs (carbon materials) gave limited specific capacitance which is not sufficient for most of the practical applications

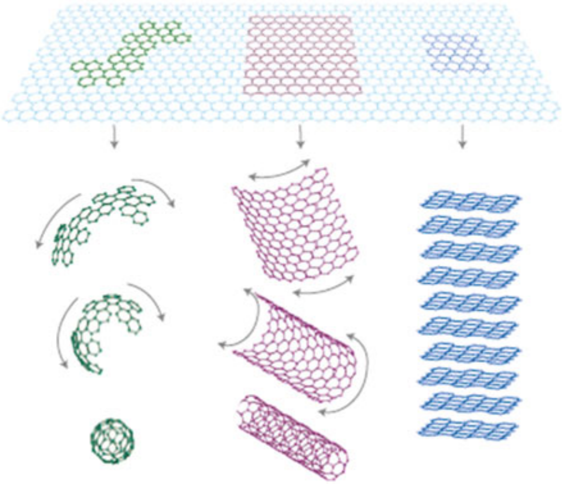

Fig. 3.3 2D graphene as the building block of bucky ball, CNTs and graphite. Reproduced with permission from Geim and Novoselov (2007)

(Zhang et al. 2009). On the other hand, the pseudo capacitive materials (conductive polymers and metal oxides) show 10–100 folds higher specific capacitance compared to the EDLCs because of their fast and reversible faradic reactions (Hu et al. 2007). Thus, substantial research interests have been consecrated to develop the pseudocapacitive electrode materials towards the designing of electrochemical capacitors.

3.1.2 Conducting Polymers (CPs)

The low cost, excellent conductivity (in doped state), negligible environmental impact, wide operational potential window (up to 3.1 V in non-aqueous electrolyte) and tuneable redox activity (by altering the chemical composition) made the conducting polymers (CPs) as the suitable material for supercapacitor development (Kalaji et al. 1999; Prasad et al. 2004; Fan and Maier 2006; Gupta and Miura 2006). The charge storage mechanism in CP based supercapacitors involve the oxidation and reduction of both the surface and bulk of the polymeric backbone of electrode material (Sharma and Bhatti 2010). Depending on the charge developed on CPs during the oxidation or reduction reactions, they are categorised into the following three types; (a) p-doped (PANI; polyaniline, Ppy; polypyrrol etc.), (b) n-doped (polythiophene derivatives) and (c) n-p doped (PTh; polythiophene, poly (3-fluorophenyl) thiophene) CPs (Clemente et al. 1996; Laforgue et al. 1999; Naoi et al. 2000; Mastragostino et al. 2000; Ryu et al. 2002). On the other hand, based on the arrangement of CPs materials, the super capacitors are classified as Type-I (both electrodes are same p-type CP), Type-II (two different p-type CPs) and Type-III (having both n- and p-doped CPs as electrodes) supercapacitors (Rudge et al. 1994; Mastragostino et al. 1996; Conway 1999; Vol'fkovich and Serdyuk 2002; Hashmi and Upadhyaya 2002; Villers et al. 2003). It has been observed that the CPs work well in a restricted potential window. Beyond the confined potential range, either degradation of the CPs takes place (at more positive potential) or the CPs transfers to an insulating state (at more negative potential) (Lota et al. 2004; Snook et al. 2011). Therefore, the selection of a suitable potential window is very much essential for smooth operation of CPs based supercapacitor. Many reports are there on the bare CPs and their composite with carbon materials for supercapacitor electrode development (Lota et al. 2004; Khomenko et al. 2005; Zhang et al. 2008). But unfortunately, they decompose losing the capacitive performance after just about 1000 repeated cycles (Naudin et al. 2001; Sivaraman et al. 2006; Sharma et al. 2008). Also during the intercalation process, swelling and shrinking leads to mechanical degradation of the CPs/CPs composite based supercapacitor electrodes. Therefore, efforts have been devoted to increase the operational stability of these CPs based supercapacitor electrodes. Some research groups have tried to increase the cycle life of the CP based supercapacitors by (i) manipulating the morphology of the CPs, (ii) making hybrid of the polymers, (iii) fabricating the composites with metal oxide/hydroxides/sulphide etc. However, more work still needed to increase the cyclic stability of the CPs based electrode materials towards supercapacitor application (Du Pasquier et al. 2002; Laforgue et al. 2003; Lota et al. 2004; Wang et al. 2006; Sharma et al. 2008).

3.1.3 Metal Oxides

Metal oxides in supercapacitors show better energy storage efficacy over the traditional carbon materials and excellent long cycle performance compared to the CPs based electrode materials. Therefore, efforts have been made to develop higher conductive metal oxides with variable valence states in a cost effective way. Among different transition metal oxides, the likes of RuO_2, MnO_2, cobalt oxides, nickel oxides etc. have been well documented. These oxide based electrode materials stores the electrical charge by both physical accumulation and surface redox reactions in the specified working potential window (Zhao et al. 2007).

Among the transition metal oxides, RuO_2 has been extensively studied for supercapacitor application due to its variable oxidation states, better electrical conductivity, excellent reversibility, robust cyclic stability, wide operational potential window etc. (Sakiyama et al. 1993; Jia et al. 1996; Kim and Kim 2006; Lee et al. 2010a). The charge storage in the RuO_2 based supercapacitors takes place by both the double layer and pseudo capacitive mechanism, demonstrating its candidature for supercapacitor electrode material (Wang et al. 2012a). But the high cost and environmental issues restrict the commercialization of RuO_2 based supercapacitor devices (Fan et al. 2007a). Therefore, other low-cost and environmentally benign metal oxides, e.g. MnO_x, V_2O_5, SnO_2, NiO, CoO, Fe_2O_3 etc. have recently gone under extensive research (Lee and Goodenough 1999; Jayalakshmi et al. 2006; Nam et al. 2008; Wang et al. 2009a; Chen et al. 2009; Wee et al. 2010; Babakhani and Ivey 2010b; Kandalkar et al. 2011). Moreover, the electrochemical performance of the metal oxide based electrode materials towards supercapacitor is highly dependent on the following parameters;

(a) *Specific surface area*: Since the pseudo capacitive performance of the oxide material is a surface phenomenon (i.e. on increasing the surface area, more will be the redox active sites available to interact with the electrolyte), so for higher specific capacitance the specific surface area needs to be increase (Kim et al. 2005; Lee et al. 2006a; Yu et al. 2006). Many effort have been invested to prepare the porous structure materials with a variety of surface morphologies. Among them the one dimensional porous structure are found to be more eminent for the supercapacitor application (Hu et al. 2006; Yuan et al. 2009).

(b) *Surface wettability*: The physically/chemically bound water molecules have a significant role in the enhancement of specific capacitance value in case of oxide based materials. Actually, reversible redox reactions strongly depend on the process involved in the exchange of cations/protons and by electron hopping. It has been observed that, the diffusion of cations taking place by hopping of the electrolyte ions and protons between the OH^- and H_2O sites, demonstrating the increased mobility of hydrogen atoms in the hydrated samples compared to the rigid one (Fu et al. 2002). Therefore, the hydrated electrode materials show enhanced cation diffusion inside the electrode layer, leading to more capacitive performance (Liu et al. 1997; Doubova et al. 2004). During the synthesis process, the high temperature annealing results the lower conductive oxide materials. It strongly inhibits the proton intercalation and shows poor ionic conductivity, leading to a decreased pseudo capacitive performance (Rajendra Prasad and Miura 2004; Sugimoto et al. 2006; Wen et al. 2009). So, optimization of the annealing temperature for the material synthesis is highly required.

(c) *Crystallinity*: The energy storage ability of the oxide material also depends on the phase or the crystallinity/crystal structure of that particular material. The increased crystallinity makes the oxide material more rigid and compact surface, restricting the diffusion of electrolyte ions into the bulk (Wang et al. 2012a). So the redox performance of the whole material gets inhibited and the lower capacitance results only from the surface reaction. Whereas, in case of amorphous materials, the capacitance comes from both the surface as well as bulk of the electrode material (Zheng et al. 1995). This can be controlled by manipulating the synthesis procedures followed and starting precursors taken for synthesis (Zheng et al. 1995; Pico et al. 2009). For example, in the case of RuO_2, on increasing the crystallinity, the specific capacitance value decreases (Kim and Popov 2002). This may be due to the restricted diffusion of the protons/electrolyte ions to the bulk of the crystallised electrode material. In the case of MnO_x, it exists in four different crystal structures as α, β, γ and δ-MnO_2 (Zhang and Chen 2008; Donne et al. 2010). Out of different crystal structures, the δ-MnO_2 shows better cation intercalation/deintercalation with very negligible structural deformation leading to higher specific capacitance values (Ma et al. 2004; Athouël et al. 2008).

(d) *Particle size*: In comparison to bulk, nanostructure particles show superior electrochemical performances towards the supercapacitor application (Sugimoto et al. 2004, 2006; Hu et al. 2006; Dubal et al. 2010; Xia et al. 2010). This is due to the availability of high accessible surface area and short path length requirement for the diffusion of the ions/electrons. Thus the smaller sized particle shows high gravimetric capacitance values with more utilization of electrode material surface (Kim and Popov 2002; Pico et al. 2009). The particle size of the oxide materials can be easily manipulated by following the controlled reaction pathways selecting suitable starting precursors (Ramani et al. 2001; Kim and Popov 2002). For example, the specific capacitance of RuO_2 can be brought closer to the theoretical value in its nanoscale dimensions (Sugimoto et al. 2003, 2005).

In view of the above parameters, extensive efforts have been devoted to synthesize a variety of metal oxide nanostructures with a huge number of surface morphologies for the development of supercapacitor electrodes. However, it has been found that the lower electrical conductivity, high consumption of the precious metal (like Ru, Ni etc.), difficulty to control the grain size further proved too much of a challenge for the development of an alternative material. It has been observed that, on introduction of different metals into one of the selected metal oxide can affect the particle size (addition of niobium, vanadium and tin helps to decrease the size of RuO_2 particles), enhance the electrical conductivity (the electrical conductivity of NiO_x increases by inserting the cobalt/molybdenum ions into the NiO_x matrix) and lower the consumption of the precious metal component (introduction of niobium, tin etc. into the RuO_2 matrix decreases the consumption of Ru metal) leading to an advanced electrode material for supercapacitor application (Ramesh et al. 2005; Yokoshima et al. 2006; Fan et al. 2007b; Hu et al. 2007; Brumbach et al. 2010; Wang et al. 2012a; Ratha et al. 2017). Moreover, in some instances it has been found that, during the synthesis of single/binary metal oxides, aggregation of the particles take place and is associated with lower electrical conductivity values. In order to counter these issues, the composite with conductive carbon materials (CNTs, activated carbon, graphene, reduced graphene oxide etc.) have been developed and explored their energy storage performances (Lin et al. 1999; Jeong and Manthiram 2001; Panić et al. 2003; Pico et al. 2008). Fortunately, the highly dispersion of oxide particles was observed with improved access to the whole nanoparticle surface reducing the ionic resistance, thus experienced with enhanced specific capacitance values (Kim et al. 2005; Barranco et al. 2009). Hence, many electrode materials have been developed for designing the supercapacitors. But different materials are associated with their own limitations which are very important to be addressed. The higher specific surface area, porous structure and better conductivity of the carbon materials make them a suitable candidate for the production of commercial supercapacitor devices, but till now they are associated with low specific capacitance values. The as-developed conductive polymers shows higher specific capacitance values, but their shrinking/swelling during the operation leads to poor cycle life. On the other hand, although the amorphous RuO_2 shows better performances towards the supercapacitor application, but the high cost, limited availability and environmental issues restrict its commercial production.

3.1.4 Metal Nitrides

In contrast to metal oxides, enhanced conductivity has been reported in the case of metal nitrides which are emerging as high performance pseudocapacitive materials for asymmetric supercapacitor devices. Due to the high electrical conductivities in comparison to metal oxides, metal nitrides are expected to possess improved power density (Bouhtiyya et al. 2012; Balogun et al. 2015; Das et al. 2015). Lithiated metal nitrides (Li_3N), transition metal nitrides (Mo_2N, VN, TiN) have already shown intriguing electrochemical activities (Bouhtiyya et al. 2012; Balogun et al. 2015). Though application of these metal nitrides is comparatively limited in supercapacitor devices, their robust chemical properties and excellent lithiation/delithiation property could effectively implemented for both asymmetric and hybrid supercapacitor technologies. In comparison to pseudocapacitive metal oxides, they are capable of generating superior power density. Among the mentioned nitrides, titanium nitride (TiN) has been the most widely studied anode due to its high electrical conductivity and mechanical stability (Grigoras et al. 2016; Kim et al. 2016). However, irreversible oxidation in aqueous media limits its implementation in practical devices. Despite of it, in recent reports, TiN has been combined with more stable materials like graphene, TiO_2, VN, MnO_2, and conducting polymers to form core–shell structures to improve its cycle stability, prevent undesired decomposition to form oxides and rate performances (Balogun et al. 2015).

3.1.5 Composite Materials

As discussed in the previous section, among other carbon based electrode materials, graphene has comparatively higher theoretical specific capacitance and surface area (Raccichini et al. 2015). But it is too difficult to achieve such high values in practice (Sugimoto et al. 2003; Stankovich et al. 2006). Therefore, composite materials of graphene (reduced graphene oxide) with the carbon nanomaterials (carbon nanotubes, activated carbon, carbon spheres, carbon black etc.), metal oxides (MnO_2, RuO_2, Fe_2O_3, Nb_2O_5, NiO etc.) and conducting polymers have been developed (Wu et al. 2010a, b; Yan et al. 2010; Liu et al. 2010; Chen et al. 2011b; Xia et al. 2011; Zhang et al. 2011; Guo and Li 2011; Byon et al. 2011; Yu et al. 2011; Kong et al. 2014, 2015; Grover et al. 2015; Lehtimäki et al. 2015). These additives prevent the restacking process in the reduced graphene oxide generating availability of more accessible surface area to the electrolyte in electrochemical supercapacitors, thus increasing the specific capacitance values. But the complex procedure and requirement of specific instrumental set ups for the synthesis of these composites require intense research and optimization in order to create more opportunities for the development of efficient and high performance electrode materials.

Besides the electrode materials discussed in the previous sections, another class of electrode material consisting of tiny carbon nanoparticles i.e. carbon quantum dots (CQDs) have drawn significant attention in recent past (Xu et al. 2004). These are the quasi spherical carbon particles having very interesting optical performances with tunable electronic properties (Luo et al. 2013; Wang and Hu 2014). These can be synthesized from a variety of precursors by following two main approaches (Fig. 3.4), i.e.

(i) Top-down approach
(ii) Bottom-up approach

In case of the Top-down approach, the quantum dots are derived by breakdown of larger carbonaceous materials. It comprises many of the synthetic strategies like solvothermal/hydrothermal processes, chemical oxidation, arc discharge,

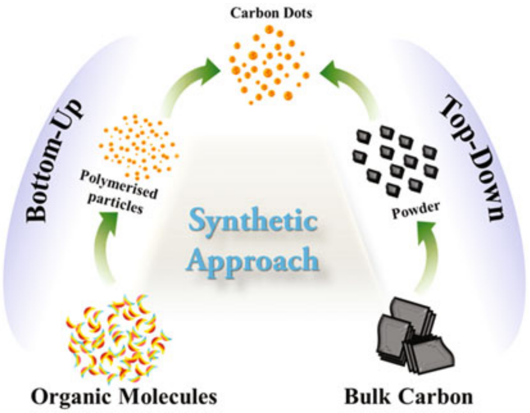

Fig. 3.4 Schematic showing the approaches for synthesis of CQDs

electrochemical cutting, plasma treatment etc. and produces the CQDs from bulk carbon precursors like graphene, carbon fiber and so on (Xu et al. 2004; Pan et al. 2010; Zhu et al. 2011; Shinde and Pillai 2012; Wang et al. 2012b; Li et al. 2012; Peng et al. 2012). Whereas, small carbon containing molecules like carbohydrates, proteins, citric acid etc. produce the CQDs by following the solvothermal/hydrothermal carbonization, microwave treatment, chemical vapor deposition methods under the bottom-up synthetic approach (Hsu and Chang 2012; Zhai et al. 2012; Tang et al. 2012; Shen et al. 2013; Samantara et al. 2016). The electronic properties of these CQDs can be easily tuned either by inserting the hetero atoms into the carbon skeleton during the synthesis or by the post surface modification of the CQDs (Wang et al. 2010; Yang et al. 2012; Prasad et al. 2013; Sun et al. 2013). Because of the ease of synthesis in bulk quantities without any environmental issues and tunable electronic properties, the CQDs are chosen as the suitable carbon material for the composite preparation with graphene. That will restricts the restacking of individual graphene layers, thus giving enhanced capacitance performance. Thereafter the scalable synthesis of the rGO/CQDs composite in a facile synthetic method and the electrochemical analysis for supercapacitor application is highly desired. So a challenge is there to,

- To enhance the specific capacitance of the carbon materials (by optimising the reaction conditions using suitable starting precursors)
- To choose a low cost starting precursor and a facile synthetic method for the bulk synthesis of the CQDs
- To develop binary metal oxides having better electrical conductivity with porous structure (Augustyn et al. 2014)
- Designing of one dimensional porous nanostructures (due to the reduced diffusion path and more accessible surface area the 1D materials shows better supercapacitor performances)
- To synthesize the composite of metal oxides/metal nitrides with carbon material based electrodes for future supercapacitor devices.

3.2 Electrolyte Materials

The primary challenge in the supercapacitor development is to enhance the energy density value, which can be obtained by either increasing the capacitance of electrode material or by widening the working potential of the device. Ideally, broadening of potential window will be advantageous for increasing the energy density of the device (this is due to the fact that the energy density is a function of square of working potential window) and also in reducing the stacking numbers to reach higher potential differences. Increment in the cell voltage is thus more effective compared to increasing the capacitance of electrode materials for energy density enhancement. As the cell potential strongly depends on the electrochemical stability of electrolyte used in order to avoid exhaustive/parasitic reactions, thus efforts have been made to select a suitable electrolyte material for the supercapacitor development. As a result, a variety of electrolytes have been developed and used in supercapacitors with variable potential windows; aqueous electrolyte based supercapacitors (1.0–1.3 V), organic electrolytes based supercapacitors (2.5–2.7 V), ionic liquid supercapacitors (3.5–4.0 V) etc. The selection of an ideal electrolyte not only enhances the energy density values but also has a significant role in improving cycle life, minimization of internal resistance, increase in the specific power output, control over the operational temperature and to decrease the self-discharge process. A brief classification chart has been illustrated in Fig. 3.5.

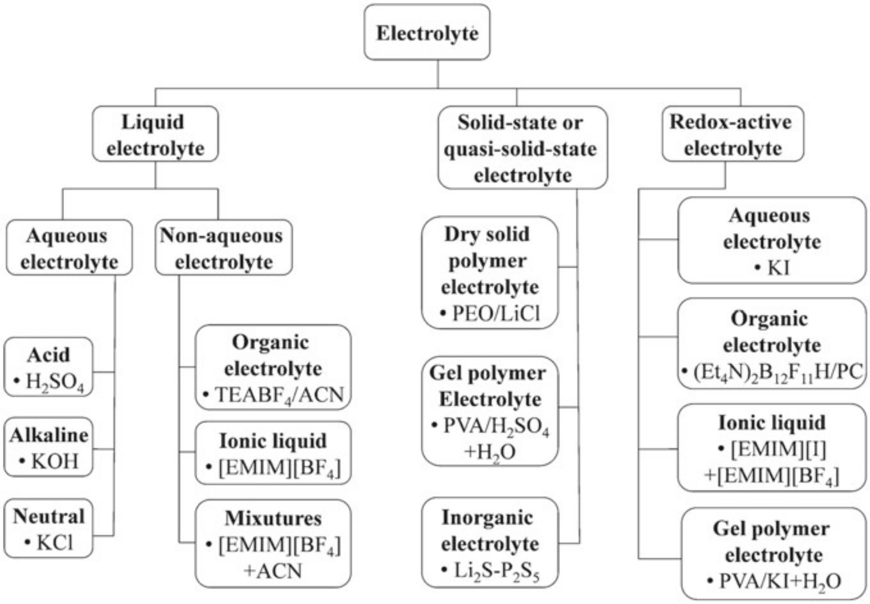

Fig. 3.5 Various categories of electrolytes that have been implemented in the fabrication of supercapacitor devices. Reproduced with permission from Zhong et al. (2015a)

Supercapacitors are developed keeping in mind that they would be able to provide an alternative to Li-ion batteries, thus the quality and quantity of the electrolytic material has a significant role play in tuning a supercapacitor device to obtain desirable output. Preferably, the electrolyte should be lightweight, have good electrochemical activity, high electrical conductivity and large tolerance towards decomposition/degradation. There are varieties of electrolytes that are being employed in supercapacitor devices to validate their overall impact on the capacitive performance. They can be classified into the following broad categories.

3.2.1 Liquid Electrolytes

Choice of electrolytic material for supercapacitor device is the most essential part which is why wide investigation has been done on a large number of liquid electrolytic materials. These liquid electrolytes can further be categorized into aqueous and non-aqueous electrolytes. Further the non-aqueous electrolytes can be categorized into two groups,

1. Organic electrolytes and
2. Ionic liquids.

3.2.1.1 Aqueous Electrolytes

These electrolytes are basically aqueous solution of a group of salts and several inorganic compounds. Aqueous solutions are highly conducting (due to availability of solvated/separated ions) in nature and are beneficial for enhancing the power density (due to low electrolytic resistance resulting in decreased ESR value) in a non-hazardous and cost-effective method. Ease of handling and simplified preparation procedure make the aqueous electrolytes suitable for supercapacitor devices (Zhong et al. 2015a). The aqueous electrolytes are further categorized on the basis of solution pH such as, acidic (H_2SO_4), alkaline (KOH, NaOH, LiOH etc.) and neutral electrolytes (Na_2SO_4, K_2SO_4, Li_2SO_4, $NaNO_3$, KCl etc.) (Long et al. 2011; Fic et al. 2012; Mun et al. 2013; Wang et al. 2014; Dhibar et al. 2014; Abbas et al. 2014; Misnon et al. 2014; Samantara et al. 2015). However, the low potential window, narrow operating temperature range and possible leakage, restricts the use of aqueous electrolyte in commercial supercapacitors (Zhong et al. 2015a). In supercapacitor devices, using aqueous electrolyte, the potential window and operating temperature should be taken care of in order to prevent any kind of decomposition/evaporation which can be catastrophic for the fabricated device. There are instances where it has been found that the neutral electrolyte (aqueous solution of Li_2SO_4) can achieve a wide potential window of 4.0 V and show very low internal resistances in comparison to the organic/ionic liquid based electrolytes (Shimizu et al. 2013). Therefore, the use of aqueous electrolytes in the supercapacitor application might provide a cost effective and environmentally benign route to enhanced energy storage.

3.2.1.2 Non-aqueous Electrolytes

These types of electrolytes are basically organic salt solutions or fused ions (ionic liquids) which are able to sustain higher working potential windows without showing any sign of decomposition/degradation. They are robust in comparison to aqueous electrolytes and are favorable for commercialization purpose. However, the high cost, high toxicity, low conductivity hinders their large scale production. There are three basic categories of non-aqueous electrolytes as discussed in the following Sections.

1. **Organic Electrolytes**

Organic electrolytes are prepared by dissolving a conducting salt in an organic solvent. Because of the wide potential window (2.5–2.8 V), most of the commercial supercapacitors have been fabricated by using organic electrolytes. This wide cell potential not only provides more energy density but also helps to increase the overall thermal and cyclic stability of as-fabricated supercapacitor devices (Brandt et al. 2012; Jung et al. 2013; Perricone et al. 2013; Zheng et al. 2014). Many of the works on organic electrolyte based supercapacitors make use of tetraethyl ammonium tetrafluoroborate ($TEABF_4$), spiro-(1,1′)-bipyrrolidinium tetrafluoroborate ($SBPBF_4$), triethylmethylammonium tetrafluoroborate ($TEMABF_4$) etc. in acetonitrile/propylene carbonate solvents (Perricone et al. 2013; Sevilla and Fuertes 2014; Zheng et al. 2014). However, supercapacitor devices fabricated using organic electrolytes are of high cost, having lower specific capacitance, higher internal resistance, low ionic conductivity, highly flammable, are toxic and require sophisticated instrumentations for their fabrication. Also, in some instances the degradation in capacitance value and self-discharge issues have been observed (Conway 1999). Besides that, the EDLC performance in these types of electrolytes is considerably poor due to large solvated ions and low dielectric constants. Thus, improvement of the electrolyte material is an essential task for high power/energy electrochemical supercapacitor development.

2. **Ionic Liquids (ILs)**

Ionic liquids are made of salts that have room temperature melting point (<100 °C) and contain an asymmetric organic cation coordinated with an inorganic/organic anion. These ionic liquids are often dissolved in organic solvents or taken in their pure form (solvent free electrolyte) to investigate the overall impact on the performance of a supercapacitor device. These ILs provide ample choice to be designed by selecting different cation-anion pair in order to optimize the working potential window. In many of the literatures, the ionic liquid employed for the supercapacitor fabrication comprises of cations such as phosphonium, sulfonium, pyrrolidinium, ammonium etc. and anions such as tetrafluoroborate (BF_4^-), dicyanamide (DCA^-), bis(trifluoromethanesulfonyl)imide ($TFSI^-$) etc. (Zhong et al. 2015a). They have higher ionic conductivities and wider cell voltages (3.5–4.0 V) in comparison to the organic electrolytes (Shi et al. 2014a). Despite having wider potential windows in comparison to aqueous and organic electrolytes, few factors such as low capacitance values, high cost and higher viscosity of the ionic electrolytes restrict their implementation in commercial supercapacitor devices (Xu et al. 2008; Chen et al. 2011a).

3.2.1.3 Redox-Active Aqueous Electrolytes

With conventional supercapacitors relying solely on the redox activity of the electrode materials, it will be interesting if the electrolyte itself can contribute toward the overall capacitive performance of supercapacitor device (Akinwolemiwa et al. 2015). In general, the electrolyte acts as a media for the movement of charge and/or ions between the two electrodes and remains passive without any contribution towards the net capacitance of the device. This is undesired as most of the supercapacitors contain significant amount of liquid electrolyte in order to induce higher pseudocapacitance. Thus, it sounds promising to extract similar redox based capacitance from the electrolyte itself. Hydroquinones, m-phenylenediamine, KI, lignosulfonates, etc. are some of the commonly used compounds which have shown excellent redox behavior as electrolytes (Yan et al. 2014).

Though large pseudocapacitance is obtained via redox activities from the active components, these redox-active electrolytes have the disadvantage of compromising with the rate performance and cycling stability of the supercapacitor devices owing primarily to their deficient electrochemical stability. Besides, a number of electrolytes tend to generate disproportionately high capacitance at the positive electrode with low capacitance at the other electrode, making it difficult to exploit the exceptionally high specific capacitance. Furthermore, some electrolyte systems seem to contribute high electrochemical activity only in acidic media, thus requiring specialized corrosion resistant current collectors, which is undesired considering the high cost associated with the fabrication of such specific current collectors. This significantly hinders the practical implementation of these electrolytes. Therefore, numerous research efforts still should be focused on scalable synthesis of fairly stable and highly effective redox mediators.

3.2.1.4 Redox-Active Non-aqueous Electrolytes

In a quest to achieve elevated cell voltage which would push for a higher energy density value, several non-aqueous electrolytes including organic and IL-based electrolytes have been investigated and reported in the literature. Inclusion of redox-active polyfluorododecaborate cluster ions (i.e., $[B_{12}F_xH_{12-x}]^{2-}$) into an organic mixture solvent containing propylene carbonate (PC) and dimethyl carbonate (DMC) has shown effective pseudocapacitive contribution to the total capacitance of the carbon based supercapacitors (Béguin et al. 2014; Zhong et al. 2015a). Furthermore, tetraethylammonium undecafluorododecaborate ($(Et_4N)_2B_{12}F_{11}H$) when combined with a mixture of PC–DMC, was able to provide overcharge protection for supercapacitor devices due to the presence of redox-active anions (Béguin et al. 2014; Zhong et al. 2015a). Similarly for ionic liquid based electrolytes, it has been demonstrated that an addition of 5 wt% 1-ethyl-3-methylimidazolium iodide ([EMIM][I]) into [EMIM][BF_4] ionic liquid could boost the specific capacitance of a supercapacitor device by nearly ~50% when compared to bare [EMIM][BF_4] ionic liquid electrolyte (Béguin et al. 2014; Yan et al. 2014; Zhong et al. 2015a). Also, another ionic liquid electrolyte, *N*-ethyl-*N*-methylpyrrolidinium fluorohydrogenate ($EMPyr(FH)_{2.3}F$) could significantly contribute extra specific capacitance to a supercapacitor through the redox reaction (Béguin et al. 2014; Zhong et al. 2015a).

3.2.2 Solid and Quasi-Solid (Gel) Type Electrolytes

Though they tend to promote the redox reaction due to better ionic conductivity, leakage and solution resistance plays a limiting role for liquid type electrolytes to be used in large scale. Also, in the case of wearable electronic devices and other portable electronic devices, implementation of liquid based supercapacitors is highly discouraged. Widespread investigation is thus being carried out for more robust and reliable electrolytes to minimize spill, leakage which will make supercapacitor devices more convenient to be implemented for next generation practical applications. In this context, significant research has been carried out for both solid and quasi-solid (gel) type electrolytes (Liao et al. 2015). These non-liquid based electrolytes are generating greater interest due to rapid miniaturization in the electronic industries. A typical gel type electrolyte is composed of a polymer matrix embedded with a liquid electrolyte, specifically designed to retain its flexibility. The liquid electrolyte may be an aqueous electrolyte, an organic solvent, an ionic liquid or a redox active electrolytic mixture.

A number of polymers such as poly(vinyl alcohol) (PVA), poly(methylmethacrylate) (PMMA), potassium/sodium salt of polyacrylic acid (potassium/sodium polyacrylate), poly(ether ether ketone) (PEEK), poly(acrylonitrile)-block-poly(ethylene glycol)-block-poly(acrylonitrile) (PAN-b-PEG-b-PAN), and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) etc. have been investigated for their possible application as a suitable polymer matrix so as to form a desired GPE assembly (Zhong et al. 2015a). A class of GPE known as hydrogels is formed when water is used as the plasticizer. In these hydrogel type GPEs, the water molecules are readily trapped by the complex polymer matrices through surface tension and result in interesting three dimensional network structures (Zhong et al. 2015a). Besides water, few organic solvents such as PC,330 EC and DMF331 or their mixtures (e.g., PC–EC,332 PC–EC–DMC,333 and PC–EC331) have also been commonly used as the plasticizers in GPEs. The level of plasticization in a typical GPE is controlled by the percentage mixture of the polymer matrix and the liquid electrolyte content. The advantage of implementing these GPEs in supercapacitor devices is that they allow for the development of flexible and tunable shapes and structures which are significant in the bendable electronic devices. Various flexible, stretchable, and micro supercapacitor devices have been reported using hydrogels extracted from PVA. Hydrogels based on PVA are synthesized by mixing it with aqueous solutions like H_2SO_4 (acidic), KOH (alkaline) and LiCl (neutral) etc. (Ma et al. 2014; Zhong et al. 2015b). The preference towards the use of PVA as the most suitable polymer matrix comes from its excellent hydrophilicity, simple synthesis technique, non-toxic effect and cost-effectiveness. Hydrogels based on several alternative conducting polymers such as polythiophene, polyaniline and polypyrrole are showing interesting electrolytic properties too (Shi et al. 2014b; Huang et al. 2016; Batisse and Raymundo-Piñero 2017).

Similar to GPEs, solid state electrolytes have recently attracted significant attention with the rapidly increasing demand for reliable and stable storage devices in the areas like portable/wearable electronics, micro-electronic devices (where compactness is highly desired), printable and flexible electronic devices etc. Ease of fabrication and packaging of solid electrolyte based supercapacitors gives a clear advantage over traditional supercapacitor devices those running on liquid based electrolytes. This will also minimize the undesired leakage erstwhile common in the case of liquid electrolyte based supercapacitors.

However, major focus has been put on polymer based elctrolytes for the fabrication of symmetric/asymmetric/hybrid supercapacitors. Only a few works has been reported on the possible implementation of inorganic solid materials such as ceramic electrolytes till date. Polymer based electrolytes can further be grouped into three distinct categories such as solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs) and polyelectrolytes. The gel polymer type electrolytes are often termed as quasi-solid electrolytes due to the presence of liquid content. In contrast, a solid polymer electrolyte consists of a mixture of polymer and inorganic salt (e.g. LiCl) having zero liquid content. The polymer content of a solid polymer electrolyte provides robust framework which supports both liquid (GPEs) and solid (SPEs) contents, however, the ionic conductivity of GPEs are better than those of SPEs. For this reason, GPE-based supercapacitors currently dominate the solid electrolyte-based supercapacitor devices, and studies on dry SPEs are rather limited. The schematic presentation of both SPE and GPE has been provided in Fig. 3.6.

However, depending on their composition and at high operating temperatures, the reliability and stability of GPEs may degrade significantly due to poor mechanical strength and a narrow operative temperature range particularly when water is used as the solvent. Furthermore, the weak mechanical strength of some GPEs is the main concern, as it may lead to internal short circuits, raising safety concerns. As reported in the literature, solid electrolytes have been used in several types of supercapacitors such as EDLCs, pseudocapacitors and hybrid supercapacitors taking different kinds of electrode materials (Liao et al. 2015). Following

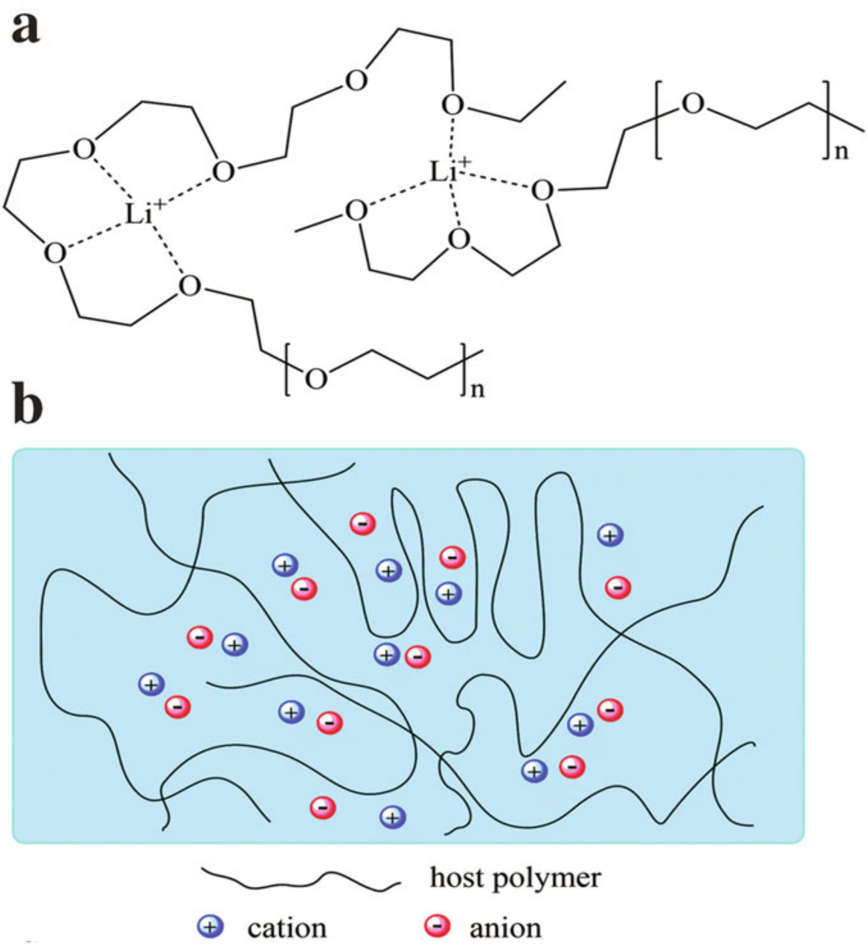

Fig. 3.6 Schematic showing **a** a solid polymer electrolyte and **b** gel polymer electrolyte. Reproduced with permission from Zhong et al. (2015a)

criteria should be considered while developing solid electrolytes for supercapacitor devices: (a) high ionic conductivity, (b) high chemical, electrochemical and thermal stability, and (c) sufficient mechanical strength and dimensional stability. In practice, it is difficult for a solid-sate electrolyte to meet all of these requirements. There are often some trade-off between ionic conductivity and mechanical strength. In this aspect, several reviews have been published recently.

3.3 Current Collector

The electrode and electrolyte materials are the active components of supercapacitors, whereas the current collector is a passive component. But, like the electrode/electrolyte materials, it plays a crucial role towards the durability and cell potential enhancement of a supercapacitor device (Zhong et al. 2015a). The selection of a current collector solely depends on the type of electrolyte taken and electrode material with which the supercapacitor device has been fabricated. In case of strong acid based electrolytes, corrosion resistive metal foil current collectors (like Au) have been used. Furthermore, to minimize the cost of supercapacitor devices, materials like ITO plates (indium tin oxide) and carbon based materials have been developed (Cho et al. 2012; Ryu et al. 2014). In the case of alkaline electrolyte based supercapacitors, the low cost nickel (Ni) based materials are chosen as suitable current collectors. Ni foam has gained popularity as excellent current collector having higher surface area than regular metal foils and capable of utilizing the electrochemical activity of the active electrode material (Gong et al. 2014). It has been found that, the Ni foam current collector contributes a small pseudo capacitance value (due to the presence of $NiO/Ni(OH)_x$ on the surface) to the total capacitance of the supercapacitors particularly when the small amount of the electrode material was taken (Gong et al. 2014). In addition to Ni based materials, other metal (stainless steel foils/foams etc.), alloy (Inconel 600) and few carbon based materials (carbon fabrics, carbon fiber paper, graphite foam, carbon cloth etc.) are found to be suitable current collector in alkaline electrolytes (Xing et al. 2011; Xu et al. 2013; Huang et al. 2013; Xiang et al. 2014; Gong et al. 2014). On the other hand, due to the non-corrosive nature of the neutral electrolytes, a variety of material like ITO, stainless steel, Ni, carbon nanotubes (CNT), titanium oxynitride etc. have been used as the current collector for supercapacitors (Xiao et al. 2014; Ratajczak et al. 2014). In the case of non-aqueous electrolyte (organic electrolytes and ionic liquids) based supercapacitors, the aluminum current collectors are broadly used (Bittner et al. 2012; Brandt et al. 2013). Although a variety of current collectors were developed, but each has some advantages and drawbacks and require further investigation.

Selection of both an electrode material and a suitable current collector is not only essential but also critical for the performance of a supercapacitor device. Incompatibility between current collector (indirect fabrication methods such as drop casting, spin coating, vacuum drying, mechanical pressing etc.) significantly affects the capacitive performance due to the equivalent series resistance (ESR). Therefore, in many recent reports, researchers have followed different synthetic techniques so as to grow the desired electrode materials directly on various high conducting, robust and electrochemically inactive current collectors such as Ni-foam, Ni-foil, Cu-foil, graphene, carbon cloth, stainless steel foil etc. Furthermore, both the current collector and electrode material have different properties toward different types of electrolytes. Interaction between the electrode material and electrolyte plays determining factor toward the stability and reliability of a supercapacitor device. Care should also be taken to consider the interface between electrode material and current collector in the presence of electrolytes which will be helpful to optimize/stabilize the whole system.

3.4 Binders

Binders have long been used by mixing with the powdered active electrode material that not only helps to maintain the structural integrity of the electrode material film but also help in achieving better adhesion between the active material and current collector. Generally, fluorinated polymeric materials like, PVDF [poly(vinylidene fluoride)], PTFE (Polytetrafluoroethylene), Nafion, natural cellulose, PVP (polyvinyl pyrrolidone), PAA (polyacrylic acid) and conductive polymers (polypyrrol, polyaniline etc.) have been employed as the binder for the fabrication of supercapacitors (Lee et al. 2010b, 2011; Kang et al. 2014; Varzi et al. 2014; Aslan et al. 2014). It has been observed that the performance of the supercapacitors strongly affected by the content and type of binder used (Tsay et al. 2012; Abbas et al. 2014). However, the presence of binders such as PTFE in excess concentration could have inhibiting effect on the supercapacitor performance due to their hydrophobic property and hinders the electrolyte penetration leading to lower capacitance performance (Tsay et al. 2012). In some of the cases, mixtures of binders in an optimized proportion have been used to get more wettability and electrolyte access. Due to the adverse effects like lower conductivity, reduced active surface and wettability of the electrode material, most of the current supercapacitor technologies are aiming to develop binder free electrodes which would lead to better utilization of the electrochemical activity of the electrode material. The desired adhesion between the electrode material and the current collector has been achieved via direct growth method or by mechanical crimping with the help of hydraulic technique.

3.5 Separators

Similar to current collectors and binders, separator is a passive component of electrochemical capacitors. Although it has no contribution to the capacitive performance, but plays an important role by preventing any physical contact between the electrodes and facilitating electron transfer between them. The separator's properties like (i) electrical insulator, (ii) ion transfer capability, (iii) chemical/electrochemical inertness, (iv) high mechanical strength (v) optimal thickness, (vi) porosity and (vii) surface morphology etc. influences the performance and durability of a supercapacitor (Tõnurist et al. 2012; Zhong et al. 2015a). There are wide range of materials from which various separators can be fabricated such as, polypropylene, PVDF, PTFE, cellulose polymer membranes (cellulose nitrate, cellulose acetate membranes etc.), glass fiber, Celgard, Nafion 115, graphene oxide films, eggshell membrane etc. (Liu and Pickup 2008; Bittner et al. 2012; Yu et al. 2012; Tõnurist et al. 2012; Shulga et al. 2014).

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