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Aneeya K. Samantara  
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Materials Development  
for Active/Passive  
Components of a  
Supercapacitor  
Background, Present  
Status and Future  
Perspective

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# Materials Development for Active/Passive Components of a Supercapacitor

Background, Present Status and Future  
Perspective

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# Preface

This book deals with the fabrication and working principle of electrochemical capacitors taking into account the current energy crisis and requirement of highly efficient and long-term energy storage solution. Besides alternatives like rechargeable batteries, electrochemical capacitors could help in addressing the global remedy for cleaner, greener and safer energy storage. This would not only preserve the already depleting non-renewable energy resources (and the environmental hazards resulting out of their consumption) but also provide much required support for renewable energy harvesting resources (i.e. solar, wind, hydro and geothermal).

Though electrochemical capacitors have extraordinary charge accumulation capabilities in comparison to conventional dielectric capacitors, they lag behind rechargeable batteries when it comes to energy per weight ratio (energy density). Therefore, urgent attention is required for further development and optimisation so as to achieve higher energy density in currently available electrochemical capacitors. To accomplish this objective, the book closely examines various important parameters controlling the fabrication and characterisation of electrochemical capacitors of various forms. From these analyses, readers can investigate the role of key components such as electrode/electrolyte materials, separators, current collector and binders on the energy storage performance of electrochemical capacitors.

The first part of this book furnishes detailed emphasis on background, classification, principle of charge storage in electrochemical capacitors. Rest of the discussion is focussed to the current limitations and possible strategies to overcome the same. This book has been written keeping in mind that the broad readership would be graduate students, academic researchers and industries involved in sustainable energy and growth. No other publication has addressed these areas so comprehensively, and therefore, this book can be considered to be highly original in content, with no competing texts.

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## About the Book

This brief deals with various forms of supercapacitors starting from traditional carbon based supercapacitors to advanced next generation hybrid supercapacitors. The primary focus is to investigate the successive evolution in the core components of a typical supercapacitor which will bring significant observations regarding their feasibility and overall impact on the charge storage capacity so as to reach at par with the current battery technology. The authors present a critical review of the current collectors, electrode materials and electrolytic components which have distinctive impact on both the power and energy density of a supercapacitor. Emerging trends in the fabrication of hybrid supercapacitor technology bring together the exceptional power density of a double layer capacitor and energy density of a rechargeable battery, which promises a brighter future for the electrical energy storage system.

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## About the Authors

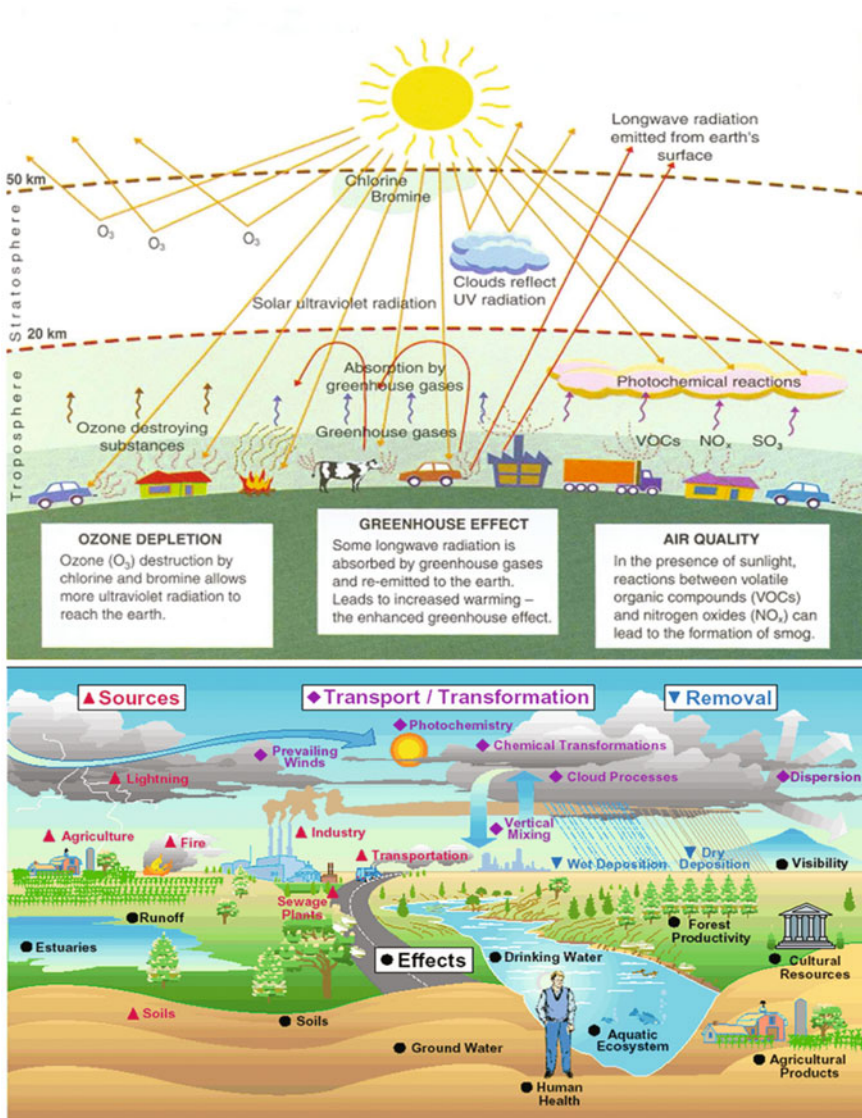
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# Chapter 1

## Introduction

Global population inflation demands for high energy resources to fit the requirements, especially for the emerging economic regions. A sizeable portion of this energy is essential in the field of heavy/local transportation, industrial production, extensive range of electronic gadgets etc. In this context, the future energy requirement is to be shared mostly by the renewable resources such as solar power, wind power, bioenergy, hydro power etc. Harvesting energy from these renewable resources has shown significant improvement considering the fact that hydro power, wind energy and bioenergy (combined) have shown profound growth in their contribution to the world energy production in recent years (RENEWABLES 2016-GLOBAL STATUS REPORT). Though solar power still have not been able to generate enough energy (only 1% share in global energy production), (RENEWABLES 2016-GLOBAL STATUS REPORT) however, rapidly declining costs of solar photovoltaic (PV) technology have created more opportunity for further optimization of the system. As important is the implementation of these renewable energy sources to support the sustainability of our rapidly depleting natural resources, parallel development of high capacity and efficient devices for the storage of the energy harvested from the renewable sources is urgent. Consumption of these non-renewable energy resources, in an unregulated manner would not only destabilize our natural reserves but also affect our environment drastically by releasing particulates and hazardous gaseous pollutants like CO<sub>2</sub>, greenhouse gases, sulphur, nitrogen oxide etc. (Fig. 1.1) (Crippa et al. 2016). In order to curb the exhaustion of our priceless natural reserves (for the sake of our future generations) and to protect our surroundings, immediate focus should be put on the generation of clean energy such as electricity, which will ease out the stress on our already degrading environment and though costly (for now), would bring uncompromised and unparalleled balance/benefit to the living world. The compulsion to combat such rapidly changing climatic conditions is the resultant of unregulated consumption of natural resources combined with their disastrous after effects. Realization of renewable energies is a must in order to tackle such catastrophic changes to our living earth. Though these renewable energy sources produce



**Fig. 1.1** Figure showing the types of air pollutants released due to the consumption of fossil fuels and their direct/indirect consequences on varieties of habitats and their adverse effects (reproduced with permission from Crippa et al. 2016)

enormous amount of energies, they are however, dispersed and thus require localized storage options capable of gathering the enormous bursts of energy generated. Furthermore, the poorly developed storage technologies have long been pushing for the development of efficient, environmentally friendly, cost-effective and safe energy storage options.

Unlike fossil fuels, electrical energy is volatile in nature. Post production, it should immediately be put to carry out effective work and is difficult to store. Therefore, electrical energy storage (EES) requires urgent attention in order to store and disseminate electrical energy properly (Lewis 2007; Yang et al. 2014; Simon et al. 2014). It is to be noted that, electric energy can only be stored via devices like batteries, capacitors and inductors. The battery technology is by far the most evolved and commercially viable option for EES. However, slow charge uptake, bulky design and short cycle life does not allow the battery technology to penetrate critical areas such as high power electric vehicles, lightweight and wearable devices, portable electronics and transparent and flexible displays. Also, hazardous and highly toxic chemical content inside most of these batteries pose great danger to the surrounding environment and require careful management/recycling (Li et al. 2016a). Li-ion technology in recent years has gained prominence due to being highly compact and their low toxic content. Despite the fact that the Li-ion based energy storage shares a sizable portion when it comes to EES, lower values of power density and risk of thermal decomposition at elevated temperature still hinders its implementation in broader context (Jain et al. 2015). Therefore, devices having higher power densities and higher cyclic stability are required to complement the excellent energy density possessed by batteries. The current focus is on the capacitor technology, i.e. to store charge via electrostatic technique. As there are no vigorous chemical reactions taking place, these devices therefore can charge and discharge at lightning speed. Supercapacitors are a new class of devices employing electrostatic mechanism of charge trapping. They possess excellent cyclic stability, ultra-fast charging and discharging and operate through a simple mechanism. Unlike batteries, these devices do not require bulky electrodes and therefore are lightweight, non-toxic, and don't pose complex disposal issues. Supercapacitors possess a capacitance which is  $>10^6$  times of the capacitance found in the case of conventional dielectric capacitors. A typical supercapacitor has superior power density than Li-ion battery and higher energy density than a conventional capacitor. Thus, supercapacitor devices can bring a perfect balance between rapid storage of electrical energy and controlled distribution of the same. Therefore, investing a great level of attention into the development and implementation of supercapacitor devices in EES is urgently required.

Besides addressing the issues that were found in the case of Li-ion batteries, supercapacitors can be realized in wider range of applications starting from heavy duty electric vehicles (supporting both the battery stack and effectively replacing the flywheel technology to improve regenerative braking) to sophisticated low-dimension and portable electronic technologies such as biomechanical energy harvester, flexible and miniature electronic appliances, personal digital assistant (PDA) etc.

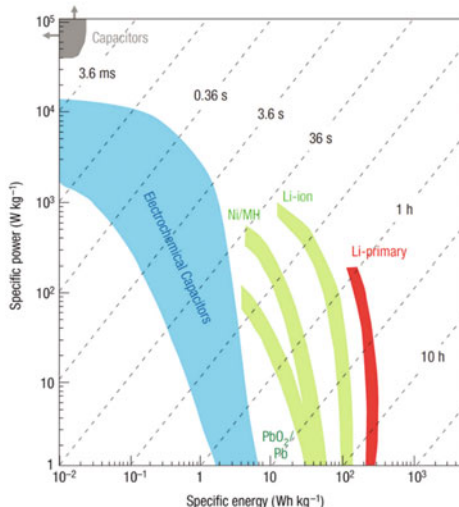
The concept of supercapacitors is relatively recent and its practical investigation initiated with the use of carbon based electrodes having exceptionally high surface areas and excellent stability (more than  $>500,000$  operational cycles) (Miller and Burke 2008). Their charge storage is governed by the formation of two distinct layers of charge/ions constituting a double layer. The charge storage is due to the

combined effect of both electrochemical adsorptions (electrochemical) and coulombic interaction (electrostatic) at the electrode/electrolyte interface. The charge trapping triggered by adsorption and static attraction effect enables the device to charge and discharge rapidly without losing stability, thus generating more power density than a typical battery.

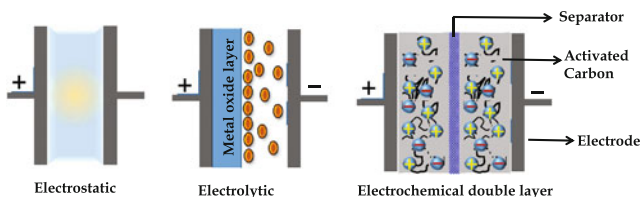
In the recent past, supercapacitor devices have gone through intense structural and morphological modifications in order to replicate the success story of Li-ion technology. Their morphological appearance and subsequent effective capacitance determines their application in specific field. They can be used in bulk through integration with the battery stacks in heavy duty electric vehicles where they protect the battery units from overcharging and/or deep discharge. They can also be effective in lower-dimensional structures (in-plane supercapacitors) with minimum space requirements (Wu et al. 2013; Li et al. 2016b; Liu et al. 2016, 2017). Charge storage performance is also dependent on the fabrication process. The detailed structural, morphological varieties and effect of both on the supercapacitor performance have been discussed in the following sections.

As mentioned in the previous section, storage of the harvested energy plays a critical role in future high power energy applications, which motivates the development of alternatives for the authentic, cost effective energy storage devices (Largeot et al. 2008; Simon et al. 2014). Although varieties of such alternatives have been considered, the electrochemical energy storage (EES) devices, show greater degree of interest because of their cost effectiveness, scalability and excellent ability to store and deliver energy. Devices like the fuel cells, batteries and supercapacitors etc. are the core components of EES. Although these devices are used for the storage of electrical energy, their fabrication, storage/deliver efficiency and the working principles are different (Gogotsi and Simon 2011; Zhang et al. 2015). Battery and the fuel cell store the electrical energy in terms of chemical reactions, whereas supercapacitors store energy in terms of electric potential developed due to the intercalation/electrosorption of opposite charges under the influence of an external applied field. Conventional supercapacitors store energy via Helmholtz double layer mechanism at the interface of the electrode and electrolyte. While the impressive power density of these devices easily surpasses that of a typical Li-ion battery, their lower value of energy density however, is a primary concern. In order to enhance the energy density without sacrificing the power density, efforts have been made to improve the storage/deliver efficiency of these devices through manipulation of some of the fundamental parameters. Primarily, the specific energy (Wh/kg) and specific power (W/kg) are the two main factors used for the performance evaluation of these storage systems (Fig. 1.2) (Simon and Gogotsi 2008). The capacity of the device has been measured to store the energy and the rate at which the device acquires/deliver energy from/to the supply/load, respectively. Generally, the power and energy of these devices are either normalized with respect to the mass (gravimetric), area (areal) or the volume (volumetric) of the electrode/electrode material.

Capacitors can be classified into three broad categories, (i) Electrostatic, (ii) Electrolytic and (iii) Electrochemical capacitors. Although all three are used to



**Fig. 1.2** Ragone plots showing representative energy storage devices of capacitors, batteries, and supercapacitors (reproduced with permission from Simon and Gogotsi 2008)



**Fig. 1.3** Schematic presentation of the types of capacitors with different configuration

store the stationary electrical energy but they are classified based on their construction and storage mechanism (Fig. 1.3). The electrostatic capacitors are regarded as the first generation of capacitor that contain two metallic plates separated by an insulating (having dielectric property) medium like air, mica sheet, paper, ceramic materials etc. After applying the potential gradient, charges of opposite nature tend to move away from each other and accumulate on the separated electrodes whose polarity is determined by the polarity of the applied field. Capacitance of these capacitors is very low achieving the order of few pico or nano farads. The second generation capacitors are different considering the fact that they have an additional electrolytic content along with the dielectric medium.

It also comprises two electrodes, one of which is a metal foil taken as the positive electrode (anode) and the conducting electrolyte itself acts as the negative electrode (cathode) used to polarize the charges during the charging process. The metal foil (anode) have a thin oxide layer on its surface made through etching

process which acts as the dielectric layer and enables to retain the charge for a longer time. The capacitance value of a typical electrolytic capacitor is more than that of an electrostatic capacitor and can reach milli farads. Third generation of capacitors constituted the ceramic type capacitors. These were made from fine granules of ferroelectric materials mixed with ceramic substance to produce desired capacitance. These ceramic type capacitors are the most reliable, robust and have higher capacitance values in comparison to both dielectric and electrolytic capacitors. That is why ceramic capacitors have been implemented in sophisticated electronic circuits as well as military grade applications (Muhammad et al. 2016). It is to be noted that, except electrolytic capacitors, which are polarized, both ceramic type and conventional dielectric capacitors are non-polarized. Also, all of the above mentioned capacitors were not made exclusively for the purpose of energy storage. They were found mainly in the electronic/electrical circuitry for the purpose of coupling, phase shifting, filtering AC (alternative current) signals (ripples) etc.

The next generation capacitors are electrochemical capacitor otherwise known as the electrochemical double layer capacitor (EDLC). In this case, the carbon material is taken as both the cathode and anode separated by an organic or aqueous electrolyte. Here, the charge storage takes place mainly due to the accumulation of the charges/ions on the surface of the electrode material driven by an externally applied potential difference. The capacitance value of these devices are of the order of farads ( $>10^{12}$  to  $10^9$  times the capacitance of a dielectric capacitor and  $>10^6$  to  $10^3$  times that of electrolytic/ceramic capacitor).

## References

- Crippa M, Janssens-Maenhout G, Dentener F et al (2016) Forty years of improvements in European air quality: regional policy-industry interactions with global impacts. *Atmos Chem Phys* 16:3825–3841. <https://doi.org/10.5194/acp-16-3825-2016>
- Gogotsi Y, Simon P (2011) True performance metrics in electrochemical energy storage. *Science* 334(80):917–918
- Jain A, Hautier G, Ong SP et al (2015) Relating voltage and thermal safety in Li-ion battery cathodes: a high-throughput computational study. *Phys Chem Chem Phys* 17:5942–5953. <https://doi.org/10.1039/C5CP00250H>
- Largeot C, Portet C, Chmiola J et al (2008) Relation between the ion size and pore size for an electric double-layer capacitor. *J Am Chem Soc* 130:2730–2731. <https://doi.org/10.1021/ja7106178>
- Lewis NS (2007) Toward cost-effective solar energy use. *Science* 315(80):798–801
- Li M, Liu J, Han W (2016a) Recycling and management of waste lead-acid batteries: a mini-review. *Waste Manag Res* 34:298–306. <https://doi.org/10.1177/0734242X16633773>
- Li R-Z, Peng R, Kihm KD et al (2016b) High-rate in-plane micro-supercapacitors scribed onto photo paper using in situ femtolasers-reduced graphene oxide/Au nanoparticle microelectrodes. *Energy Environ Sci* 9:1458–1467. <https://doi.org/10.1039/C5EE03637B>
- Liu Z, Wu Z-S, Yang S et al (2016) Ultraflexible in-plane micro-supercapacitors by direct printing of solution-processable electrochemically exfoliated graphene. *Adv Mater* 28:2217–2222. <https://doi.org/10.1002/adma.201505304>

- Liu Z, Liu S, Dong R et al (2017) High power in-plane micro-supercapacitors based on mesoporous polyaniline patterned graphene. *Small* 13:1603388. <https://doi.org/10.1002/sml.201603388>
- Miller JR, Burke AF (2008) Electrochemical capacitors: challenges and opportunities for real-world applications. *Electrochem Soc Interface* 17:53–57
- Muhammad R, Iqbal Y, Reaney IM (2016) BaTiO<sub>3</sub>-Bi(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub> ceramics for high-temperature capacitor applications. *J Am Ceram Soc* 99:2089–2095. <https://doi.org/10.1111/jace.14212>
- Simon P, Gogotsi Y (2008) Materials for electrochemical capacitors. *Nat Mater* 7:845–854. <https://doi.org/10.1038/nmat2297>
- Simon P, Gogotsi Y, Dunn B (2014) Where do batteries end and supercapacitors begin? *Science* 343(80):1210–1211. <https://doi.org/10.1126/science.1249625>
- Wu Z, Parvez K, Feng X, Müllen K (2013) Graphene-based in-plane micro-supercapacitors with high power and energy densities. *Nat Commun* 4:2487
- Yang B, Hooper-Burkhardt L, Wang F et al (2014) An inexpensive aqueous flow battery for large-scale electrical energy storage based on water-soluble organic redox couples. *J Electrochem Soc* 161:A1371–A1380. <https://doi.org/10.1149/2.1001409jes>
- Zhang C, Lv W, Tao Y, Yang Q-H (2015) Towards superior volumetric performance: design and preparation of novel carbon materials for energy storage. *Energy Environ Sci* 8:1390–1403. <https://doi.org/10.1039/C5EE00389J>



## Chapter 2

# Historical Background and Present Status of the Supercapacitors

The capacitive performance of the double layer at solid/electrolyte interface is a known phenomenon since 1879, first predicted by Hermann von Helmholtz. But, the practical use of double layered capacitance was first accomplished after the patent on carbon based electrolytic capacitors booked by Becker at the General Electric Corporation (Becker 1957). After Becker, Sohio Corporation, Cleveland, in the year 1969, manufactured the first electric double layer capacitor for the commercial purpose using porous carbon in a non-aqueous solvent comprising tetra alkyl ammonium salt based electrolyte (Boos 1970). In 1978, NEC (a Japanese multinational Information Technology provider) marketed the double layer capacitor technology as “supercapacitor” for the memory back up in computers. Although the product had been placed in the market, but still it was associated with the lower specific energy values. Thereafter, so many efforts have been made to design supercapacitors with higher efficiency. It has been observed that, up to 1990, no such improvement in the material design and technology development for low cost manufacturing of supercapacitors were carried out. Then Conway’s group developed the concept of pseudocapacitance by introducing RuO<sub>2</sub> having higher specific capacitance and low series resistance (Conway 1991). Renewed interest toward the development of supercapacitors occurred after recognizing its importance in the hybrid vehicles in the late 90s. These pseudocapacitive materials (especially the transition metal based oxides, polymers etc.) show ~10–100 fold higher energy storage performance in comparison to the EDLCs. This enhanced storage properties are due to the highly reversible redox (faradic) process, which is completely different from that of EDLCs. These types of capacitors involve both the non-faradic (electrical double layer) and faradic (redox) charge storage processes (Zhang et al. 2011). In the present stage, the capacitors available in market constitute both the higher surface area carbon materials (activated carbon) apart from highly redox active RuO<sub>2</sub> (Hu et al. 2006). Because of the high powered supercapacitors, the concept of hybrid energy storage system came into existence that contains supercapacitors integrated either to a fuel cell or a battery.

## References

- Becker HI (1957) Low voltage electrolytic capacitor. United States Pat. Off. 2–4
- Boos DL (1970) Electrolytic capacitor having carbon paste electrodes. 1–10
- Conway BE (1991) Transition from “supercapacitor” to “battery” behavior in electrochemical energy storage. *J Electrochem Soc* 138:1539–1548. <https://doi.org/10.1149/1.2085829>
- Hu C-C, Chang K-H, Lin M-C, Wu Y-T (2006) Design and tailoring of the nanotubular arrayed architecture of hydrous RuO<sub>2</sub> for next generation supercapacitors. *Nano Lett* 6:2690–2695. <https://doi.org/10.1021/nl061576a>
- Zhang X, Shi W, Zhu J et al (2011) High-power and high-energy-density flexible pseudocapacitor electrodes made from porous CuO nanobelts and single-walled carbon nanotubes. *ACS Nano* 5:2013–2019. <https://doi.org/10.1021/nn1030719>

## 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).

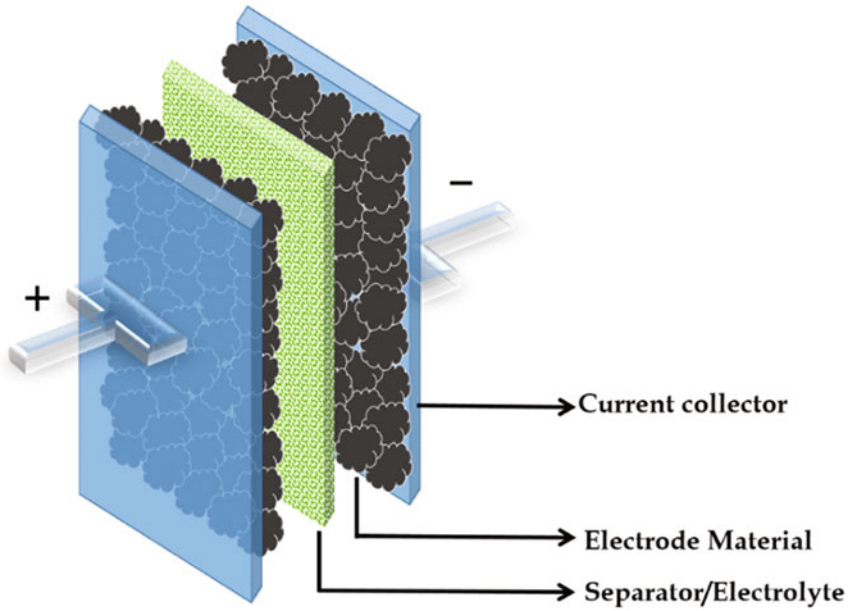


Fig. 3.1 Components of supercapacitor

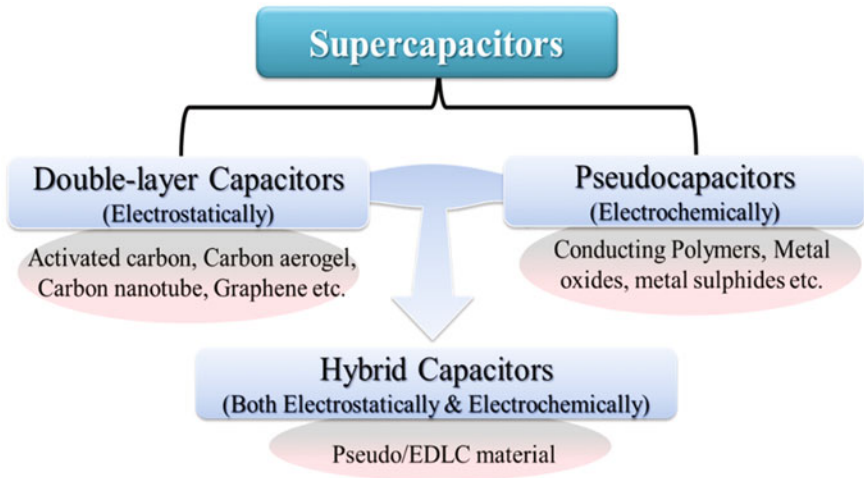


Fig. 3.2 Classification of supercapacitors based on the electrode material and the charge storage mechanism

### 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  $\sim 0.8$ – $0.4$  or  $\sim 0.7$  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

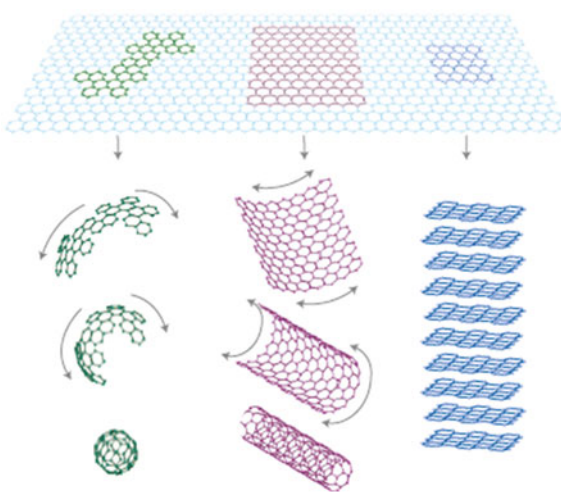
specific capacitance performances. Unfortunately, the high contact resistance between the individual carbon particles increases the series resistance of the electrode, thus the electrochemical supercapacitor performance decreases (Zhang et al. 2009). Therefore the development of more conductive carbon 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 ( $2675 \text{ m}^2/\text{g}$ ) and higher intrinsic specific capacitance value ( $550 \text{ F/g}$ ), 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  $\text{RuO}_2$ ,  $\text{MnO}_2$ , 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,  $\text{RuO}_2$  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  $\text{RuO}_2$  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  $\text{RuO}_2$  based supercapacitor devices (Fan et al. 2007a). Therefore, other low-cost and environmentally benign metal oxides, e.g.  $\text{MnO}_x$ ,  $\text{V}_2\text{O}_5$ ,  $\text{SnO}_2$ ,  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{Fe}_2\text{O}_3$  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  $\text{OH}^-$  and  $\text{H}_2\text{O}$  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  $\text{RuO}_2$ , 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  $\text{MnO}_x$ , it exists in four different crystal structures as  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ - $\text{MnO}_2$  (Zhang and Chen 2008; Donne et al. 2010). Out of different crystal structures, the  $\delta$ - $\text{MnO}_2$  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  $\text{RuO}_2$  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  $\text{RuO}_2$  particles), enhance the electrical conductivity (the electrical conductivity of  $\text{NiO}_x$  increases by inserting the cobalt/molybdenum ions into the  $\text{NiO}_x$  matrix) and lower the consumption of the precious metal component (introduction of niobium, tin etc. into the  $\text{RuO}_2$  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  $\text{RuO}_2$  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 ( $\text{Li}_3\text{N}$ ), transition metal nitrides ( $\text{Mo}_2\text{N}$ , 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<sub>2</sub>, VN, MnO<sub>2</sub>, 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

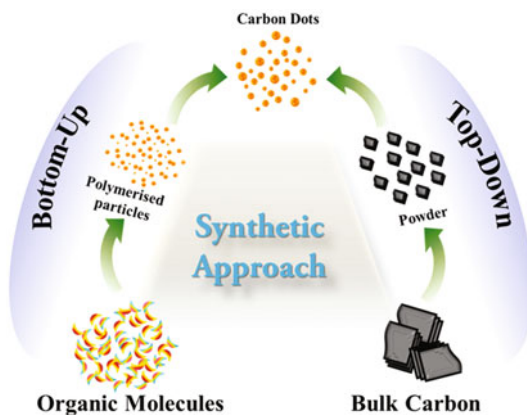
As discussed in the previous section, among other carbon based electrode materials, graphene has comparatively higher theoretical specific capacitance and surface area (Raccichini et al. 2015). But it is too difficult to achieve such high values in practice (Sugimoto et al. 2003; Stankovich et al. 2006). Therefore, composite materials of graphene (reduced graphene oxide) with the carbon nanomaterials (carbon nanotubes, activated carbon, carbon spheres, carbon black etc.), metal oxides (MnO<sub>2</sub>, RuO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, 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

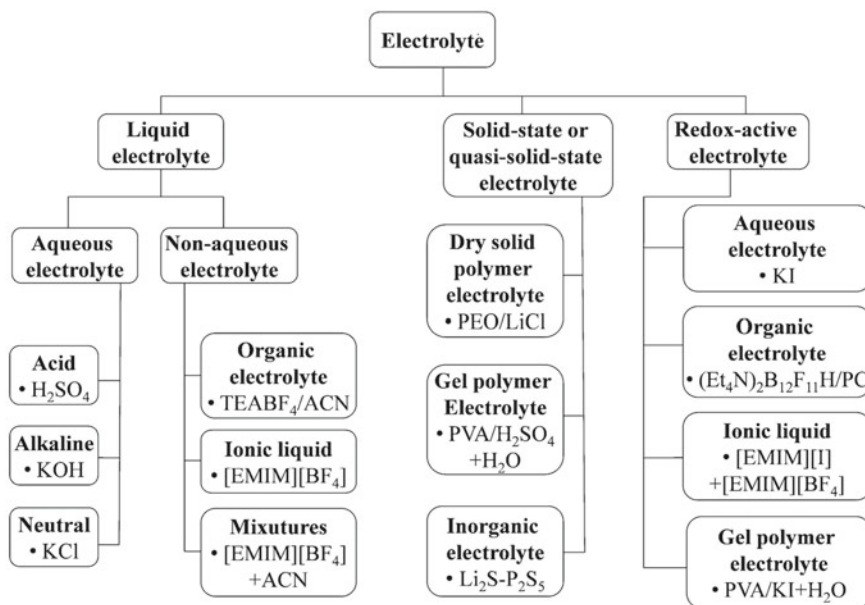


electrochemical cutting, plasma treatment etc. and produces the CQDs from bulk carbon precursors like graphene, carbon fiber and so on (Xu et al. 2004; Pan et al. 2010; Zhu et al. 2011; Shinde and Pillai 2012; Wang et al. 2012b; Li et al. 2012; Peng et al. 2012). Whereas, small carbon containing molecules 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 ( $\text{H}_2\text{SO}_4$ ), alkaline (KOH, NaOH, LiOH etc.) and neutral electrolytes ( $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{NaNO}_3$ , 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  $\text{Li}_2\text{SO}_4$ ) 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<sub>4</sub>), spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBPBF<sub>4</sub>), triethylmethylammonium tetrafluoroborate (TEMABF<sub>4</sub>) 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<sub>4</sub><sup>-</sup>),

dicyanamide ( $\text{DCA}^-$ ), bis(trifluoromethanesulfonyl)imide ( $\text{TFSI}^-$ ) 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.,  $[\text{B}_{12}\text{F}_x\text{H}_{12-x}]^{2-}$ ) 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  $((\text{Et}_4\text{N})_2\text{B}_{12}\text{F}_{11}\text{H})$  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<sub>4</sub>] ionic liquid could boost the specific capacitance of a supercapacitor device by nearly ~50% when compared to bare [EMIM][BF<sub>4</sub>] 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 (EMPyrr(FH)<sub>2,3</sub>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.

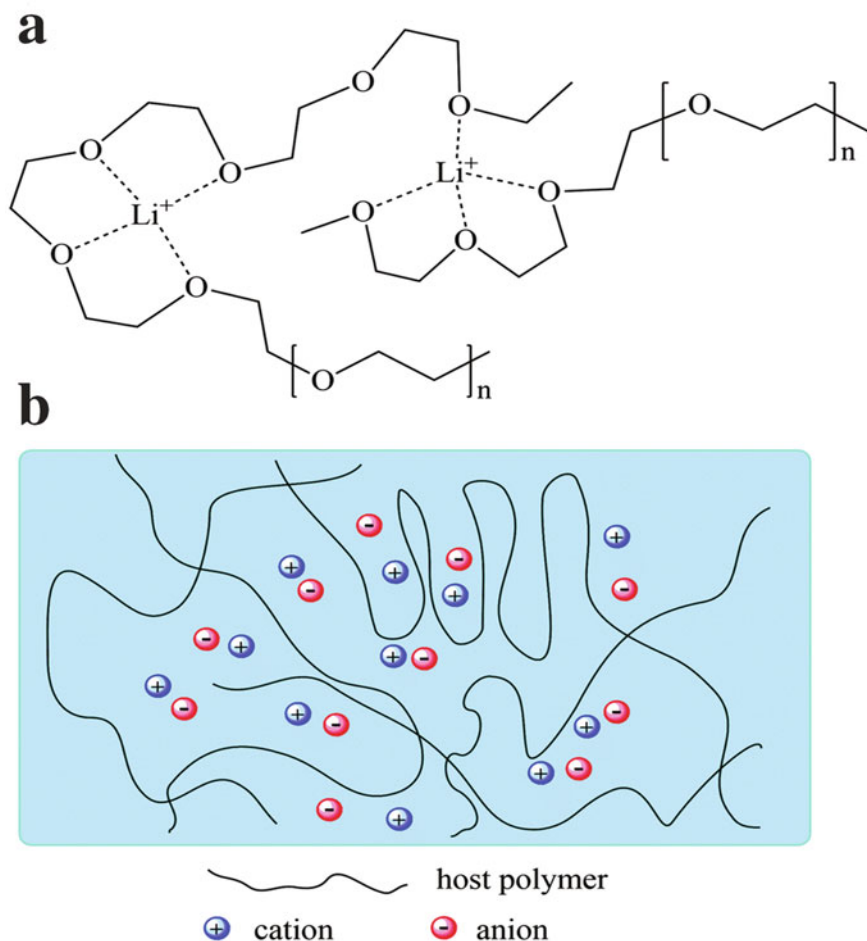
A number of polymers such as poly(vinyl alcohol) (PVA), poly(methyl-methacrylate) (PMMA), potassium/sodium salt of polyacrylic acid (potassium/sodium polyacrylate), poly(ether ether ketone) (PEEK), poly(acrylonitrile)-block-poly(ethylene glycol)-block-poly(acrylonitrile) (PAN-b-PEG-b-PAN), and poly(vinylidene 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  $\text{H}_2\text{SO}_4$  (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 electrolytes 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-state 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  $\text{NiO/Ni(OH)}_x$  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; Tönurist et al. 2012; Shulga et al. 2014).

## References

- Abbas Q, Pajak D, Frackowiak E, Béguin F (2014) Effect of binder on the performance of carbon/carbon symmetric capacitors in salt aqueous electrolyte. *Electrochim Acta* 140:132–138. doi:[10.1016/j.electacta.2014.04.096](https://doi.org/10.1016/j.electacta.2014.04.096)
- Akinwolemiwa B, Peng C, Chen GZ (2015) Redox electrolytes in supercapacitors. *J Electrochem Soc* 162:A5054–A5059. doi:[10.1149/2.0111505jes](https://doi.org/10.1149/2.0111505jes)
- An KH, Kim WS, Park YS et al (2001) Supercapacitors using single-walled carbon nanotube electrodes. *Adv Mater* 13:497–500. doi:[10.1002/1521-4095\(200104\)13:7<497::AID-ADMA497>3.0.CO;2-H](https://doi.org/10.1002/1521-4095(200104)13:7<497::AID-ADMA497>3.0.CO;2-H)
- Aslan M, Weingarh D, Jäckel N et al (2014) Polyvinylpyrrolidone as binder for castable supercapacitor electrodes with high electrochemical performance in organic electrolytes. *J Power Sour* 266:374–383. doi:[10.1016/j.jpowsour.2014.05.031](https://doi.org/10.1016/j.jpowsour.2014.05.031)
- Athouël L, Moser F, Dugas R et al (2008) Variation of the MnO<sub>2</sub> birnessite structure upon charge/discharge in an electrochemical supercapacitor electrode in aqueous Na<sub>2</sub>SO<sub>4</sub> electrolyte. *J Phys Chem C* 112:7270–7277. doi:[10.1021/jp0773029](https://doi.org/10.1021/jp0773029)
- Augustyn V, Simon P, Dunn B (2014) Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ Sci* 7:1597–1614. doi:[10.1039/C3EE44164D](https://doi.org/10.1039/C3EE44164D)
- Babakhani B, Ivey DG (2010a) Improved capacitive behavior of electrochemically synthesized Mn oxide/PEDOT electrodes utilized as electrochemical capacitors. *Electrochim Acta* 55:4014–4024. doi:[10.1016/j.electacta.2010.02.030](https://doi.org/10.1016/j.electacta.2010.02.030)
- Babakhani B, Ivey DG (2010b) Anodic deposition of manganese oxide electrodes with rod-like structures for application as electrochemical capacitors. *J Power Sources* 195:2110–2117. doi:[10.1016/j.jpowsour.2009.10.045](https://doi.org/10.1016/j.jpowsour.2009.10.045)
- Balogun M-S, Qiu W, Wang W et al (2015) Recent advances in metal nitrides as high-performance electrode materials for energy storage devices. *J Mater Chem A* 3:1364–1387. doi:[10.1039/C4TA05565A](https://doi.org/10.1039/C4TA05565A)
- Barisci JN, Wallace GG, Baughman RH (2000) Electrochemical characterization of single-walled carbon nanotube electrodes. *J Electrochem Soc* 147:4580–4583. doi:[10.1149/1.1394104](https://doi.org/10.1149/1.1394104)
- Barranco V, Pico F, Ibañez J et al (2009) Amorphous carbon nanofibres inducing high specific capacitance of deposited hydrous ruthenium oxide. *Electrochim Acta* 54:7452–7457. doi:[10.1016/j.electacta.2009.07.080](https://doi.org/10.1016/j.electacta.2009.07.080)
- Batiste N, Raymundo-Piñero E (2017) A self-standing hydrogel neutral electrolyte for high voltage and safe flexible supercapacitors. *J Power Sources* 348:168–174. doi:[10.1016/j.jpowsour.2017.03.005](https://doi.org/10.1016/j.jpowsour.2017.03.005)
- Béguin F, Szostak K, Lota G, Frackowiak E (2005) A self-supporting electrode for supercapacitors prepared by one-step pyrolysis of carbon nanotube/polyacrylonitrile blends. *Adv Mater* 17:2380–2384. doi:[10.1002/adma.200402103](https://doi.org/10.1002/adma.200402103)
- Béguin F, Presser V, Balducci A, Frackowiak E (2014) Carbons and electrolytes for advanced supercapacitors. *Adv Mater* 26:2219–2251. doi:[10.1002/adma.201304137](https://doi.org/10.1002/adma.201304137)
- Bittner AM, Zhu M, Yang Y et al (2012) Ageing of electrochemical double layer capacitors. *J Power Sour* 203:262–273. doi:[10.1016/j.jpowsour.2011.10.083](https://doi.org/10.1016/j.jpowsour.2011.10.083)
- Bouhitiyya S, Lucio-Porto R, Ducros J-B et al (2012) Transition metal nitrides thin films for supercapacitor applications. *Meet Abstr MA2012-02:494*

- Brandt A, Isken P, Lex-Balducci A, Balducci A (2012) Adiponitrile-based electrochemical double layer capacitor. *J Power Sour* 204:213–219. doi:[10.1016/j.jpowsour.2011.12.025](https://doi.org/10.1016/j.jpowsour.2011.12.025)
- Brandt A, Ramirez-Castro C, Anouti M, Balducci A (2013) An investigation about the use of mixtures of sulfonium-based ionic liquids and propylene carbonate as electrolytes for supercapacitors. *J Mater Chem A* 1:12669–12678. doi:[10.1039/C3TA12737K](https://doi.org/10.1039/C3TA12737K)
- Brumbach MT, Alam TM, Nilson RH et al (2010) Ruthenium oxide–niobium hydroxide composites for pseudocapacitor electrodes. *Mater Chem Phys* 124:359–370. doi:[10.1016/j.matchemphys.2010.06.047](https://doi.org/10.1016/j.matchemphys.2010.06.047)
- Burke A (2000) Ultracapacitors: why, how, and where is the technology. *J Power Sour* 91:37–50. doi:[10.1016/S0378-7753\(00\)00485-7](https://doi.org/10.1016/S0378-7753(00)00485-7)
- Byon HR, Lee SW, Chen S et al (2011) Thin films of carbon nanotubes and chemically reduced graphenes for electrochemical micro-capacitors. *Carbon N Y* 49:457–467. doi:[10.1016/j.carbon.2010.09.042](https://doi.org/10.1016/j.carbon.2010.09.042)
- Chen J, Huang K, Liu S (2009) Hydrothermal preparation of octadecahedron Fe<sub>3</sub>O<sub>4</sub> thin film for use in an electrochemical supercapacitor. *Electrochim Acta* 55:1–5. doi:[10.1016/j.electacta.2009.04.017](https://doi.org/10.1016/j.electacta.2009.04.017)
- Chen J, Li C, Shi G (2013) Graphene materials for electrochemical capacitors. *J Phys Chem Lett* 4:1244–1253. doi:[10.1021/jz400160k](https://doi.org/10.1021/jz400160k)
- Chen Y, Zhang X, Zhang D et al (2011a) High performance supercapacitors based on reduced graphene oxide in aqueous and ionic liquid electrolytes. *Carbon N Y* 49:573–580. doi:[10.1016/j.carbon.2010.09.060](https://doi.org/10.1016/j.carbon.2010.09.060)
- Chen Z, Augustyn V, Wen J et al (2011b) High-performance supercapacitors based on intertwined CNT/V<sub>2</sub>O<sub>5</sub> nanowire nanocomposites. *Adv Mater* 23:791–795. doi:[10.1002/adma.201003658](https://doi.org/10.1002/adma.201003658)
- Cho HW, Hepowit LR, Nam H-S et al (2012) Synthesis and supercapacitive properties of electrodeposited polyaniline composite electrode on acrylonitrile-butadiene rubber as a flexible current collector. *Synth Met* 162:410–413. doi:[10.1016/j.synthmet.2011.12.025](https://doi.org/10.1016/j.synthmet.2011.12.025)
- Clemente A, Panero S, Spila E, Scrosati B (1996) Solid-state, polymer-based, redox capacitors. *Solid State Ionics* 85:273–277. doi:[10.1016/0167-2738\(96\)00070-7](https://doi.org/10.1016/0167-2738(96)00070-7)
- Conway BE (1999) *Electrochemical supercapacitors scientific fundamentals and technological applications*. Kluwer Academic/Plenum, New York
- Das B, Behm M, Lindbergh G et al (2015) High performance metal nitrides, MN (M = Cr, Co) nanoparticles for non-aqueous hybrid supercapacitors. *Adv Powder Technol* 26:783–788. doi:[10.1016/j.apt.2015.02.001](https://doi.org/10.1016/j.apt.2015.02.001)
- Dhibar S, Bhattacharya P, Hatui G et al (2014) Transition metal-doped polyaniline/single-walled carbon nanotubes nanocomposites: efficient electrode material for high performance supercapacitors. *ACS Sustain Chem Eng* 2:1114–1127. doi:[10.1021/sc5000072](https://doi.org/10.1021/sc5000072)
- Donne SW, Hollenkamp AF, Jones BC (2010) Structure, morphology and electrochemical behaviour of manganese oxides prepared by controlled decomposition of permanganate. *J Power Sour* 195:367–373. doi:[10.1016/j.jpowsour.2009.06.103](https://doi.org/10.1016/j.jpowsour.2009.06.103)
- Doubova LM, De Battisti A, Daolio S et al (2004) Effect of surface structure on behavior of RuO<sub>2</sub> electrodes in sulfuric acid aqueous solution. *Russ J Electrochem* 40:1115–1122. doi:[10.1023/B:RUEL.0000048642.73284.4f](https://doi.org/10.1023/B:RUEL.0000048642.73284.4f)
- Du Pasquier A, Laforgue A, Simon P et al (2002) A nonaqueous asymmetric hybrid Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/poly(fluorophenylthiophene) energy storage device. *J Electrochem Soc* 149:A302–A306. doi:[10.1149/1.1446081](https://doi.org/10.1149/1.1446081)
- Dubal DP, Dhawale DS, Salunkhe RR, Lokhande CD (2010) Conversion of interlocked cube-like Mn<sub>3</sub>O<sub>4</sub> into nanoflakes of layered birnessite MnO<sub>2</sub> during supercapacitive studies. *J Alloys Compd* 496:370–375. doi:[10.1016/j.jallcom.2010.02.014](https://doi.org/10.1016/j.jallcom.2010.02.014)
- Eikerling M, Kornyshev AA, Lust E (2005) Optimized structure of nanoporous carbon-based double-layer capacitors. *J Electrochem Soc* 152:E24–E33. doi:[10.1149/1.1825379](https://doi.org/10.1149/1.1825379)
- Endo M, Maeda T, Takeda T et al (2001) Capacitance and pore-size distribution in aqueous and nonaqueous electrolytes using various activated carbon electrodes. *J Electrochem Soc* 148:A910–A914. doi:[10.1149/1.1382589](https://doi.org/10.1149/1.1382589)



- Fan L-Z, Maier J (2006) High-performance polypyrrole electrode materials for redox supercapacitors. *Electrochim Commun* 8:937–940. doi:[10.1016/j.elecom.2006.03.035](https://doi.org/10.1016/j.elecom.2006.03.035)
- Fan JY, Wu XL, Li HX et al (2006) Si-based solid blue emitters from 3C-SiC nanocrystals. *Appl Phys A* 82:485–487. doi:[10.1007/s00339-005-3445-4](https://doi.org/10.1007/s00339-005-3445-4)
- Fan L-Z, Hu Y-S, Maier J et al (2007a) High electroactivity of polyaniline in supercapacitors by using a hierarchically porous carbon monolith as a support. *Adv Funct Mater* 17:3083–3087. doi:[10.1002/adfm.200700518](https://doi.org/10.1002/adfm.200700518)
- Fan Z, Chen J, Cui K et al (2007b) Preparation and capacitive properties of cobalt–nickel oxides/carbon nanotube composites. *Electrochim Acta* 52:2959–2965. doi:[10.1016/j.electacta.2006.09.029](https://doi.org/10.1016/j.electacta.2006.09.029)
- Fang B, Binder L (2006) A modified activated carbon aerogel for high-energy storage in electric double layer capacitors. *J Power Sour* 163:616–622. doi:[10.1016/j.jpowsour.2006.09.014](https://doi.org/10.1016/j.jpowsour.2006.09.014)
- Fic K, Lota G, Meller M, Frackowiak E (2012) Novel insight into neutral medium as electrolyte for high-voltage supercapacitors. *Energy Environ Sci* 5:5842–5850. doi:[10.1039/C1EE02262H](https://doi.org/10.1039/C1EE02262H)
- Frackowiak E (2007) Carbon materials for supercapacitor application. *Phys Chem Chem Phys* 9:1774–1785. doi:[10.1039/B618139M](https://doi.org/10.1039/B618139M)
- Frackowiak E, Delpoux S, Jurewicz K et al (2002) Enhanced capacitance of carbon nanotubes through chemical activation. *Chem Phys Lett* 361:35–41. doi:[10.1016/S0009-2614\(02\)00684-X](https://doi.org/10.1016/S0009-2614(02)00684-X)
- Fu R, Ma Z, Zheng JP (2002) Proton NMR and dynamic studies of hydrous ruthenium oxide. *J Phys Chem B* 106:3592–3596. doi:[10.1021/jp013860q](https://doi.org/10.1021/jp013860q)
- Geim AK, Novoselov KS (2007) The rise of graphene. *Nat Mater* 6:183–191
- Gong X, Cheng JP, Liu F et al (2014) Nickel-Cobalt hydroxide microspheres electrodeposited on nickel cobaltite nanowires grown on Ni foam for high-performance pseudocapacitors. *J Power Sour* 267:610–616. doi:[10.1016/j.jpowsour.2014.05.120](https://doi.org/10.1016/j.jpowsour.2014.05.120)
- Grigoras K, Keskinen J, Grönberg L et al (2016) Conformal titanium nitride in a porous silicon matrix: a nanomaterial for in-chip supercapacitors. *Nano Energy* 26:340–345. doi:[10.1016/j.nanoen.2016.04.029](https://doi.org/10.1016/j.nanoen.2016.04.029)
- Grover S, Goel S, Sahu V et al (2015) Asymmetric supercapacitive characteristics of PANI embedded holey graphene nanoribbons. *ACS Sustain Chem Eng* 3:1460–1469. doi:[10.1021/acssuschemeng.5b00184](https://doi.org/10.1021/acssuschemeng.5b00184)
- Guo CX, Li CM (2011) A self-assembled hierarchical nanostructure comprising carbon spheres and graphene nanosheets for enhanced supercapacitor performance. *Energy Environ Sci* 4:4504–4507. doi:[10.1039/C1EE01676H](https://doi.org/10.1039/C1EE01676H)
- Gupta V, Miura N (2006) High performance electrochemical supercapacitor from electrochemically synthesized nanostructured polyaniline. *Mater Lett* 60:1466–1469. doi:[10.1016/j.matlet.2005.11.047](https://doi.org/10.1016/j.matlet.2005.11.047)
- Hadjipaschalis I, Poullikkas A, Efthimiou V (2009) Overview of current and future energy storage technologies for electric power applications. *Renew Sustain Energy Rev* 13:1513–1522. doi:[10.1016/j.rser.2008.09.028](https://doi.org/10.1016/j.rser.2008.09.028)
- Hashmi SA, Upadhyaya HM (2002) Polypyrrole and poly(3-methyl thiophene)-based solid state redox supercapacitors using ion conducting polymer electrolyte. *Solid State Ionics* 153:883–889. doi:[10.1016/S0167-2738\(02\)00390-9](https://doi.org/10.1016/S0167-2738(02)00390-9)
- Hsu P-C, Chang H-T (2012) Synthesis of high-quality carbon nanodots from hydrophilic compounds: role of functional groups. *Chem Commun* 48:3984–3986. doi:[10.1039/C2CC30188A](https://doi.org/10.1039/C2CC30188A)
- Hu C-C, Chang K-H, Lin M-C, Wu Y-T (2006) Design and tailoring of the nanotubular arrayed architecture of hydrous RuO<sub>2</sub> for next generation supercapacitors. *Nano Lett* 6:2690–2695. doi:[10.1021/nl061576a](https://doi.org/10.1021/nl061576a)
- Hu C-C, Wang C-C, Chang K-H (2007) A comparison study of the capacitive behavior for sol-gel-derived and co-annealed ruthenium–tin oxide composites. *Electrochim Acta* 52:2691–2700. doi:[10.1016/j.electacta.2006.09.026](https://doi.org/10.1016/j.electacta.2006.09.026)
- Huang L, Chen D, Ding Y et al (2013) Hybrid composite Ni(OH)<sub>2</sub>@NiCO<sub>2</sub>O<sub>4</sub> grown on carbon fiber paper for high-performance supercapacitors. *ACS Appl Mater Interfaces* 5:11159–11162. doi:[10.1021/am403367u](https://doi.org/10.1021/am403367u)



- Huang H, Yao J, Li L et al (2016) Reinforced polyaniline/polyvinyl alcohol conducting hydrogel from a freezing–thawing method as self-supported electrode for supercapacitors. *J Mater Sci* 51:8728–8736. doi:[10.1007/s10853-016-0137-8](https://doi.org/10.1007/s10853-016-0137-8)
- Hulicova D, Yamashita J, Soneda Y et al (2005) Supercapacitors prepared from melamine-based carbon. *Chem Mater* 17:1241–1247. doi:[10.1021/cm049337g](https://doi.org/10.1021/cm049337g)
- Hulicova D, Kodama M, Hatori H (2006) Electrochemical performance of nitrogen-enriched carbons in aqueous and non-aqueous supercapacitors. *Chem Mater* 18:2318–2326. doi:[10.1021/cm060146i](https://doi.org/10.1021/cm060146i)
- Ivanovskii AL (2012) Graphene-based and graphene-like materials. *Russ Chem Rev* 81:571–605. doi:[10.1070/RC2012v081n07ABEH004302](https://doi.org/10.1070/RC2012v081n07ABEH004302)
- Jayalakshmi M, Venugopal N, Raja KP, Rao MM (2006) Nano SnO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> mixed oxide and SnO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–carbon composite oxides as new and novel electrodes for supercapacitor applications. *J Power Sour* 158:1538–1543. doi:[10.1016/j.jpowsour.2005.10.091](https://doi.org/10.1016/j.jpowsour.2005.10.091)
- Jeong YU, Manthiram A (2001) Amorphous tungsten oxide/ruthenium oxide composites for electrochemical capacitors. *J Electrochem Soc* 148:A189–A193. doi:[10.1149/1.1345869](https://doi.org/10.1149/1.1345869)
- Jia QX, Song SG, Wu XD et al (1996) Epitaxial growth of highly conductive RuO<sub>2</sub> thin films on (100) Si. *Appl Phys Lett* 68:1069–1071. doi:[10.1063/1.115715](https://doi.org/10.1063/1.115715)
- Jung N, Kwon S, Lee D et al (2013) Synthesis of chemically bonded graphene/carbon nanotube composites and their application in large volumetric capacitance supercapacitors. *Adv Mater* 25:6854–6858. doi:[10.1002/adma.201302788](https://doi.org/10.1002/adma.201302788)
- Kalaji M, Murphy PJ, Williams GO (1999) The study of conducting polymers for use as redox supercapacitors. *Synth Met* 102:1360–1361. doi:[10.1016/S0379-6779\(98\)01334-4](https://doi.org/10.1016/S0379-6779(98)01334-4)
- Kandalkar SG, Lee H-M, Chae H, Kim C-K (2011) Structural, morphological, and electrical characteristics of the electrodeposited cobalt oxide electrode for supercapacitor applications. *Mater Res Bull* 46:48–51. doi:[10.1016/j.materresbull.2010.09.041](https://doi.org/10.1016/j.materresbull.2010.09.041)
- Kang M, Lee JE, Shim HW et al (2014) Intrinsically conductive polymer binders for electrochemical capacitor application. *RSC Adv* 4:27939–27945. doi:[10.1039/C4RA03261F](https://doi.org/10.1039/C4RA03261F)
- Khomenko V, Frackowiak E, Béguin F (2005) Determination of the specific capacitance of conducting polymer/nanotubes composite electrodes using different cell configurations. *Electrochim Acta* 50:2499–2506. doi:[10.1016/j.electacta.2004.10.078](https://doi.org/10.1016/j.electacta.2004.10.078)
- Kim H, Popov BN (2002) Characterization of hydrous ruthenium oxide/carbon nanocomposite supercapacitors prepared by a colloidal method. *J Power Sour* 104:52–61. doi:[10.1016/S0378-7753\(01\)00903-X](https://doi.org/10.1016/S0378-7753(01)00903-X)
- Kim I-H, Kim K-B (2006) Electrochemical characterization of hydrous ruthenium oxide thin-film electrodes for electrochemical capacitor applications. *J Electrochem Soc* 153:A383. doi:[10.1149/1.2147406](https://doi.org/10.1149/1.2147406)
- Kim Y-T, Tadai K, Mitani T (2005) Highly dispersed ruthenium oxide nanoparticles on carboxylated carbon nanotubes for supercapacitor electrode materials. *J Mater Chem* 15:4914–4921. doi:[10.1039/B511869G](https://doi.org/10.1039/B511869G)
- Kim DJ, Kim JK, Lee JH et al (2016) Scalable and bendable organized mesoporous TiN films templated by using a dual-functional amphiphilic graft copolymer for solid supercapacitors. *J Mater Chem A* 4:12497–12503. doi:[10.1039/C6TA03475F](https://doi.org/10.1039/C6TA03475F)
- Kong L, Zhang C, Zhang S et al (2014) High-power and high-energy asymmetric supercapacitors based on Li<sup>+</sup>-intercalation into a T-Nb<sub>2</sub>O<sub>5</sub>/graphene pseudocapacitive electrode. *J Mater Chem A* 2:17962–17970. doi:[10.1039/C4TA03604B](https://doi.org/10.1039/C4TA03604B)
- Kong L, Zhang C, Wang J et al (2015) Free-standing T-Nb<sub>2</sub>O<sub>5</sub>/graphene composite papers with ultrahigh gravimetric/volumetric capacitance for Li-Ion intercalation pseudocapacitor. *ACS Nano* 9:11200–11208. doi:[10.1021/acs.nano.5b04737](https://doi.org/10.1021/acs.nano.5b04737)
- Laforgue A, Simon P, Sarrazin C, Fauvarque J-F (1999) Polythiophene-based supercapacitors. *J Power Sour* 80:142–148. doi:[10.1016/S0378-7753\(98\)00258-4](https://doi.org/10.1016/S0378-7753(98)00258-4)
- Laforgue A, Simon P, Fauvarque JF et al (2003) Activated carbon/conducting polymer hybrid supercapacitors. *J Electrochem Soc* 150:A645–A651. doi:[10.1149/1.1566411](https://doi.org/10.1149/1.1566411)
- Lee HY, Goodenough JB (1999) Supercapacitor behavior with KCl Electrolyte. *J Solid State Chem* 144:220–223. doi:[10.1006/jssc.1998.8128](https://doi.org/10.1006/jssc.1998.8128)

- Lee J-K, Pathan HM, Jung K-D, Joo O-S (2006a) Electrochemical capacitance of nanocomposite films formed by loading carbon nanotubes with ruthenium oxide. *J Power Sour* 159:1527–1531. doi:[10.1016/j.jpowsour.2005.11.063](https://doi.org/10.1016/j.jpowsour.2005.11.063)
- Lee J, Kim J, Hyeon T (2006b) Recent progress in the synthesis of porous carbon materials. *Adv Mater* 18:2073–2094. doi:[10.1002/adma.200501576](https://doi.org/10.1002/adma.200501576)
- Lee H, Cho MS, Kim IH et al (2010a) RuO<sub>x</sub>/polypyrrole nanocomposite electrode for electrochemical capacitors. *Synth Met* 160:1055–1059. doi:[10.1016/j.synthmet.2010.02.026](https://doi.org/10.1016/j.synthmet.2010.02.026)
- Lee K-T, Tsai C-B, Ho W-H, Wu N-L (2010b) Superabsorbent polymer binder for achieving MnO<sub>2</sub> supercapacitors of greatly enhanced capacitance density. *Electrochem Commun* 12:886–889. doi:[10.1016/j.elecom.2010.04.012](https://doi.org/10.1016/j.elecom.2010.04.012)
- Lee H, Kim H, Cho MS et al (2011) Fabrication of polypyrrole (PPy)/carbon nanotube (CNT) composite electrode on ceramic fabric for supercapacitor applications. *Electrochim Acta* 56:7460–7466. doi:[10.1016/j.electacta.2011.06.113](https://doi.org/10.1016/j.electacta.2011.06.113)
- Lehtimäki S, Suominen M, Damlin P et al (2015) Preparation of supercapacitors on flexible substrates with electrodeposited PEDOT/graphene composites. *ACS Appl Mater Interfaces* 7:22137–22147. doi:[10.1021/acsami.5b05937](https://doi.org/10.1021/acsami.5b05937)
- Leitner K, Lerf A, Winter M et al (2006) Nomex-derived activated carbon fibers as electrode materials in carbon based supercapacitors. *J Power Sour* 153:419–423. doi:[10.1016/j.jpowsour.2005.05.078](https://doi.org/10.1016/j.jpowsour.2005.05.078)
- Li Y, Zhao Y, Cheng H et al (2012) Nitrogen-doped graphene quantum dots with oxygen-rich functional groups. *J Am Chem Soc* 134:15–18. doi:[10.1021/ja206030c](https://doi.org/10.1021/ja206030c)
- Liao G, Geier S, Mahrholz T et al (2015) Li<sub>1.4</sub>Al<sub>0.4</sub>Ti<sub>1.6</sub>(PO<sub>4</sub>)<sub>3</sub> used as solid electrolyte for structural supercapacitors. V001T01A006
- Lin C, Ritter JA, Popov BN (1999) Development of carbon-metal oxide supercapacitors from sol-gel derived carbon-ruthenium xerogels. *J Electrochem Soc* 146:3155–3160. doi:[10.1149/1.1392448](https://doi.org/10.1149/1.1392448)
- Liu X, Pickup PG (2008) Performance and low temperature behaviour of hydrous ruthenium oxide supercapacitors with improved power densities. *Energy Environ Sci* 1:494–500. doi:[10.1039/B809939A](https://doi.org/10.1039/B809939A)
- Liu T, Pell WG, Conway BE (1997) Self-discharge and potential recovery phenomena at thermally and electrochemically prepared RuO<sub>2</sub> supercapacitor electrodes. *Electrochim Acta* 42:3541–3552. doi:[10.1016/S0013-4686\(97\)81190-5](https://doi.org/10.1016/S0013-4686(97)81190-5)
- Liu A, Li C, Bai H, Shi G (2010) Electrochemical deposition of polypyrrole/sulfonated graphene composite films. *J Phys Chem C* 114:22783–22789. doi:[10.1021/jp108826e](https://doi.org/10.1021/jp108826e)
- Long JW, Bélanger D, Brousse T et al (2011) Asymmetric electrochemical capacitors—stretching the limits of aqueous electrolytes. *MRS Bull* 36:513–522. doi:[10.1557/mrs.2011.137](https://doi.org/10.1557/mrs.2011.137)
- Lota K, Khomenko V, Frackowiak E (2004) Capacitance properties of poly(3, 4-ethylenedioxythiophene)/carbon nanotubes composites. *J Phys Chem Solids* 65:295–301. doi:[10.1016/j.jpcs.2003.10.051](https://doi.org/10.1016/j.jpcs.2003.10.051)
- Luo PG, Sahu S, Yang S-T et al (2013) Carbon “quantum” dots for optical bioimaging. *J Mater Chem B* 1:2116–2127. doi:[10.1039/C3TB00018D](https://doi.org/10.1039/C3TB00018D)
- Ma R, Bando Y, Zhang L, Sasaki T (2004) Layered MnO<sub>2</sub> nanobelts: hydrothermal synthesis and electrochemical measurements. *Adv Mater* 16:918–922. doi:[10.1002/adma.200306592](https://doi.org/10.1002/adma.200306592)
- Ma G, Li J, Sun K et al (2014) High performance solid-state supercapacitor with PVA–KOH–K3 [Fe(CN)<sub>6</sub>] gel polymer as electrolyte and separator. *J Power Sour* 256:281–287. doi:[10.1016/j.jpowsour.2014.01.062](https://doi.org/10.1016/j.jpowsour.2014.01.062)
- Mastragostino M, Arbizzani C, Meneghello L, Paraventi R (1996) Electronically conducting polymers and activated carbon: electrode materials in supercapacitor technology. *Adv Mater* 8:331–334. doi:[10.1002/adma.19960080409](https://doi.org/10.1002/adma.19960080409)
- Mastragostino M, Paraventi R, Zanelli A (2000) Supercapacitors based on composite polymer electrodes. *J Electrochem Soc* 147:3167–3170. doi:[10.1149/1.1393878](https://doi.org/10.1149/1.1393878)
- Mison II, Aziz RA, Zain NKM et al (2014) High performance MnO<sub>2</sub> nanoflower electrode and the relationship between solvated ion size and specific capacitance in highly conductive electrolytes. *Mater Res Bull* 57:221–230. doi:[10.1016/j.materresbull.2014.05.044](https://doi.org/10.1016/j.materresbull.2014.05.044)

- Momma T, Liu X, Osaka T et al (1996) Electrochemical modification of active carbon fiber electrode and its application to double-layer capacitor. *J Power Sour* 60:249–253. doi:[10.1016/S0378-7753\(96\)80018-8](https://doi.org/10.1016/S0378-7753(96)80018-8)
- Morishita T, Soneda Y, Tsumura T, Inagaki M (2006) Preparation of porous carbons from thermoplastic precursors and their performance for electric double layer capacitors. *Carbon N Y* 44:2360–2367. doi:[10.1016/j.carbon.2006.04.030](https://doi.org/10.1016/j.carbon.2006.04.030)
- Mun Y, Jo C, Hyeon T et al (2013) Simple synthesis of hierarchically structured partially graphitized carbon by emulsion/block-copolymer co-template method for high power supercapacitors. *Carbon N Y* 64:391–402. doi:[10.1016/j.carbon.2013.07.092](https://doi.org/10.1016/j.carbon.2013.07.092)
- Nam K-W, Kim K-H, Lee E-S et al (2008) Pseudocapacitive properties of electrochemically prepared nickel oxides on 3-dimensional carbon nanotube film substrates. *J Power Sour* 182:642–652. doi:[10.1016/j.jpowsour.2008.03.090](https://doi.org/10.1016/j.jpowsour.2008.03.090)
- Naoi K, Suematsu S, Manago A (2000) Electrochemistry of poly(1, 5-diaminoanthraquinone) and its application in electrochemical capacitor materials. *J Electrochem Soc* 147:420–426. doi:[10.1149/1.1393212](https://doi.org/10.1149/1.1393212)
- Naudin É, El Mehdi N, Soucy C et al (2001) Poly(3-arylthiophenes): syntheses of monomers and spectroscopic and electrochemical characterization of the corresponding polymers. *Chem Mater* 13:634–642. doi:[10.1021/cm0007656](https://doi.org/10.1021/cm0007656)
- Pan D, Zhang J, Li Z, Wu M (2010) Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots. *Adv Mater* 22:734–738. doi:[10.1002/adma.200902825](https://doi.org/10.1002/adma.200902825)
- Panić V, Vidaković T, Gojković S et al (2003) The properties of carbon-supported hydrous ruthenium oxide obtained from RuO<sub>x</sub>Hy sol. *Electrochim Acta* 48:3805–3813. doi:[10.1016/S0013-4686\(03\)00514-0](https://doi.org/10.1016/S0013-4686(03)00514-0)
- Peng J, Gao W, Gupta BK et al (2012) Graphene quantum dots derived from carbon fibers. *Nano Lett* 12:844–849. doi:[10.1021/nl2038979](https://doi.org/10.1021/nl2038979)
- Perricone E, Chamas M, Cointeaux L et al (2013) Investigation of methoxypropionitrile as co-solvent for ethylene carbonate based electrolyte in supercapacitors. A safe and wide temperature range electrolyte. *Electrochim Acta* 93:1–7. doi:[10.1016/j.electacta.2013.01.084](https://doi.org/10.1016/j.electacta.2013.01.084)
- Pico F, Ibañez J, Lillo-Rodenas MA et al (2008) Understanding RuO<sub>2</sub>·xH<sub>2</sub>O/carbon nanofibre composites as supercapacitor electrodes. *J Power Sour* 176:417–425. doi:[10.1016/j.jpowsour.2007.11.001](https://doi.org/10.1016/j.jpowsour.2007.11.001)
- Pico F, Morales E, Fernandez JA et al (2009) Ruthenium oxide/carbon composites with microporous or mesoporous carbon as support and prepared by two procedures. A comparative study as supercapacitor electrodes. *Electrochim Acta* 54:2239–2245. doi:[10.1016/j.electacta.2008.10.028](https://doi.org/10.1016/j.electacta.2008.10.028)
- Prasad KR, Koga K, Miura N (2004) Electrochemical deposition of nanostructured indium oxide: high-performance electrode material for redox supercapacitors. *Chem Mater* 16:1845–1847. doi:[10.1021/cm0497576](https://doi.org/10.1021/cm0497576)
- Prasad KS, Pallela R, Kim DM, Shim YB (2013) Microwave-assisted one-pot synthesis of metal-free nitrogen and phosphorus dual-doped nanocarbon for electrocatalysis and cell imaging. *Part Part Syst Charact* 30:557–564. doi:[10.1002/ppsc.201300020](https://doi.org/10.1002/ppsc.201300020)
- Qu D, Shi H (1998) Studies of activated carbons used in double-layer capacitors. *J Power Sour* 74:99–107. doi:[10.1016/S0378-7753\(98\)00038-X](https://doi.org/10.1016/S0378-7753(98)00038-X)
- Raccichini R, Varzi A, Passerini S, Scrosati B (2015) The role of graphene for electrochemical energy storage. *Nat Mater* 14:271–279
- Rajendra Prasad K, Miura N (2004) Electrochemically synthesized MnO<sub>2</sub>-based mixed oxides for high performance redox supercapacitors. *Electrochem Commun* 6:1004–1008. doi:[10.1016/j.electcom.2004.07.017](https://doi.org/10.1016/j.electcom.2004.07.017)
- Ramani M, Haran BS, White RE et al (2001) Studies on activated carbon capacitor materials loaded with different amounts of ruthenium oxide. *J Power Sources* 93:209–214. doi:[10.1016/S0378-7753\(00\)00575-9](https://doi.org/10.1016/S0378-7753(00)00575-9)
- Ramesh TN, Kamath PV, Shivakumara C (2005) Correlation of structural disorder with the reversible discharge capacity of nickel hydroxide electrode. *J Electrochem Soc* 152:A806–A810. doi:[10.1149/1.1865852](https://doi.org/10.1149/1.1865852)

- Ratajczak P, Jurewicz K, Skowron P et al (2014) Effect of accelerated ageing on the performance of high voltage carbon/carbon electrochemical capacitors in salt aqueous electrolyte. *Electrochim Acta* 130:344–350. doi:[10.1016/j.electacta.2014.02.140](https://doi.org/10.1016/j.electacta.2014.02.140)
- Ratha S, Samantara AK, Singha KK et al (2017) Urea-assisted room temperature stabilized metastable  $\beta$ -NiMoO<sub>4</sub>: experimental and theoretical insights into its unique bifunctional activity toward oxygen evolution and supercapacitor. *ACS Appl Mater Interfaces* 9:9640–9653. doi:[10.1021/acsami.6b16250](https://doi.org/10.1021/acsami.6b16250)
- Raymundo-Piñero E, Cazorla-Amorós D, Linares-Solano A et al (2002) High surface area carbon nanotubes prepared by chemical activation. *Carbon N Y* 40:1614–1617. doi:[10.1016/S0008-6223\(02\)00134-3](https://doi.org/10.1016/S0008-6223(02)00134-3)
- Raymundo-Piñero E, Kierzek K, Machnikowski J, Béguin F (2006) Relationship between the nanoporous texture of activated carbons and their capacitance properties in different electrolytes. *Carbon N Y* 44:2498–2507. doi:[10.1016/j.carbon.2006.05.022](https://doi.org/10.1016/j.carbon.2006.05.022)
- Regisser F, Lavoie M-A, Champagne GY, Bélanger D (1996) Randomly oriented graphite electrode. Part 1. Effect of electrochemical pretreatment on the electrochemical behavior and chemical composition of the electrode. *J Electroanal Chem* 415:47–54. doi:[10.1016/S0022-0728\(96\)04636-0](https://doi.org/10.1016/S0022-0728(96)04636-0)
- Rudge A, Davey J, Raistrick I et al (1994) Conducting polymers as active materials in electrochemical capacitors. *J Power Sour* 47:89–107. doi:[10.1016/0378-7753\(94\)80053-7](https://doi.org/10.1016/0378-7753(94)80053-7)
- Ryu KS, Kim KM, Park N-G et al (2002) Symmetric redox supercapacitor with conducting polyaniline electrodes. *J Power Sources* 103:305–309. doi:[10.1016/S0378-7753\(01\)00862-X](https://doi.org/10.1016/S0378-7753(01)00862-X)
- Ryu I, Yang M, Kwon H et al (2014) Coaxial RuO<sub>2</sub>-ITO nanopillars for transparent supercapacitor application. *Langmuir* 30:1704–1709. doi:[10.1021/la4044599](https://doi.org/10.1021/la4044599)
- Sakiyama K, Onishi S, Ishihara K et al (1993) Deposition and properties of reactively sputtered ruthenium dioxide films. *J Electrochem Soc* 140:834–839. doi:[10.1149/1.2056168](https://doi.org/10.1149/1.2056168)
- Salitra G, Soffer A, Eliad L et al (2000) Carbon electrodes for double-layer capacitors I. Relations between ion and pore dimensions. *J Electrochem Soc* 147:2486–2493. doi:[10.1149/1.1393557](https://doi.org/10.1149/1.1393557)
- Samantara AK, Chandra Sahu S, Ghosh A, Jena BK (2015) Sandwiched graphene with nitrogen, sulphur co-doped CQDs: an efficient metal-free material for energy storage and conversion applications. *J Mater Chem A* 3:16961–16970. doi:[10.1039/C5TA03376D](https://doi.org/10.1039/C5TA03376D)
- Samantara AK, Maji S, Ghosh A et al (2016) Good's buffer derived highly emissive carbon quantum dots: excellent biocompatible anticancer drug carrier. *J Mater Chem B* 4:2412–2420. doi:[10.1039/C6TB00081A](https://doi.org/10.1039/C6TB00081A)
- Sarangapani S, Tilak BV, Chen C-P (1996) Materials for electrochemical capacitors: theoretical and experimental constraints. *J Electrochem Soc* 143:3791–3799. doi:[10.1149/1.1837291](https://doi.org/10.1149/1.1837291)
- Seredych M, Hulicova-Jurcakova D, Lu GQ, Bandosz TJ (2008) Surface functional groups of carbons and the effects of their chemical character, density and accessibility to ions on electrochemical performance. *Carbon N Y* 46:1475–1488. doi:[10.1016/j.carbon.2008.06.027](https://doi.org/10.1016/j.carbon.2008.06.027)
- Sevilla M, Fuertes AB (2014) Direct synthesis of highly porous interconnected carbon nanosheets and their application as high-performance supercapacitors. *ACS Nano* 8:5069–5078. doi:[10.1021/nm501124h](https://doi.org/10.1021/nm501124h)
- Sharma P, Bhatti TS (2010) A review on electrochemical double-layer capacitors. *Energy Convers Manag* 51:2901–2912. doi:[10.1016/j.enconman.2010.06.031](https://doi.org/10.1016/j.enconman.2010.06.031)
- Sharma RK, Rastogi AC, Desu SB (2008) Manganese oxide embedded polypyrrole nanocomposites for electrochemical supercapacitor. *Electrochim Acta* 53:7690–7695. doi:[10.1016/j.electacta.2008.04.028](https://doi.org/10.1016/j.electacta.2008.04.028)
- Shen L, Zhang L, Chen M et al (2013) The production of pH-sensitive photoluminescent carbon nanoparticles by the carbonization of polyethylenimine and their use for bioimaging. *Carbon N Y* 55:343–349. doi:[10.1016/j.carbon.2012.12.074](https://doi.org/10.1016/j.carbon.2012.12.074)
- Shi M, Kou S, Yan X (2014a) Engineering the electrochemical capacitive properties of graphene sheets in ionic-liquid electrolytes by correct selection of anions. *Chemsuschem* 7:3053–3062. doi:[10.1002/cssc.201402275](https://doi.org/10.1002/cssc.201402275)

- Shi Y, Pan L, Liu B et al (2014b) Nanostructured conductive polypyrrole hydrogels as high-performance, flexible supercapacitor electrodes. *J Mater Chem A* 2:6086–6091. doi:[10.1039/C4TA00484A](https://doi.org/10.1039/C4TA00484A)
- Shimizu W, Makino S, Takahashi K et al (2013) Development of a 4.2 V aqueous hybrid electrochemical capacitor based on MnO<sub>2</sub> positive and protected Li negative electrodes. *J Power Sour* 241:572–577. doi:[10.1016/j.jpowsour.2013.05.003](https://doi.org/10.1016/j.jpowsour.2013.05.003)
- Shinde DB, Pillai VK (2012) Electrochemical preparation of luminescent graphene quantum dots from multiwalled carbon nanotubes. *Chem A Eur J* 18:12522–12528. doi:[10.1002/chem.201201043](https://doi.org/10.1002/chem.201201043)
- Shiraishi S, Kurihara H, Okabe K et al (2002) Electric double layer capacitance of highly pure single-walled carbon nanotubes (HiPco<sup>TM</sup> Buckytubes<sup>TM</sup>) in propylene carbonate electrolytes. *Electrochem Commun* 4:593–598. doi:[10.1016/S1388-2481\(02\)00382-X](https://doi.org/10.1016/S1388-2481(02)00382-X)
- Shulga YM, Baskakov SA, Smirnov VA et al (2014) Graphene oxide films as separators of polyaniline-based supercapacitors. *J Power Sour* 245:33–36. doi:[10.1016/j.jpowsour.2013.06.094](https://doi.org/10.1016/j.jpowsour.2013.06.094)
- Simon P, Gogotsi Y (2008) Materials for electrochemical capacitors. *Nat Mater* 7:845–854. doi:[10.1038/nmat2297](https://doi.org/10.1038/nmat2297)
- Sivaraman P, Thakur A, Kushwaha RK et al (2006) Poly(3-methyl thiophene)-activated carbon hybrid supercapacitor based on gel polymer electrolyte. *Electrochem Solid-State Lett* 9:A435–A438. doi:[10.1149/1.2213357](https://doi.org/10.1149/1.2213357)
- Snook GA, Kao P, Best AS (2011) Conducting-polymer-based supercapacitor devices and electrodes. *J Power Sour* 196:1–12. doi:[10.1016/j.jpowsour.2010.06.084](https://doi.org/10.1016/j.jpowsour.2010.06.084)
- Stankovich S, Dikin DA, Dommett GHB et al (2006) Graphene-based composite materials. *Nature* 442:282–286
- Sugimoto W, Iwata H, Murakami Y, Takasu Y (2004) Electrochemical capacitor behavior of layered ruthenic acid hydrate. *J Electrochem Soc* 151:A1181–A1187. doi:[10.1149/1.1765681](https://doi.org/10.1149/1.1765681)
- Sugimoto W, Iwata H, Yasunaga Y et al (2003) Preparation of ruthenic acid nanosheets and utilization of its interlayer surface for electrochemical energy storage. *Angew Chemie Int Ed* 42:4092–4096. doi:[10.1002/anie.200351691](https://doi.org/10.1002/anie.200351691)
- Sugimoto W, Iwata H, Yokoshima K et al (2005) Proton and electron conductivity in hydrous ruthenium oxides evaluated by electrochemical impedance spectroscopy: the origin of large capacitance. *J Phys Chem B* 109:7330–7338. doi:[10.1021/jp044252o](https://doi.org/10.1021/jp044252o)
- Sugimoto W, Yokoshima K, Murakami Y, Takasu Y (2006) Charge storage mechanism of nanostructured anhydrous and hydrous ruthenium-based oxides. *Electrochim Acta* 52:1742–1748. doi:[10.1016/j.electacta.2006.02.054](https://doi.org/10.1016/j.electacta.2006.02.054)
- Sun D, Ban R, Zhang P-H et al (2013) Hair fiber as a precursor for synthesizing of sulfur- and nitrogen-co-doped carbon dots with tunable luminescence properties. *Carbon N Y* 64:424–434. doi:[10.1016/j.carbon.2013.07.095](https://doi.org/10.1016/j.carbon.2013.07.095)
- Tang L, Ji R, Cao X et al (2012) Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots. *ACS Nano* 6:5102–5110. doi:[10.1021/nn300760g](https://doi.org/10.1021/nn300760g)
- Tõnrist K, Thomberg T, Jänes A et al (2012) Specific performance of electrical double layer capacitors based on different separator materials in room temperature ionic liquid. *Electrochem Commun* 22:77–80. doi:[10.1016/j.elecom.2012.05.029](https://doi.org/10.1016/j.elecom.2012.05.029)
- Tsay K-C, Zhang L, Zhang J (2012) Effects of electrode layer composition/thickness and electrolyte concentration on both specific capacitance and energy density of supercapacitor. *Electrochim Acta* 60:428–436. doi:[10.1016/j.electacta.2011.11.087](https://doi.org/10.1016/j.electacta.2011.11.087)
- Varzi A, Balducci A, Passerini S (2014) Natural cellulose: a green alternative binder for high voltage electrochemical double layer capacitors containing ionic liquid-based electrolytes. *J Electrochem Soc* 161:A368–A375
- Villers D, Jobin D, Soucy C et al (2003) The influence of the range of electroactivity and capacitance of conducting polymers on the performance of carbon conducting polymer hybrid supercapacitor. *J Electrochem Soc* 150:A747–A752. doi:[10.1149/1.1571530](https://doi.org/10.1149/1.1571530)
- Vol'fkovich YM, Serdyuk TM (2002) Electrochemical capacitors. *Russ J Electrochem* 38:935–959. doi:[10.1023/A:1020220425954](https://doi.org/10.1023/A:1020220425954)

- Wang Y, Hu A (2014) Carbon quantum dots: synthesis, properties and applications. *J Mater Chem C* 2:6921–6939. doi:[10.1039/C4TC00988F](https://doi.org/10.1039/C4TC00988F)
- Wang Y-G, Li H-Q, Xia Y-Y (2006) Ordered whiskerlike polyaniline grown on the surface of mesoporous carbon and its electrochemical capacitance performance. *Adv Mater* 18:2619–2623. doi:[10.1002/adma.200600445](https://doi.org/10.1002/adma.200600445)
- Wang G, Shen X, Horvat J et al (2009a) Hydrothermal synthesis and optical, magnetic, and supercapacitance properties of nanoporous cobalt oxide nanorods. *J Phys Chem C* 113:4357–4361. doi:[10.1021/jp8106149](https://doi.org/10.1021/jp8106149)
- Wang Y, Shi Z, Huang Y et al (2009b) Supercapacitor devices based on graphene materials. *J Phys Chem C* 113:13103–13107. doi:[10.1021/jp902214f](https://doi.org/10.1021/jp902214f)
- Wang X, Cao L, Yang S-T et al (2010) Bandgap-like strong fluorescence in functionalized carbon nanoparticles. *Angew Chemie Int Ed* 49:5310–5314. doi:[10.1002/anie.201000982](https://doi.org/10.1002/anie.201000982)
- Wang G, Zhang L, Zhang J (2012a) A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev* 41:797–828. doi:[10.1039/C1CS15060J](https://doi.org/10.1039/C1CS15060J)
- Wang J, Wang C-F, Chen S (2012b) Amphiphilic egg-derived carbon dots: rapid plasma fabrication, pyrolysis process, and multicolor printing patterns. *Angew Chemie Int Ed* 51:9297–9301. doi:[10.1002/anie.201204381](https://doi.org/10.1002/anie.201204381)
- Wang Q, Yan J, Wang Y et al (2014) Three-dimensional flower-like and hierarchical porous carbon materials as high-rate performance electrodes for supercapacitors. *Carbon N Y* 67:119–127. doi:[10.1016/j.carbon.2013.09.070](https://doi.org/10.1016/j.carbon.2013.09.070)
- Wee G, Soh HZ, Cheah YL et al (2010) Synthesis and electrochemical properties of electrospun  $V_2O_5$  nanofibers as supercapacitor electrodes. *J Mater Chem* 20:6720–6725. doi:[10.1039/C0JM00059K](https://doi.org/10.1039/C0JM00059K)
- Wen J, Ruan X, Zhou Z (2009) Preparation and electrochemical performance of novel ruthenium–manganese oxide electrode materials for electrochemical capacitors. *J Phys Chem Solids* 70:816–820. doi:[10.1016/j.jpcs.2009.03.015](https://doi.org/10.1016/j.jpcs.2009.03.015)
- Wu Q, Xu Y, Yao Z et al (2010a) Supercapacitors based on flexible graphene/polyaniline nanofiber composite films. *ACS Nano* 4:1963–1970. doi:[10.1021/nn1000035](https://doi.org/10.1021/nn1000035)
- Wu Z-S, Wang D-W, Ren W et al (2010b) Anchoring hydrous  $RuO_2$  on graphene sheets for high-performance electrochemical capacitors. *Adv Funct Mater* 20:3595–3602. doi:[10.1002/adfm.201001054](https://doi.org/10.1002/adfm.201001054)
- Xia H, Feng J, Wang H et al (2010)  $MnO_2$  nanotube and nanowire arrays by electrochemical deposition for supercapacitors. *J Power Sour* 195:4410–4413. doi:[10.1016/j.jpowsour.2010.01.075](https://doi.org/10.1016/j.jpowsour.2010.01.075)
- Xia X, Tu J, Mai Y et al (2011) Graphene sheet/porous nio hybrid film for supercapacitor applications. *Chem—A Eur J* 17:10898–10905 doi:[10.1002/chem.201100727](https://doi.org/10.1002/chem.201100727)
- Xiang F, Zhong J, Gu N et al (2014) Far-infrared reduced graphene oxide as high performance electrodes for supercapacitors. *Carbon N Y* 75:201–208. doi:[10.1016/j.carbon.2014.03.053](https://doi.org/10.1016/j.carbon.2014.03.053)
- Xiao J, Yang S, Wan L et al (2014) Electrodeposition of manganese oxide nanosheets on a continuous three-dimensional nickel porous scaffold for high performance electrochemical capacitors. *J Power Sour* 245:1027–1034. doi:[10.1016/j.jpowsour.2013.07.024](https://doi.org/10.1016/j.jpowsour.2013.07.024)
- Xing W, Qiao S, Wu X et al (2011) Exaggerated capacitance using electrochemically active nickel foam as current collector in electrochemical measurement. *J Power Sour* 196:4123–4127. doi:[10.1016/j.jpowsour.2010.12.003](https://doi.org/10.1016/j.jpowsour.2010.12.003)
- Xu X, Ray R, Gu Y et al (2004) Electrophoretic analysis and purification of fluorescent single-walled carbon nanotube fragments. *J Am Chem Soc* 126:12736–12737. doi:[10.1021/ja040082h](https://doi.org/10.1021/ja040082h)
- Xu B, Wu F, Chen R et al (2008) Highly mesoporous and high surface area carbon: a high capacitance electrode material for EDLCs with various electrolytes. *Electrochem Commun* 10:795–797. doi:[10.1016/j.elecom.2008.02.033](https://doi.org/10.1016/j.elecom.2008.02.033)
- Xu J, Wang Q, Wang X et al (2013) Flexible asymmetric supercapacitors based upon  $Co_9S_8$  Nanorod/ $Co_3O_4@RuO_2$  nanosheet arrays on carbon cloth. *ACS Nano* 7:5453–5462. doi:[10.1021/nn401450s](https://doi.org/10.1021/nn401450s)



- Yan J, Wei T, Shao B et al (2010) Electrochemical properties of graphene nanosheet/carbon black composites as electrodes for supercapacitors. *Carbon N Y* 48:1731–1737. doi:[10.1016/j.carbon.2010.01.014](https://doi.org/10.1016/j.carbon.2010.01.014)
- Yan J, Wang Q, Wei T, Fan Z (2014) Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. *Adv Energy Mater* 4:1300816–n/a. doi:[10.1002/aenm.201300816](https://doi.org/10.1002/aenm.201300816)
- Yang Y, Cui J, Zheng M et al (2012) One-step synthesis of amino-functionalized fluorescent carbon nanoparticles by hydrothermal carbonization of chitosan. *Chem Commun* 48:380–382. doi:[10.1039/C1CC15678K](https://doi.org/10.1039/C1CC15678K)
- Yokoshima K, Shibutani T, Hirota M et al (2006) Electrochemical supercapacitor behavior of nanoparticulate rutile-type  $\text{Ru}_{1-x}\text{V}_x\text{O}_2$ . *J Power Sour* 160:1480–1486. doi:[10.1016/j.jpowsour.2006.02.053](https://doi.org/10.1016/j.jpowsour.2006.02.053)
- Yu G-Y, Chen W-X, Zheng Y-F et al (2006) Synthesis of Ru/carbon nanocomposites by polyol process for electrochemical supercapacitor electrodes. *Mater Lett* 60:2453–2456. doi:[10.1016/j.matlet.2006.01.015](https://doi.org/10.1016/j.matlet.2006.01.015)
- Yu G, Hu L, Vosgueritchian M et al (2011) Solution-processed graphene/ $\text{MnO}_2$  nanostructured textiles for high-performance electrochemical capacitors. *Nano Lett* 11:2905–2911. doi:[10.1021/nl2013828](https://doi.org/10.1021/nl2013828)
- Yu H, Tang Q, Wu J et al (2012) Using eggshell membrane as a separator in supercapacitor. *J Power Sour* 206:463–468. doi:[10.1016/j.jpowsour.2012.01.116](https://doi.org/10.1016/j.jpowsour.2012.01.116)
- Yuan J, Liu Z-H, Qiao S et al (2009) Fabrication of  $\text{MnO}_2$ -pillared layered manganese oxide through an exfoliation/reassembling and oxidation process. *J Power Sour* 189:1278–1283. doi:[10.1016/j.jpowsour.2008.12.148](https://doi.org/10.1016/j.jpowsour.2008.12.148)
- Zhai X, Zhang P, Liu C et al (2012) Highly luminescent carbon nanodots by microwave-assisted pyrolysis. *Chem Commun* 48:7955–7957. doi:[10.1039/C2CC33869F](https://doi.org/10.1039/C2CC33869F)
- Zhang SW, Chen GZ (2008) Manganese oxide based materials for supercapacitors. *Energy Mater* 3:186–200. doi:[10.1179/174892409X427940](https://doi.org/10.1179/174892409X427940)
- Zhang H, Cao G, Wang Z et al (2008) Tube-covering-tube nanostructured polyaniline/carbon nanotube array composite electrode with high capacitance and superior rate performance as well as good cycling stability. *Electrochem Commun* 10:1056–1059. doi:[10.1016/j.elecom.2008.05.007](https://doi.org/10.1016/j.elecom.2008.05.007)
- Zhang Y, Feng H, Wu X et al (2009) Progress of electrochemical capacitor electrode materials: a review. *Int J Hydrogen Energy* 34:4889–4899. doi:[10.1016/j.ijhydene.2009.04.005](https://doi.org/10.1016/j.ijhydene.2009.04.005)
- Zhang K, Ang BT, Zhang LL et al (2011) Pyrolyzed graphene oxide/resorcinol-formaldehyde resin composites as high-performance supercapacitor electrodes. *J Mater Chem* 21:2663–2670. doi:[10.1039/C0JM02850A](https://doi.org/10.1039/C0JM02850A)
- Zhao D-D, Bao S-J, Zhou W-J, Li H-L (2007) Preparation of hexagonal nanoporous nickel hydroxide film and its application for electrochemical capacitor. *Electrochem Commun* 9:869–874. doi:[10.1016/j.elecom.2006.11.030](https://doi.org/10.1016/j.elecom.2006.11.030)
- Zheng JP, Cygan PJ, Jow TR (1995) Hydrrous ruthenium oxide as an electrode material for electrochemical capacitors. *J Electrochem Soc* 142:2699–2703. doi:[10.1149/1.2050077](https://doi.org/10.1149/1.2050077)
- Zheng C, Yoshio M, Qi L, Wang H (2014) A 4 V-electrochemical capacitor using electrode and electrolyte materials free of metals. *J Power Sour* 260:19–26. doi:[10.1016/j.jpowsour.2014.02.098](https://doi.org/10.1016/j.jpowsour.2014.02.098)
- Zhong C, Deng Y, Hu W et al (2015a) A review of electrolyte materials and compositions for electrochemical supercapacitors. *Chem Soc Rev* 44:7484–7539. doi:[10.1039/C5CS00303B](https://doi.org/10.1039/C5CS00303B)
- Zhong J, Fan L-Q, Wu X et al (2015b) Improved energy density of quasi-solid-state supercapacitors using sandwich-type redox-active gel polymer electrolytes. *Electrochim Acta* 166:150–156. doi:[10.1016/j.electacta.2015.03.114](https://doi.org/10.1016/j.electacta.2015.03.114)
- Zhu S, Zhang J, Qiao C et al (2011) Strongly green-photoluminescent graphene quantum dots for bioimaging applications. *Chem Commun* 47:6858–6860. doi:[10.1039/C1CC11122A](https://doi.org/10.1039/C1CC11122A)

## Chapter 4

# Asymmetric and Hybrid Supercapacitor

Both EDLCs and pseudocapacitor produce enough power density easily surpassing that of a battery, but their energy density is too low which is why they are currently employed only as backup devices for the purpose of rapid storage and discharge process. There are attempts made to combine electrodes of contrasting properties in order to achieve higher operating potential and to prevent electrolytic decomposition. For example, a strategic combination of carbonaceous material based electrode (EDLC electrode) and another electrode made out of pseudocapacitive material could exploit the altogether different potential windows so that the total working potential is the resultant of their individual working potential window optimized via suitable electrochemical method. Such tactical manipulation in selecting two asymmetric electrodes is highly essential. The primary goal is to devise a supercapacitor that would possess desired energy density (due to the presence of pseudocapacitive material) without sacrificing its characteristic power density (maintained by the EDLC type electrode).

Furthermore, approach has been made to combine both the basic principles of battery and supercapacitor to fabricate a device that could emulate the exceptional energy density of a battery and unmatched power density of a supercapacitor. Such devices are called as hybrid supercapacitors or more appropriately battery-supercapacitor hybrid devices (BSH) (Li et al. 2015a, b). Unlike electric double layer supercapacitor (EDLS) and pseudocapacitors, a BSH makes use of an EDLC material (activated carbon/grapheme/CNTs etc.) as the cathode and a suitable battery electrode as the anode. While the battery electrode (anode) acts as the energy source, the cathode (capacitor material) operates as the power source so as to replace the battery technology. Such an assembly of two dissimilar electrodes is meant to bring a balance between both power and energy density. Similar to asymmetric supercapacitor (ASC) devices, electrodes in the hybrid supercapacitors operate at different potential windows. Taking advantage of this unique property, the overall potential window can be escalated to attain higher values which in turn will enhance the energy density without hindering the power density. Therefore, to



achieve high energy and power density, the designing and development of suitable electrode materials is highly essential.

However, the selection and fabrication process is not as simple as is observed in the case of a typical EDLC and/or pseudocapacitor device. First, the optimum working potential window is achieved for both the electrodes using a standard three-electrode electrochemical cell (half-cell arrangement). From the half-cell measurements, details such as the loaded mass, capacitance value, and potential window are calculated and used to evaluate the required mass for each of the electrode material so as to maintain the mass-charge balance which is critical for the stability and efficient operation of the ASC device. Following equation is used to evaluate the mass ratio of the two electrodes (Shen et al. 2015; Wu et al. 2017):

$$\frac{m_+}{m_-} = \frac{C_- \Delta E_-}{C_+ \Delta E_+} \quad (1)$$

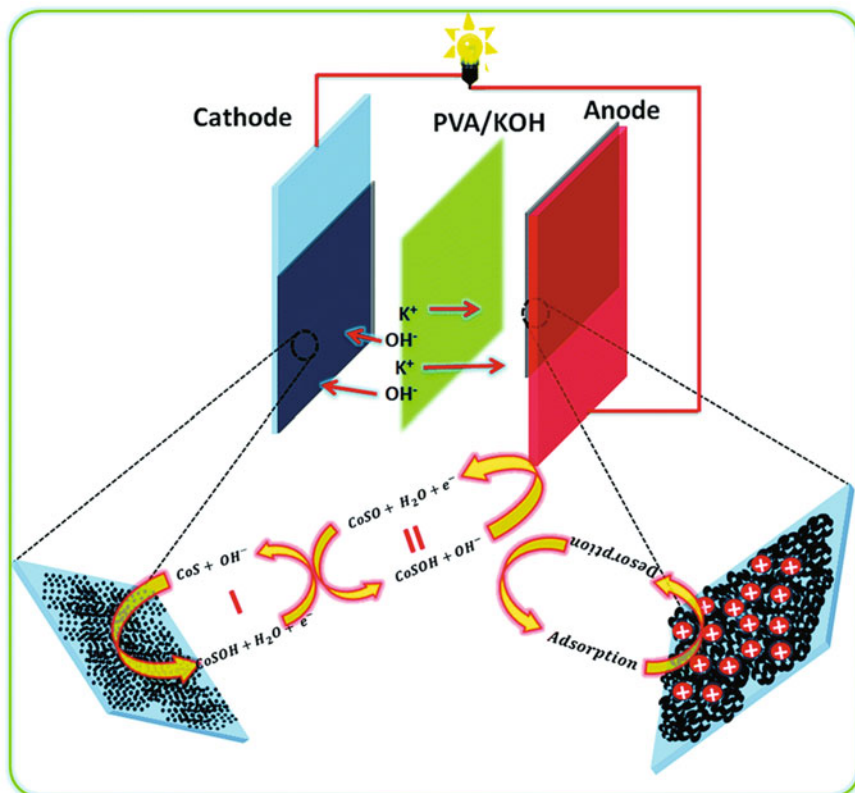
where  $m$ ,  $C$ , and  $\Delta E$  are the electrode mass, supercapacitor, and the potential range in the charge/discharge process for both electrodes, respectively.

## 4.1 Asymmetric Supercapacitor (ASC)

ASCs consist of a cathode, fabricated using a carbonaceous material having high specific surface area (SSA) and an anode comprising high performance and cost effective pseudocapacitor materials such as metal oxides ( $\text{MnO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{RuO}_2$ ,  $\text{MoO}_3$ ,  $\text{PbO}_2$  and  $\text{Fe}_2\text{O}_3$  etc.), conducting polymers such as PANI, PPy etc. (Zhi et al. 2013; Grote and Lei 2014; Long et al. 2014; Zhou et al. 2014a, b; Liu et al. 2015; Wu et al. 2017). The strategically tuned potential window in such ASCs can go beyond the decomposition potential of water (in the case of aqueous electrolytes) which clearly gives significant advantage over the symmetric supercapacitor devices having lower potential window ( $\sim 1.0$  V) in the presence of aqueous electrolytes. Apart from the compounds mentioned above, metal sulfides such as NiS (Guan et al. 2017), CoS (Shi et al. 2015),  $\text{NiCO}_2\text{S}_4$  etc. (Shen et al. 2015) have shown promising results as anode materials for ASC devices. Though the cycle life of an ASC device is lower than that of EDLC type supercapacitor, it effortlessly makes up with its exceptionally balanced power and energy density. Following Fig. 4.1 is a schematic of a typical asymmetric supercapacitor device.

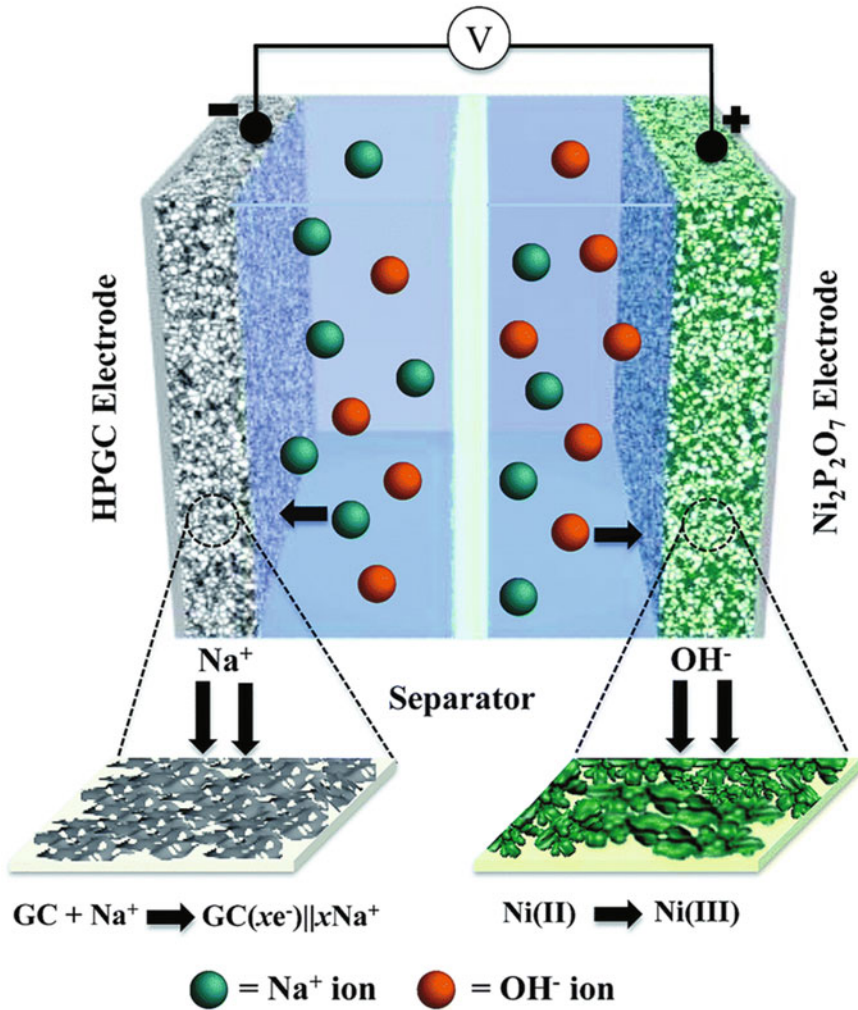
## 4.2 Hybrid Supercapacitor

Considering the current development of the EES devices, Li-ion batteries and supercapacitors are the most sought after devices which boast promising potential to be implemented in wide range of practical applications. The concept of lithium



**Fig. 4.1** Schematic showing an asymmetric supercapacitor device consisting of a gel polymer electrolyte (PVA/KOH). As can be seen, two different electrode materials are sandwiching the GPE in between them. Reproduced with permission from Subramani et al. (2017)

storage is promising considering the excellent electrochemical activity of Li, its abundance and it being lightweight in nature. There are numerous interesting literature reports on the high yielding lithium storage techniques which are essential in improving the LIB technology further. Efforts have been made to combine a material that has high lithium storage property with a capacitor material in order to derive high energy density like that of a Li-ion battery, still retaining the power density, typical of a supercapacitor. The Li-ion capacitor consists of a positive electrode (anode) made of capacitor material (carbonaceous) and a cathode used in typical Li-ion batteries such as  $\text{LiMn}_2\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{MnFe}_2\text{O}_4$ , and  $\text{LiTi}_2(\text{PO}_4)_3$  etc. (Aravindan et al. 2014; Yan et al. 2014). Sodium-ion hybrid capacitors have also emerged as potential energy storage devices recently (Senthilkumar et al. 2015). Figure 4.2 illustrates a basic principle behind the fabrication of a sodium-ion hybrid capacitor. These hybrid devices come with some promising specifications such as,



**Fig. 4.2** Schematic elucidating basic mechanism behind the sodium-ion hybrid capacitor device. Reproduced with permission from Senthilkumar et al. (2015)

- (i) Low self-discharge,
- (ii) High reliability,
- (iii) Wide operating temperature,
- (iv) Long cycle life and
- (v) High degree of safety.

These advantageous properties are gradually being exploited in various areas such as automatic guided vehicles, stacker cranes, construction machines, and instantaneous potential drop compensators.

## References

- Aravindan V, Gnanaraj J, Lee Y-S, Madhavi S (2014) Insertion-type electrodes for nonaqueous li-ion capacitors. *Chem Rev* 114:11619–11635. doi:[10.1021/cr5000915](https://doi.org/10.1021/cr5000915)
- Grote F, Lei Y (2014) A complete three-dimensionally nanostructured asymmetric supercapacitor with high operating voltage window based on PPy and MnO<sub>2</sub>. *Nano Energy* 10:63–70. doi:[10.1016/j.nanoen.2014.08.019](https://doi.org/10.1016/j.nanoen.2014.08.019)
- Guan B, Li Y, Yin B et al (2017) Synthesis of hierarchical NiS microflowers for high performance asymmetric supercapacitor. *Chem Eng J* 308:1165–1173. doi:[10.1016/j.cej.2016.10.016](https://doi.org/10.1016/j.cej.2016.10.016)
- Li Q, Chen W, Liu Z et al (2015a) Development of energy management system based on a power sharing strategy for a fuel cell-battery-supercapacitor hybrid tramway. *J Power Sour* 279:267–280. doi:[10.1016/j.jpowsour.2014.12.042](https://doi.org/10.1016/j.jpowsour.2014.12.042)
- Li R, Wang Y, Zhou C et al (2015b) Carbon-stabilized high-capacity ferroferric oxide nanorod array for flexible solid-state alkaline battery–supercapacitor hybrid device with high environmental suitability. *Adv Funct Mater* 25:5384–5394. doi:[10.1002/adfm.201502265](https://doi.org/10.1002/adfm.201502265)
- Liu W, Liu N, Shi Y et al (2015) A wire-shaped flexible asymmetric supercapacitor based on carbon fiber coated with a metal oxide and a polymer. *J Mater Chem A* 3:13461–13467. doi:[10.1039/C5TA01105A](https://doi.org/10.1039/C5TA01105A)
- Long C, Qi D, Wei T et al (2014) Nitrogen-doped carbon networks for high energy density supercapacitors derived from polyaniline coated bacterial cellulose. *Adv Funct Mater* 24:3953–3961. doi:[10.1002/adfm.201304269](https://doi.org/10.1002/adfm.201304269)
- Senthilkumar B, Khan Z, Park S et al (2015) Highly porous graphitic carbon and Ni<sub>2</sub>P<sub>2</sub>O<sub>7</sub> for a high performance aqueous hybrid supercapacitor. *J Mater Chem A* 3:21553–21561. doi:[10.1039/C5TA04737D](https://doi.org/10.1039/C5TA04737D)
- Shen L, Wang J, Xu G et al (2015) NiCo<sub>2</sub>S<sub>4</sub> nanosheets grown on nitrogen-doped carbon foams as an advanced electrode for supercapacitors. *Adv Energy Mater* 5:n/a–n/a. doi:[10.1002/aenm.201400977](https://doi.org/10.1002/aenm.201400977)
- Shi J, Li X, He G et al (2015) Electrodeposition of high-capacitance 3D CoS/graphene nanosheets on nickel foam for high-performance aqueous asymmetric supercapacitors. *J Mater Chem A* 3:20619–20626. doi:[10.1039/C5TA04464B](https://doi.org/10.1039/C5TA04464B)
- Subramani K, Sudhan N, Divya R, Sathish M (2017) All-solid-state asymmetric supercapacitors based on cobalt hexacyanoferrate-derived CoS and activated carbon. *RSC Adv* 7:6648–6659. doi:[10.1039/C6RA27331A](https://doi.org/10.1039/C6RA27331A)
- Wu L, Hao L, Pang B et al (2017) MnO<sub>2</sub> nanoflowers and polyaniline nanoribbons grown on hybrid graphene/Ni 3D scaffolds by in situ electrochemical techniques for high-performance asymmetric supercapacitors. *J Mater Chem A* 5:4629–4637. doi:[10.1039/C6TA10757E](https://doi.org/10.1039/C6TA10757E)
- Yan J, Wang Q, Wei T, Fan Z (2014) Recent advances in design and fabrication of electrochemical supercapacitors with high energy densities. *Adv Energy Mater* 4:1300816–n/a. doi:[10.1002/aenm.201300816](https://doi.org/10.1002/aenm.201300816)
- Zhi M, Xiang C, Li J et al (2013) Nanostructured carbon-metal oxide composite electrodes for supercapacitors: a review. *Nanoscale* 5:72–88. doi:[10.1039/C2NR32040A](https://doi.org/10.1039/C2NR32040A)
- Zhou Y, Lachman N, Ghaffari M et al (2014a) A high performance hybrid asymmetric supercapacitor via nano-scale morphology control of graphene, conducting polymer, and carbon nanotube electrodes. *J Mater Chem A* 2:9964–9969. doi:[10.1039/C4TA01785D](https://doi.org/10.1039/C4TA01785D)

Zhou Y, Xu H, Lachman N et al (2014b) Advanced asymmetric supercapacitor based on conducting polymer and aligned carbon nanotubes with controlled nanomorphology. *Nano Energy* 9:176–185. doi:[10.1016/j.nanoen.2014.07.007](https://doi.org/10.1016/j.nanoen.2014.07.007)

## Chapter 5

# Trend and Scope Beyond Traditional Supercapacitors

Primitive type supercapacitors that were made of pure carbon or carbon derived electrode materials have gone through rapid evolution since few decades. Most of these traditional supercapacitor devices are of symmetric nature, i.e. both electrodes are fabricated from the same material which reduces any chances of enhancing the working potential window. The first stage evolution took place with the concept of taking two different materials as electrodes to form an asymmetric supercapacitor device which not only will provide the option for wider potential window but also suppress decomposition of electrolytic content (specifically for aqueous based electrolytes). Thus asymmetric supercapacitors are promising storage options and should be put to further research in order to promote its commercial viability. Extensive research should also be done on electrolytic materials as they play a key role in the performance of a supercapacitor device.

Apart from the above asymmetric supercapacitor prototype, further work need to be carried out to try and test the feasibility of various other cost-effective materials as supercapacitor electrodes. As discussed in the previous sections, there are challenges while trying to obtain a system of two electrodes using a suitable electrolytic material. There are other aspects too such as the post-fabrication performance of the supercapacitor device, safety, reliability and stability. Also, more attention is to be devoted towards the development and practical implementation of hybrid supercapacitors by designing a combination of electrodes and electrolyte.

To create a high performance asymmetric and/or hybrid storage device (supercapacitor), there are few key points which should be taken care of;

1. Designing a current collector which should be able to provide excellent contact formation. It should be highly resistant toward any physical and/or chemical hazards. Preferably, a highly conducting, robust, non-corrosive, and flexible material such as metal foam/foil is to be applied as the current collector.
2. Suitable electrode materials for the purpose to fabricate both cathode and anode. For the cathode, a material with high porosity, chemical stability, mechanical/

tensile strength, superior adsorption capability will be ideal in order to promote EDLC.

In contrast, for the anode, a material with high pseudocapacitive/lithium intercalation property, high electrical conductivity would suffice. For ASCs, though metal oxides provide plenty of options to try out, research should be extended toward more promising materials such as metal nitrides having better electrical conductivities which would have significant impact on the supercapacitor performances.

Similar approach toward the futuristic development of lithium storage material is the key to the designing of high power density and energy density supercapacitors which could assist the battery technology to ward off issues of sluggish charge uptake time, overcharging etc. Lithiated metal nitrides and/or lithium compounds are found to be ideal for this purpose.

Furthermore, electrode material synthesis is an important aspect which should be carried out with utmost care. Most of the materials that have been grown indirectly using substrate/template assisted growth can be successfully replaced with those grown directly using various substrates and can directly be taken as current collector/electrode assembly. That would bring much better adhesion between the both which is desired for a supercapacitor device.

3. Judicious selection of electrolyte materials (liquid, gel or solid) is also critical as it would have significant impact on the stability and ionic conductivity of the solid electrolyte interphase (SEI). The compactness, rigidity and long cycle life of a supercapacitor device will be determined by the type of electrolyte used. For supercapacitors employing liquid electrolytes, a suitable separator should be selected to facilitate ion/charge transportation and for maintaining a barrier between the two electrodes and protect the device from short circuit.
4. Though rigorous research has been done on huge number of metal oxides as cheap and high performance pseudocapacitive material, extended interest should be vested in few promising compounds such as metal nitrides, metal borides etc. which would facilitate the selection and development of efficient high performance supercapacitor electrodes.