

CHAPTER 1

INTRODUCTION

This chapter embodies an overview of different types of electrochemical energy storage devices such as batteries, fuel cells, electrolytic capacitors and electrochemical supercapacitors. The importance of supercapacitors, their historical background, classification, charge storage mechanisms and applications in diverse fields have been dealt with. The chapter discusses different types of electrode and electrolyte materials that have been investigated for supercapacitor applications with a detailed description of conducting polymer and graphene electrodes. Different aspects of swift heavy ion irradiation and the energy loss processes during their passage through materials are discussed. The chapter ends with the scope of the thesis and statement of the thesis problem.

1.1 Overview of electrochemical energy storage devices

The rapid increase in energy consumption based on the growing population worldwide and increasing combustion of fossil fuels have caused major concerns on the accelerating global warming and environmental pollution. At current energy consumption rate, it is expected that the global energy needs will almost double by 2050 [1]. Predictions are that the global energy demand will be dominated by fossil fuels accounting for 78% by 2030 [2]. To meet the high energy demand and to mitigate environmental pollution, there has been an urgent demand for the development of clean, sustainable and renewable alternative energy sources that can replace fossil fuels. Renewable energy sources such as solar and wind energies are available in abundance and are potentially cheaper technologies. However, these energy sources are intermittent and cannot fulfil the energy demands at peak hours leading to power fluctuations. Utilizing energy storage devices to regulate their supply is a chief requirement to improve their usability for mass production. The other renewable energy sources like biomass, biofuel and hydropower are comparatively stable means of energy production, but energy storage is essential for their effective usage during depletion time. Hence all renewable energy sources suffer from power fluctuations and share a common requirement of the need for

reliable energy storage systems. Therefore the requirement of efficient, environmentally benign and low-cost energy storage systems has become indispensable to fulfil the energy demand and emerging ecological concerns. There are different types of energy storage systems where energy could be stored in various forms such as kinetic energy (flywheels), thermal energy (solar-thermal plants), potential energy (pumped hydroelectric storage), pneumatic energy (compressed air storage), magnetic energy (superconducting magnetic storage) and electrochemical energy (batteries, supercapacitors) [3]. Amongst various energy storage systems, electrochemical energy storage systems have been developed as efficient, sustainable and safe energy storage technologies to meet the requirements of high energy and power devices, the classifications of which are discussed below:

1.1.1 Conventional capacitors

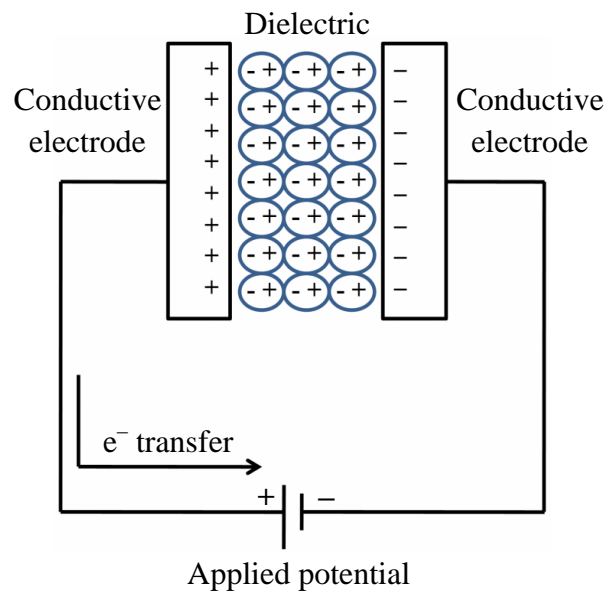


Figure 1.1: Schematic of a conventional capacitor.

A conventional capacitor is a device that stores energy in the form of electrical charge. The energy stored is in the range of microfarads and their charging-discharging time is very fast, which makes them useful for pulsed power applications [4]. Capacitors store charge electrostatically between two parallel conductive plates called electrodes separated by a dielectric medium as shown in Figure 1.1. When an external potential is applied, electrons are attracted towards the positive potential and are transferred from the positively charged metallic plate to the negatively charged

plate. Thus an electron deficiency occurs at the positive potential side and an electron surplus develops at the negative side that gives rise to a potential difference between the two metallic plates. This charge gets stored as electrical energy in the capacitor which can be utilized by connecting an external load. The ratio of charge stored on either conductor (Q) to the applied potential (V) is a constant of proportionality known as the capacitance and is given by $C = Q/V = \epsilon A/d$, where ϵ is the dielectric permittivity, A is the area of the electrodes and d is the thickness of the dielectric [5]. The energy and power stored in a capacitor are calculated as: $E = \frac{1}{2} CV^2$ and $P = V^2/4R$, where R is the equivalent series resistance of the circuit.

1.1.2 Electrolytic capacitors

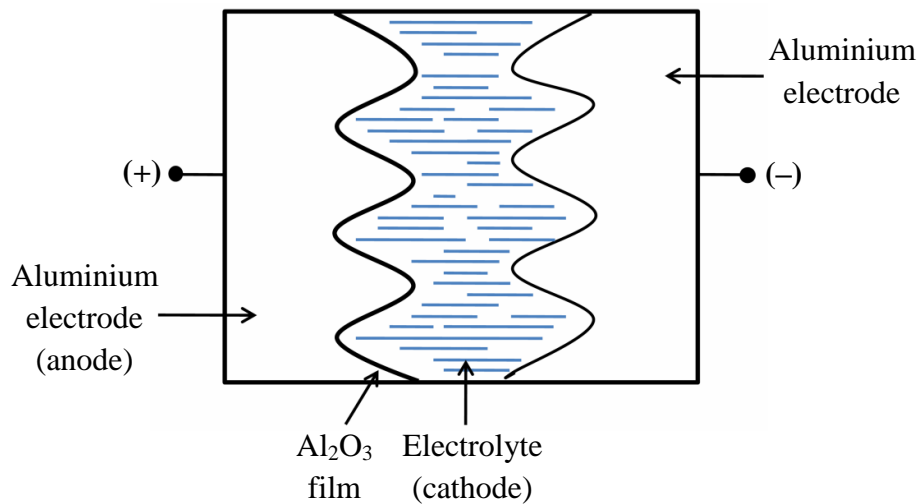


Figure 1.2: Schematic of an aluminium electrolytic capacitor.

Electrolytic capacitors are devices that comprise of a special metal as the anode and an electrolyte as the cathode, respectively. An oxide layer is formed electrochemically on the surface of the metal electrode which acts as a dielectric [6]. The formation of very thin oxide layer as dielectric offers larger capacitance to electrolytic capacitors as compared to conventional capacitors. Charles Pollak was the first to introduce the idea of electrolytic capacitors in 1886 when he found that the oxide layer formed on an aluminium electrode remained stable in a neutral or alkaline electrolyte even after the power was switched off [7]. There are generally three types of electrolytic capacitors: (i) Aluminium electrolytic capacitors, (ii) Tantalum electrolytic capacitors and (iii) Niobium electrolytic capacitors. The

electrolytes used are solid as well as liquid electrolytes between two symmetrical electrodes. The schematic illustration of an aluminium electrolytic capacitor is shown in Figure 1.2, which consists of two aluminium foils, a separating paper as the electrolyte and a thin layer of Al_2O_3 as the dielectric. The oxide layer is formed on one of the two aluminium foils that acts as the anode and the operating electrolyte serves as the cathode. The function of the other aluminium foil is to pass current to the operating electrolyte. The surface area of the aluminium foils is increased by electrochemical etching to obtain high capacitance values [8]. Aluminium electrolytic capacitors have found applications in automobiles, computers, aircraft etc.

1.1.3 Electrochemical supercapacitors

Electrochemical supercapacitors are energy storage devices that store charge at the interfaces between the electrode and the electrolyte [9]. The charge storage principle of a supercapacitor is similar to conventional capacitor except that the two electrodes are in contact with a common electrolyte separated by a porous dielectric membrane. The interface between the electrode and the electrolyte serves as the dielectric in supercapacitors which is of the order of a few angstroms, much smaller than a conventional capacitor [10]. This gives rise to very high capacitance values in the range of farads and therefore they are referred to as supercapacitors.

1.1.4 Batteries

Batteries are devices that convert the chemical energy contained in an electrochemically active material into electrical energy through faradaic redox reactions at the electrode-electrolyte interface [11]. A faradaic redox reaction implies the gain or loss of at least one electron. The faradaic reactions occur in a cell which includes two electrodes (anode and cathode), a separator and an electrolyte (liquid/solid) of high ionic conductivity. When the battery is discharged through an external load as shown in Figure 1.3 (a), electrons flow from the anode to the cathode through the external circuit and the charge neutrality is maintained by the movement of the ions through the electrolyte to both the electrodes. Therefore oxidation occurs at the anode and reduction occurs at the cathode and both the reactions proceed simultaneously until the battery is fully discharged. During

charging, an external source of electrical current is connected to the battery that reverses the flow of electrons until the battery is recharged as shown in Figure 1.3 (b). The maximum voltage that can be achieved from a battery is measured by the change in the Gibbs free energy (ΔG) of the redox processes occurring inside the battery, which is given by $\Delta G = -nF\Delta E$ where F is the Faraday constant, n is the number of electrons transferred and ΔE is the cell voltage difference [12].

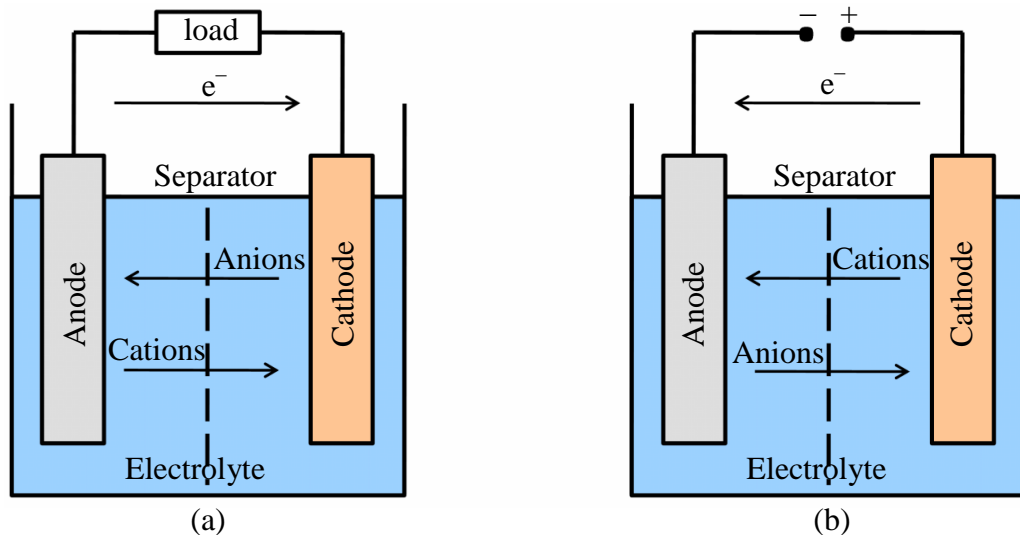


Figure 1.3: Schematic of (a) discharging and (b) charging processes of a secondary battery.

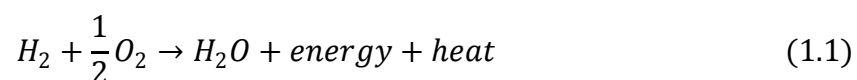
Batteries are classified as primary and secondary batteries depending on their recharging capacity [13]. The redox reactions in primary batteries are irreversible and are not rechargeable once completely discharged. The commonly used primary batteries are zinc-carbon, alkaline manganese and primary lithium batteries. The redox reactions associated with secondary batteries are reversible and can be recharged upto hundreds of cycles depending on the capacity and cyclic performance of the battery. These batteries serve as energy storage devices in many applications like computers, cell phones, hybrid vehicles, medical devices etc. Some important secondary batteries are lithium-ion, nickel-metal hydride, nickel-cadmium and lead-acid batteries [14]. Lithium-ion batteries are currently the commonly used electrochemical cells with an energy density of about 110-160 Wh/kg, moderate charge-discharge rates, rechargeable upto 500-1000 cycles, safe with a protection circuit, light weight and low maintenance [15]. It consists of a carbon material as the anode and the cathode used is a lithium intercalated compound such as LiMO_2 ($M =$

Co, Mn, Ni). During charging, lithium ions move from the cathode towards the carbon anode across the electrolyte and the reverse takes place in the discharge process. The electrons flow through the outer circuit during the processes which produce electrical current [16].

1.1.5 Fuel cells

Fuel cells are electrochemical devices that convert energy in fuels such as hydrogen directly into electrical energy and heat through the electrochemical reaction of hydrogen and oxygen to form water. Unlike batteries that must be discarded or recharged once depleted, fuel cells use a continuous supply of chemical energy and produce an electrical power output that sustains indefinitely [17]. The reaction of hydrogen atoms with oxygen atoms to form water releases electrons, which flows through the external circuit as electric current. Fuel cells have many advantages like high efficiency, low emissions, silent operation and environmentally friendly [18]. A fuel cell unit comprises of a stack that consists of a number of individual cells, where each cell has two electrodes. The two electrodes are composed of porous gas diffusion layers made up of materials having high electronic conductivity such as graphite and are separated by a solid or liquid electrolyte that transports ions between them. The reactions that produce electric current occur at the electrodes, where a catalyst is often used to accelerate the reactions [19]. The catalyst used may be different for different types of fuel cells. A schematic of a hydrogen-oxygen or proton exchange membrane fuel cell is shown in Figure 1.4, which consists of two electrodes separated by a proton conductive polymer membrane as the electrolyte.

Hydrogen is supplied to the anode and is electro-catalytically oxidized into hydrogen ions, which travel through the electrolyte to the cathode. The electrons flow through the external circuit to the cathode where oxygen reacts with protons and electrons to form water releasing heat [20]. A thin layer of platinum coated on each electrode is used as a catalyst to accelerate the reactions between hydrogen and oxygen. The overall reaction of a proton exchange membrane fuel cell can be written as:



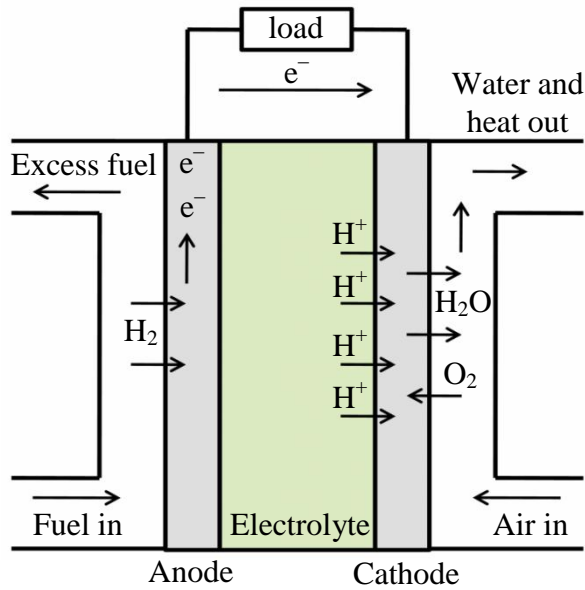


Figure 1.4: Schematic of a proton exchange membrane fuel cell.

The water and heat generated by the fuel cell must be continuously removed for its proper functioning. There are five types of fuel cells depending on the electrolyte material and the fuel source, which determine the electrode reactions and the ions that are transferred across the electrolyte. These are: (i) Alkaline fuel cell (AFC), (ii) Phosphoric acid fuel cell (PAFC), (iii) Molten carbonate fuel cell (MCFC), (iv) Solid oxide fuel cell (SOFC), and (v) Proton exchange membrane fuel cell (PEMFC) [21]. All the mentioned fuel cells require pure hydrogen fuel for their operation. Amongst them, PEMFC has the advantages of low manufacturing cost, easy handling, zero emissions and the ability to operate at relatively low temperatures. The efficiency of AFC is high and is used to generate electricity in spacecraft, but the running cost is expensive. Different types of fuel cells are utilized in different applications such as space exploration, portable electronics, transportation and other stationary and residential purposes [22]. Apart from the mentioned fuel cells, a new fuel cell known as Direct methanol fuel cell (DMFC) is under vigorous on-going research. The operating mechanism of this fuel cell is similar to that of PEMFC, but it uses methanol as a fuel instead of hydrogen [23].

1.2 Comparison of electrochemical energy storage devices

The commonly used electrochemical energy storage devices are conventional capacitors, batteries, electrochemical supercapacitors and fuel cells. These energy

storage devices exhibit different energy and power densities, which can be well understood from the Ragone plot [24] as shown in Figure 1.5. Energy density and power density are important parameters that determine the performance of an energy storage device. Energy density, measured in Wh/kg is the amount of energy per unit weight that could be stored in a device and power density (W/kg) determines how fast the energy could be stored and released [25].

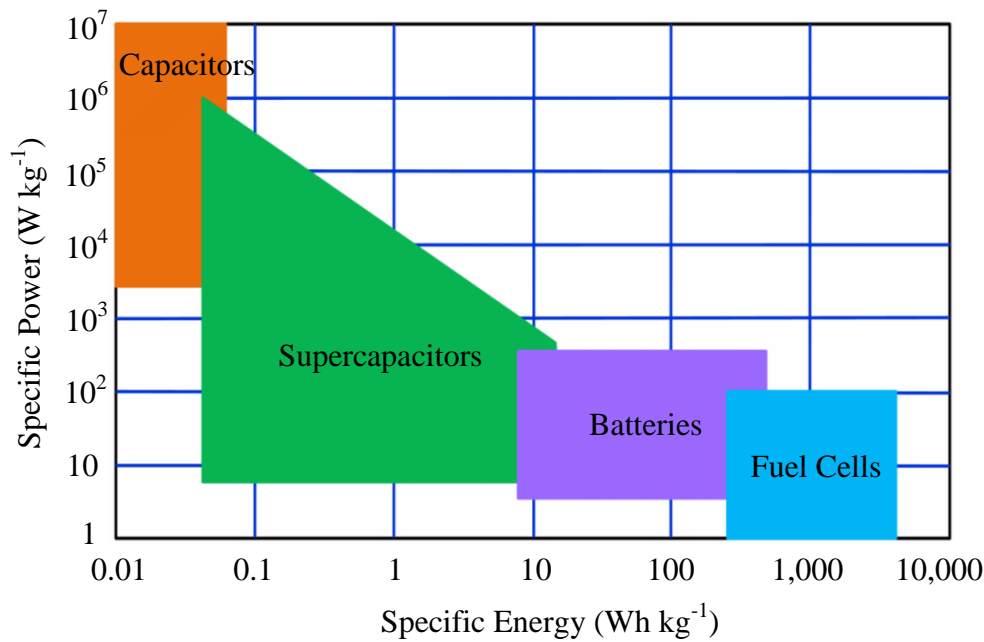


Figure 1.5: Ragone plot of different electrochemical energy storage devices.

The Ragone plot is a power density vs. energy density plot and is helpful in choosing an energy storage device for a particular application having specific requirements. It clearly shows that fuel cells show the highest energy density whereas capacitors are considered as high-power systems. The power density of batteries is lower than that of capacitors and electrochemical supercapacitors, but they have the ability to store large amounts of energy. Supercapacitors bridge the gap between capacitors and batteries with energy densities in the range of 8-10 Wh/kg and power densities greater than 10 kW/kg [26]. The cycle life of supercapacitors is very high upto 10⁶ cycles as there are no chemical conversions of the electrode materials involved with non-faradaic processes. They are safer and their internal resistance is lower than that of capacitors and batteries i.e. the energy loss to heat is less during each cycle. The charge-discharge rates of supercapacitors are highly reversible and fast and can be charged within seconds. However, batteries store

charge by slow redox reactions, which take them several hours to charge [27]. With all the aforementioned advantages, supercapacitors are efficient alternatives to batteries for hybrid vehicles and portable electronics with high power performance upto $-40\text{ }^{\circ}\text{C}$.

1.3 Historical background of supercapacitors

The concept of energy storage at the electrode-electrolyte interfaces was first patented by H. I. Becker in 1957, who used porous carbon material as an electrode in H_2SO_4 electrolyte [28]. However, the device was not commercialized. The invention of the modern device format of supercapacitor took place in 1970 when the Standard Oil Company of Ohio (SOHIO) introduced a disc shaped capacitor into the market made of carbon electrodes soaked in tetra alkyl ammonium salt electrolyte [29]. This technology was later licensed to Nippon Electric Company (NEC) in 1971 who commercialized the first supercapacitor for memory backup applications in 1978 [30]. In 1970s, another new mechanism of charge storage was proposed by B. E. Conway that was exhibited by redox-active materials, which led to the development of RuO_2 electrodes based supercapacitor [31]. Since then, the supercapacitor technology has gained importance and evolved over several decades with varying designs and found applications in hybrid electric vehicles, portable wireless communication etc. At present, a number of companies around the world like Maxwell, Panasonic, Nippon and Ness Cap manufacture and sell supercapacitors [32].

1.4 Classification of supercapacitors

Supercapacitors, also known as ultracapacitors, are promising candidates for energy storage applications due to their pulse power supply, fast charge-discharge rates, long cycle life, low self-discharge and safe operation [33]. They utilize large surface area electrode materials and very thin dielectrics such as electrode-electrolyte interface to achieve capacitances of several orders of magnitude higher than that of conventional capacitors. Supercapacitors store charge by two different mechanisms: (i) electrostatically by charge accumulation at the electrode-electrolyte interface and (ii) faradically by charge transfer reactions between the electrode and the electrolyte [34]. Depending on these two charge storage mechanisms and the electrode materials

used, supercapacitors are categorized into two types: Electric double layer capacitors and pseudocapacitors. The combination of these two charge storage mechanisms gives rise to the third classification of supercapacitors known as hybrid capacitors [35]. The block diagram of the classification of supercapacitors based on their types and electrode materials is depicted in Figure 1.6.

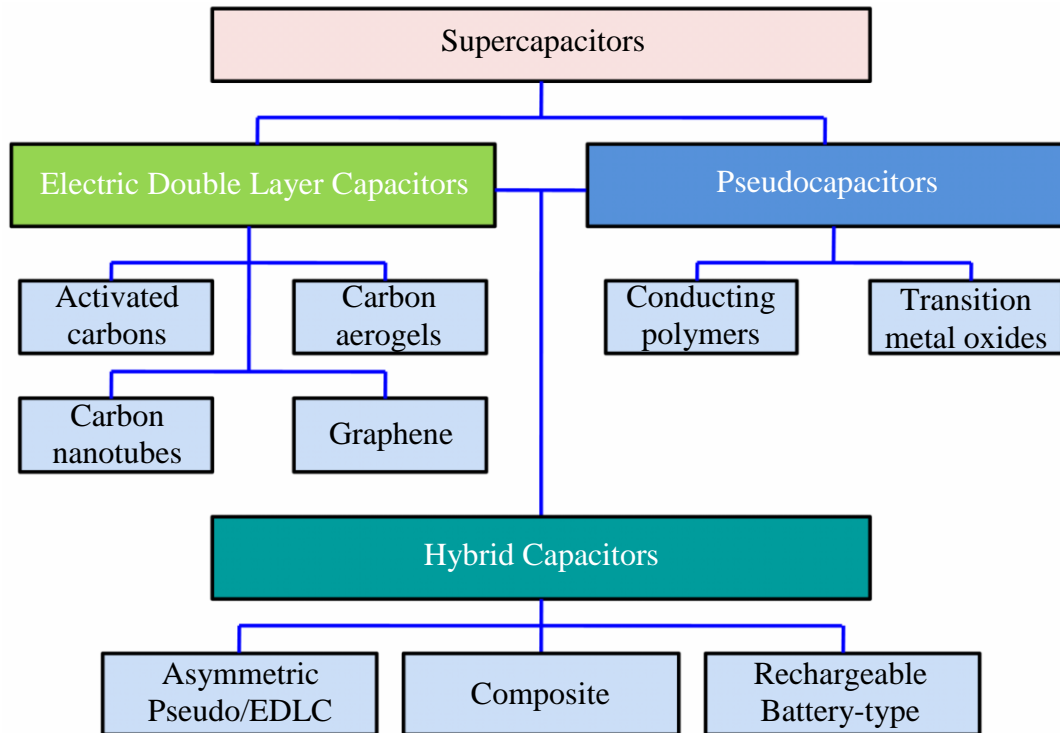


Figure 1.6: Block diagram of classification of supercapacitors.

1.4.1 Electric double layer capacitors

Electric double layer (EDL) capacitors store charge by electrostatic attraction between the electrolyte ions and the charges on the electrode surface forming two electric double layers at the electrode-electrolyte interface. The thickness of the double layer is of the order of a few Angstroms. The charge storage mechanism is purely electrostatic and no faradaic charge transfer occurs across the interface in EDL capacitors [36]. The energy storage process is associated with the movement of charge to the interfaces and no chemical changes are involved, therefore the process is fast and highly reversible. For this reason, EDL capacitors have a high power density and can operate upto 10^6 charge-discharge cycles [37]. The schematic diagram of EDL capacitors is shown in Figure 1.7, which consists of two porous carbon electrodes, an electrolyte and a separator that allows ions to pass through as

well as provides electric insulation between the electrodes. When an external potential is applied, positive and negative charges of the electrodes accumulate on the surface, which attracts electrolyte ions of opposite polarity. This forms a double layer at each electrode-electrolyte interface separated by a few Angstroms. The double layer formed at each electrode-electrolyte interface represents two capacitors connected in series. Owing to the short distance of charge separation and large surface area of porous electrodes, EDL capacitors achieve high capacitances than that of normal capacitors. Electrode materials for EDL capacitors are generally carbon-based materials with high specific surface area such as carbon aerogels, activated carbon, carbon nanotubes, graphene etc. [38, 39].

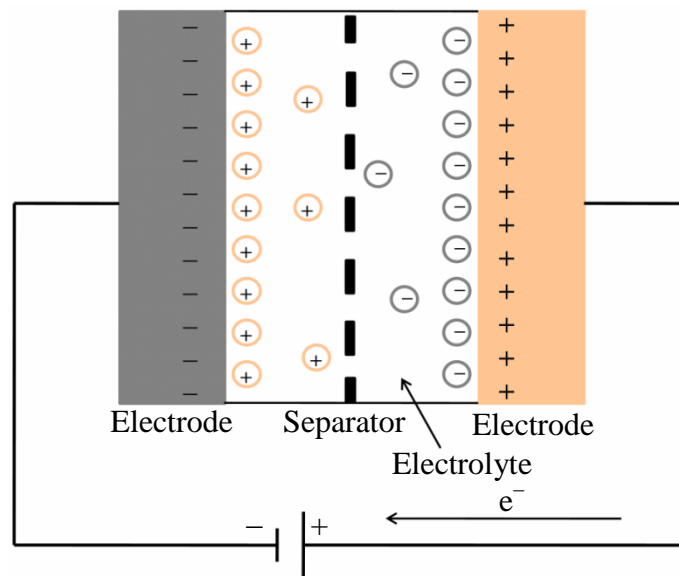


Figure 1.7: Schematic of charge storage process in electric double layer capacitors.

1.4.2 Pseudocapacitors

The charge storage in pseudocapacitors occurs by reversible faradaic redox reactions between the electrode and the electrolyte in addition to the electrostatic charge accumulation. When a potential is applied, charge transfer occurs across the electrode-electrolyte interface associated with a change in the oxidation state of the electrode, which is referred to as a faradaic process [35]. Due to the presence of faradaic reactions, they are also known as redox supercapacitors. Unlike EDL capacitors, the charge storage mechanism of pseudocapacitors is indirect, where the amount of charge transferred is a continuous function of the potential of the electrode, which is similar to a capacitor and hence is designated as

pseudocapacitance (“pseudo” implies “not real”). Pseudocapacitance is exhibited by redox-active materials like conducting polymers [polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene)], transition metal oxides (MnO₂, RuO₂, NiO), metal hydroxides [Ni(OH)₂, Co(OH)₂] etc. [40]. The schematic of the working principle of pseudocapacitor using polypyrrole (PPy) as electrode and KCl as electrolyte is shown in Figure 1.8. The faradaic reactions between the PPy electrode and KCl electrolyte during charging at the negative and positive electrode could be expressed as:

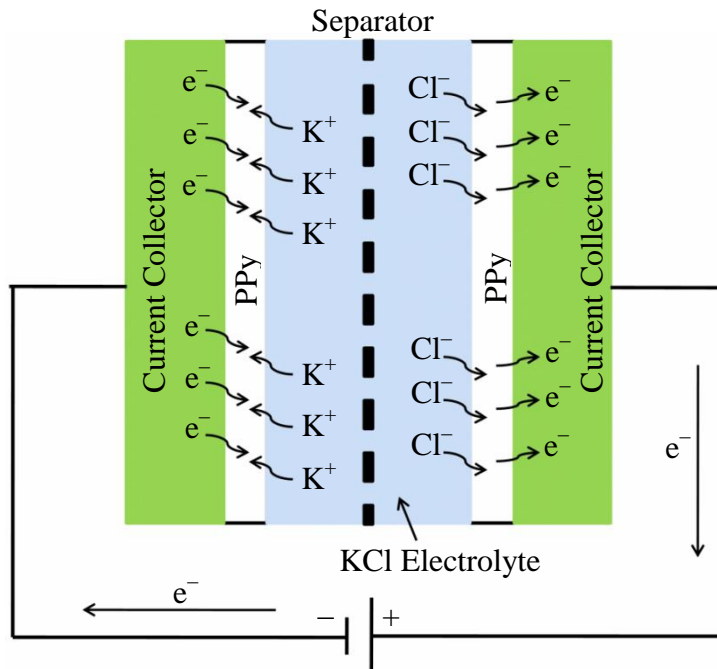
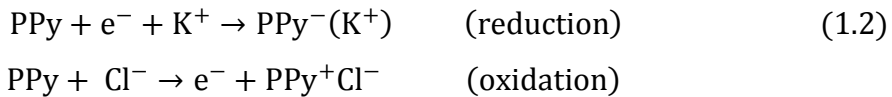


Figure 1.8: Schematic of charge storage process in pseudocapacitors.

It can be seen that both the surface and the bulk of the material are involved in pseudocapacitive charge storage. Therefore the specific capacitance of pseudocapacitors can be higher by 10-100 times than that of EDL capacitors [41]. The faradaic reactions are reversible and faster than that of rechargeable batteries, but are slower than the ion adsorption process in EDL capacitors. During the faradaic charge transfer reactions, volumetric changes are experienced by the electrode, which degrades their performance with time. Hence, pseudocapacitors are characterized by a high specific capacitance and energy density than that of EDL

capacitors but have a low power density and cycle life [42]. A comparison of the performance of EDL capacitors and pseudocapacitors is presented in Table 1.1.

Table 1.1: Comparison of different properties of EDL capacitors and pseudocapacitors

Properties	EDL capacitors	Pseudocapacitors
Charge storage process	Electrostatic (non-faradaic)	Faradaic
Specific capacitance	20-50 $\mu\text{F cm}^{-2}$	2000 $\mu\text{F cm}^{-2}$ for one-electron transfer; 200-500 mF cm^{-2} for multi-electron transfer
Energy density	Low (3-5 Wh/kg)	High (10-12 Wh/kg)
Power density	High power due to easy diffusion	Low power due to electrode kinetics limitations
Cycle life	Reversible charge-discharge upto 10^6 cycles	Moderate charge-discharge reversibility upto 10^5 cycles; degrades with time
Operating potential window	Narrow in range of 1-3 V	Large in range of 1-5 V
Leakage effect	Capacitance constant with potential	Capacitance changes with potential

1.4.3 Hybrid capacitors

Due to the relative disadvantages of EDL capacitors and pseudocapacitors, hybrid capacitors have been developed in order to combine the best properties of individual materials and mitigate their drawbacks to produce a synergistic effect for improved electrochemical performance. In hybrid capacitors, both faradaic and non-faradaic charge storage processes are utilized to achieve high specific capacitance and energy density than that of EDL capacitors without sacrificing the power density and cycle life that limit the performance of pseudocapacitors [43]. Depending on their electrode configuration, hybrid capacitors are classified into three categories: (i) composite hybrid, (ii) asymmetric hybrid and (iii) battery-type hybrid supercapacitors, respectively.

(i) Composite hybrid supercapacitors

The supercapacitors that use composite materials as electrodes are called composite hybrid supercapacitors. Here, carbon-based materials are integrated with conducting polymers or metal oxides and both the charge storage mechanisms of ion adsorption and faradaic redox reactions are utilized in a single electrode [44]. The carbon materials provide EDL capacitance (EDLC) as well as a high surface area backbone that increases the contact between the deposited pseudocapacitive materials and the electrolyte thereby increasing the faradaic charge transfer reactions. The combination of both EDLC and pseudocapacitance improves the capacitive performance of the electrode. Nanocomposites of various carbon materials and conducting polymers or metal oxides have been reported to provide with superior electrochemical performance than that of the individual components. Nanocomposite electrodes of carbon nanotubes (CNT) and conducting polymers have been actively explored and specific capacitances in the range of 320-490 F/g and 200-350 F/g have been achieved for CNT-PAni [45-47] and CNT-PPy nanocomposites [48, 49]. Combining various types of metal oxides with carbon materials yield specific capacitance values of 150-300 F/g, which are higher than that of their pristine components [50-52].

(ii) Asymmetric hybrid supercapacitors

Asymmetric hybrid supercapacitors are fabricated by using an EDLC material as one electrode and a pseudocapacitive material as the other electrode. Both the electrodes are of different materials and store charge by two different mechanisms which mitigate the problems of low operating voltage range and cycle life [53]. An appropriate combination of carbon based materials and conducting polymers has been studied to achieve superior electrochemical performance than that of individual EDL capacitors and pseudocapacitors [54]. Asymmetric electrodes based on graphene or carbon nanotubes as negative electrode and MnO_2 as positive electrode have been extensively investigated and achieved with high energy and power densities [55, 56].

(iii) Battery-type hybrid supercapacitors

Battery-type hybrids are similar to asymmetric hybrids except that they couple two different technologies of battery and supercapacitor in a single device. This device

configuration is designed to achieve a high energy density of batteries combined with the high power density and cycle life of supercapacitors [57]. Different supercapacitive electrodes combined with batteries have been proposed recently that have offered high operating cell voltage. Significant interest has been focused on the coupling of nickel hydroxide, lead dioxide etc. with graphene and activated carbon [58, 59]. An example of hybrid capacitor is based on positive activated carbon capacitive electrode combined with a negative $\text{Li}_4\text{Ti}_5\text{O}_{12}$ faradaic electrode in a mixed organic electrolyte, which showed a sloping voltage profile of 1.5-3 V [60]. A hybrid capacitor fabricated by using activated carbon as positive electrode and graphite as negative electrode resulted in an increased positive voltage upto 5 V in an organic electrolyte [61]. Asymmetric hybrids based on capacitive activated carbon (AC) electrode and faradaic MnO_2 -AC nanocomposite electrode in aqueous Na_2SO_4 electrolyte led to an extended operating voltage of 2 V and a maximum energy density of 18.2 Wh/kg after 2500 cycles [62].

1.5 Application of supercapacitors

Due to the high power density and exceptional cycle life of supercapacitors, they are utilized for a variety of applications that require large energy release in a short period of time. Some applications of supercapacitors are discussed below:

- (i) Hybrid electric vehicles: Supercapacitors are used in peak-load requirements during acceleration or climbing-up hills owing to its high power performance. Supercapacitors can be utilized to harvest energy during regenerative braking. They are also used as power supplies in hybrid cars for start/stop application. As starting and stopping the engine of vehicles require power spikes, supercapacitors are efficient than batteries. When a hybrid vehicle stops, its internal combustion engine shuts down that is restarted from the power provided by a supercapacitor. The supercapacitor is recharged as the engine resumes powering the vehicle. This helps in reducing fuel consumption. They are suitable for vehicles such as city buses, trash trucks and delivery vans that experience a large number of start/stop cycles during a day, which require long cycle life and heat dissipation generated during charge-discharge losses [63]. Buses that run using supercapacitor technology have been implemented by some countries like Germany, France and China.

- (ii) Memory back-up: Supercapacitors are incorporated into computers, mobile phones and other electronic applications that require memory protection, where even a brief interruption of power supply could cause loss of stored information [64]. They can act as back-up power supply for a short period of time in such applications. Batteries suffer from a limited lifetime and require regular replacement, which is not a problem with supercapacitors owing to their long lifetime.
- (iii) Battery improvement: Batteries are widely being used in portable power appliances such as UPS, laptops and mobile phones, which draw high-power pulsed currents instantaneously leading to reduction in battery performance and life. Combining supercapacitors with batteries are an effective alternative for such applications, which can relieve the battery of the severe load demands by providing the peak-power requirements [65]. This can result in a long-lifetime of the battery.
- (iv) Power quality: Power distribution line often suffers from voltage fluctuations, which is compensated by a static synchronous compensator system that absorbs or injects the additional power during fluctuations. The voltage perturbations are short-lived, not lasting more than 10 cycles [66]. Therefore such a system requires a DC energy storage device that can store and deliver energy in a short duration, which is a preferred choice for supercapacitors rather than batteries.
- (v) Renewable energy: Solar photovoltaic applications use batteries for their operation that need to be replaced every 3 years due to their continuous cycling. But supercapacitors can be continuously charged and discharged for a large number of cycles and requires replacement only every 20 years, which is equivalent to the life span of photovoltaic panels. Utilizing supercapacitors in such applications can reduce life cycle costs by eliminating frequent maintenance requirements [67]. Supercapacitors can also be used for adjusting the pitch of wind turbine blades for maximum utilization of wind speed for power generation. Pitch control of each of the wind turbine blades is required to ensure optimum positioning for efficient use of wind speed as well as to safe the blades from potentially damaging winds. This can be achieved electrically from the power source by supercapacitors.

(vi) Portable power supplies: Most portable electronic equipment having moderate energy demands use batteries as a power source and have long recharge time and need to be charged overnight. By replacing the batteries with supercapacitors, this problem could be overcome as supercapacitors exhibit fast charging-discharging rates.

1.6 Electrode materials for supercapacitors

Electrode materials play a significant role in the performance of supercapacitors. The surface area, structural uniformity and porosity of electrodes are important parameters to achieve high specific capacitance because these structural features govern the accessibility and diffusion rate of electrolyte ions into the bulk of the electrode [68]. Carbon is the commonly used electrode material for EDL capacitors, while metal oxides and conducting polymers are the mostly studied pseudocapacitive materials. The combination of carbon-based materials with metal oxides or conducting polymers leads to the formation of composite electrodes used in hybrid supercapacitors that utilize the advantages of individual components to enhance the device performance. The electrode materials used in all three types of supercapacitors are described in the following sub-sections.

1.6.1 Electrode materials for electric double layer capacitors

The electrode materials used for EDL capacitors are carbon-based materials due to their high specific surface area, high electrical conductivity, controlled pore size, low cost and multi-dimensionality from zero to three-dimension. These carbon-based materials can be produced in different structural forms such as sheets, tubes, ribbons, fibers, foams, quantum dots etc. [33]. The most explored carbon materials as EDL capacitor electrodes are discussed below:

1.6.1.1 Activated carbon

Activated carbons (ACs) are widely used as supercapacitor electrodes owing to their large specific surface area in the range of 500-2000 m²/g, good conductivity and relatively low cost. ACs exhibit high capacitive storage due to the presence of variable sized pores in their structure, namely micropores (< 2 nm), mesopores (2-50

nm) and macropores (> 50 nm) [69]. Such a porous structure is achieved by physical or chemical activation or both of carbonaceous organic precursors such as wood [70], coconut shells [71], rice husk [72], bamboo species [73] or of synthetic precursors such as polymers [74]. The pore size distribution and pore volume of these materials can be controlled by the process of activation. Physical activation is carried out at high temperatures of 1200 °C using oxidizing gases such as steam, CO₂ or air. Chemical activation refers to the treatment of amorphous carbons with activating agents such as alkalis, chlorides, carbonates or acids (KOH, H₃PO₄ etc.) at temperatures between 400-800 °C [75]. The specific capacitance achieved from ACs is in the range of 100 to 300 F/g in aqueous electrolytes [76, 77] and 50 to 150 F/g in organic electrolytes [78, 72]. In ionic liquid electrolyte, ACs were reported to achieve a specific capacitance of 187 F/g at room temperature, which increased to 196 F/g at a higher temperature of 60 °C [79]. However, the studies indicate that the specific capacitance of ACs does not increase linearly with the specific surface area, which is due to the low accessibility of the pores by the electrolyte ions. This occurs when the pore sizes are smaller than the size of the electrolyte ions limiting their diffusion into the pores [80]. Thus, large solvated ions could not be adsorbed in micropores as compared to that in mesopores, which becomes difficult with high charge-discharge rates. Therefore, in addition to surface area, pore size strongly influences the capacitive performance of ACs in EDL capacitors and has to be optimized according to the size of the electrolyte ions for enhanced charge storage.

1.6.1.2 Carbon aerogel

Apart from tunable porous ACs, carbon aerogels have also gained interest as EDLC electrodes due to their high specific surface area ranging from 400-1000 m²/g and good electrical conductivity of 25-100 S/cm. They are three-dimensional porous materials composed of interconnected carbon nanoparticles of size around 3-30 nm and pore size usually less than 50 nm [81]. They do not require an additional binder for electrode preparation and can self-bind to the current collector, which increase their applicability as electrodes [82]. Carbon aerogels can be produced in different forms such as monoliths, powders, thin films, composites or microspheres. They are usually synthesized by the method of sol-gel or pyrolysis, which produces carbon aerogels with good electrical conductivity as compared to that of the insulating

organic and inorganic aerogels [83]. The microstructure and properties of carbon aerogels can be controlled by varying the molar ratios of the starting precursor material giving rise to aerogels of different densities [84]. Higher density aerogels consist of more interlinked particles with high surface areas, which can provide high volumetric capacitance in energy storage devices. The specific capacitance achieved for carbon aerogels is in the range of 60 to 150 F/g [85, 86].

1.6.1.3 Carbon nanotubes

With the discovery of carbon nanotubes by Iijima in 1991 [87], carbon nanotubes (CNT) have developed as promising electrode materials for EDL capacitors due to their excellent properties like high electrical conductivity, large surface area, good mechanical and thermal stability and hollow structure with unique porosity that allows easy transport of ions [88]. CNT are categorized into two types, namely single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) [89]. SWCNT are formed by rolling a single sheet of sp^2 bonded graphite layer into a cylindrical tube, while MWCNT consists of several concentric graphite sheets rolled cylindrically. The cylindrical hollow tubes having large porous canals provide CNT with high surface areas of 100-400 m^2/g and high porosity [90]. Hence, high specific capacitance and charge-discharge rates than that of ACs could be achieved with CNT by properly adjusting the porosity and conductivity. Capacitance values in the range of 80-140 F/g have been reported using SWCNT and MWCNT, respectively [91, 92]. However, the high production cost of CNT has limited their commercial application, which stimulated further research to improve the electrochemical performance of CNT. According to reports, aligned CNT are found to be more advantageous as compared to entangled CNT for high-power performance [93]. Reports suggest that CNT directly grown onto conductive substrates eliminate the need of a binding agent and the contact resistance of the electrode is minimized thereby simplifying the electrode fabrication and improving the specific capacitance [94]. Lu et al. prepared vertically aligned CNT for supercapacitor electrodes, which exhibited a specific capacitance and power density of 440 F/g and 6.3 kW/kg in an ionic liquid [EMIM][Tf₂N] electrolyte [95]. Many research efforts have been focused on the development of composite materials of CNT with different pseudocapacitive materials to improve the specific capacitance

and energy density. Xu and co-workers synthesized PPy-CNT nanocomposites and demonstrated an increase in specific capacitance from 224 F/g to 350 F/g with an increase in CNT concentration from 30 wt% to 49 wt% [96]. Nanocomposite electrode of RuO₂-SWCNT has been printed on various substrates by ink injection method, which displayed a specific capacitance of 138 F/g and an energy density of 18 Wh/kg in PVA-H₃PO₄ solid gel-polymer electrolyte [97]. Considerable efforts have also been carried out to increase the specific surface area and wettability of CNT by surface treatment such as introducing functional groups, creating surface defects or chemical activation for improved electrode-electrolyte reactivity [98, 99].

1.6.1.4 Graphene

Graphene, a two-dimensional monolayer sheet of sp² bonded carbon atoms has recently attracted tremendous attention as novel supercapacitor electrodes among the scientific and engineering communities. The one-atomic thick 2D sheet of carbon packed in a hexagonal lattice was a ground-breaking discovery of Geim and Novoselov in 2004 by mechanical exfoliation of a single layer of graphite by ‘scotch-tape’ method for which they were awarded the Nobel Prize in Physics in 2010 [100]. Graphene is a planar monolayer of carbon atoms as shown in Figure 1.9 with a carbon-carbon bond length of 0.142 nm. It is the basic building block of carbon materials starting from which all other dimensional structures such as 3D graphite, 2D CNT and 0D fullerene can be produced by stacking, rolling and wrapping a graphene nanosheet, respectively [9].

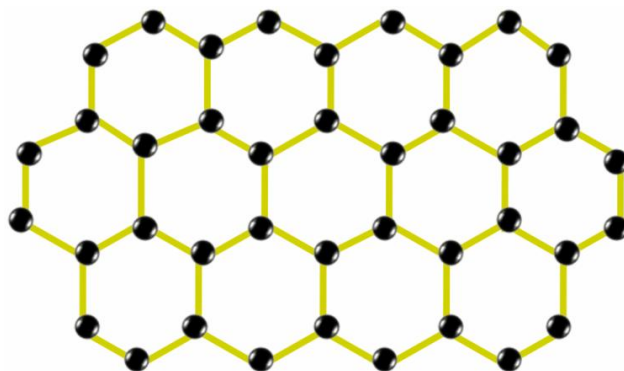


Figure 1.9: Graphene: a two-dimensional monolayer sheet of carbon.

Graphene exhibits remarkable properties such as high theoretical surface area of 2630 m²/g, outstanding electrical conductivity of 6000 S/cm, electron mobility of

200,000 cm²/V s at room temperature, superior thermal conductivity of 5300 W/mK and high Young's modulus of 1 TPa [101]. Graphene is a zero band-gap material with an overlap of the valence and conduction band and the charge carriers behave as massless relativistic particles giving rise to a host of interesting properties such as anomalous quantum Hall effect [102]. To exploit these properties for energy storage applications, various synthesis routes have been developed to prepare graphene and its derivatives that include mechanical cleavage of graphite [100], unzipping of CNT [103], chemical vapor deposition (CVD) [104], epitaxial growth on SiC [105] and chemical exfoliation of graphite [106]. Graphene obtained by mechanical exfoliation and CVD method is of high quality, but the yield is very low. In particular, chemical exfoliation of graphite is considered as a desirable alternative for large-scale production of graphene. In this method, graphite is first oxidized according to Hummers' method or the modified Hummers' method to graphite oxide followed by exfoliation in suitable solvents to obtain a stable suspension of few layered sheets termed as graphene oxide (GO) [107]. Then, reduction of GO is performed using different reducing agents such as hydrazine hydrate [108], sodium borohydride [109], vitamin C [110], hydroiodic acid [111] etc. to produce reduced graphene oxide (RGO). RGO is chemically derived bi-layered or multi-layered graphene, which consists of many oxygen functionalities in its structure that provide opportunities for tuning its electrical and optical properties [112]. The very large electrochemically active surface of RGO with functional groups and flexibility makes it a suitable candidate for energy storage and can greatly influence the electrochemical performance.

The applicability of RGO as electrodes was first reported by Ruoff et al. in 2008, which delivered a specific capacitance of 135 F/g in aqueous electrolyte and 99 F/g in organic electrolyte, respectively [113]. However, the experimentally obtained specific capacitance and surface area of RGO was much lower in comparison to the large theoretical surface area. RGO prepared by hydrothermal method also exhibited a very low surface area and specific capacitance of 14.9 m²/g and 66 F/g, respectively in aqueous electrolyte [114]. This is due to the restacking or agglomeration of RGO sheets after chemical reduction owing to the van der Waals interaction (≈ 5.9 kJ/mol) between them leading to reduced surface area, which significantly hampers their application as electrodes. To prevent the re-stacking of RGO sheets as well as to exploit its unique properties, different materials like

conducting polymers [115], metal oxides [116], metals [117] etc. have been hybridized with RGO or GO sheets to form nanocomposites, which act as effective spacers between the sheets. The advantage with GO is that it is hydrophilic due to the presence of polar oxygen functionalities like epoxide, hydroxyl, carboxylic and carbonyl groups in its basal planes and edges, which improves its dispersion in various solvents including water and eases its processability [118]. Till date, RGO based nanocomposites have been extensively explored for supercapacitor applications and have demonstrated improved electrochemical performance. For integration of RGO with conducting polymers, *in situ* reduction or polymerization has been carried out to prevent the self-aggregation or re-stacking of RGO sheets due to the presence of polymer in the solution [119]. The negatively charged oxygen functional groups present in RGO can bind with conducting polymers that carry a positive charge via electrostatic force and a stable dispersion with well separated RGO sheets could be obtained [27]. Moreover, RGO can significantly improve the conductivity of the nanocomposite, which is beneficial for superior electrochemical performance. Wu and co-workers prepared a RuO₂-graphene nanocomposite, where the graphene sheets were prevented from agglomeration by RuO₂ nanoparticles that were attached on the sheets through the oxygen functional groups. The composite exhibited a specific capacitance of 570 F/g and high cyclic stability of 97% after 1000 cycles along with an energy density of 20 Wh/kg [120]. Wang et al. fabricated graphene/polyaniline composite by *in situ* polymerization of aniline monomer on graphene-silica substrate, which exhibited a specific capacitance of 749 F/g at a current density of 0.5 A/g and 88% capacitive retention after 1000 cycles [121]. A graphene/PPy nanotube aerogel has been synthesized by self-assembly of GO and PPy nanotubes to obtain a stable and homogeneous dispersion followed by reduction, where the nanotubes act as spacers to prevent the re-stacking of graphene sheets. This hybrid nanocomposite electrode displayed a specific capacitance of 253 F/g at a current density of 0.5 A/g and impressive cyclic stability of 93% after 2000 cycles [122].

1.6.2 Electrode materials for pseudocapacitors

The materials that can undergo fast and reversible redox reactions with a subsequent conversion in its oxidation state store charge by pseudocapacitive mechanism. The

specific capacitance exhibited by these materials is greater than that of EDLCs because they can store charge not only in the electric double layers, but also by faradaic charge transfer reactions on the electrode surface. Generally, the most widely studied pseudocapacitive materials are transition metal oxides and conducting polymers.

1.6.2.1 Transition metal oxides

Transition metal oxides (TMOs) are promising pseudocapacitive electrode materials owing to their high specific capacitance and good electrochemical reversibility. TMOs exhibit variable oxidation states and have the ability to convert between different oxidation states with the insertion/extraction of cations from/to the electrolyte during reduction and oxidation [123]. These charge transfer reactions are fast and reversible, which gives rise to pseudocapacitance. There are different types of TMOs that have been investigated for supercapacitor electrodes such as RuO₂, MnO₂, NiO, SnO₂, V₂O₅, Co₃O₄ etc. out of which RuO₂ and MnO₂ are the extensively studied ones [124]. RuO₂ shows the highest specific capacitance among all metal oxides along with a high conductivity, long cycle life and high charge-discharge rates. It exhibits three oxidation states within a potential window of 1.2 V, where ruthenium switches between different oxidation states via multiple redox reactions during charging and discharging [125]. Its redox reactions in an acidic medium can be represented as:



High specific capacitances in the range of 500-900 F/g have been reported using hydrous RuO₂ based electrodes [126, 127]. However, the application of RuO₂ based electrode materials is minimized by their high cost, low availability, toxicity and limited operating voltage window (1 V). To address this problem, several attempts have been made for combining RuO₂ with low cost materials like CNT [128], SnO₂ [129], TiO₂ [130], Co₃O₄ [131] etc. without compromising the electrochemical performance. Instead, supercapacitors based on other metal oxides such as MnO₂ [132], NiO [133], Fe₂O₃ [134], V₂O₅ [135] etc. have been currently studied as alternatives to RuO₂ due to their low cost, less toxicity, high redox activity and environmental safety. However, some drawbacks still exist with these

pseudocapacitors like low conductivity, aggregation and poor structural reversibility with increasing number of cycles. Therefore, recent research has been focused on the incorporation of different conductive fillers within these metal oxides to improve their dispersion, electronic conductivity and cyclability [136, 137].

1.6.2.2 Conducting polymers

The high manufacturing cost and poor cyclic performance of other pseudocapacitive materials have attracted research interests on conducting polymers for supercapacitor electrodes. Conducting polymers (CPs) are attractive class of materials owing to its low cost, high specific capacitance and energy density, high conductivity in doped state, lightweight and easy processability [42]. The widely investigated CPs for supercapacitor electrodes are polypyrrole (PPy), polyaniline (PAni), poly(3,4-ethylene dioxythiophene) (PEDOT), polythiophene (PTh) and their derivatives [138]. The chemical structures of some significant CPs are presented in Figure 1.10. Compared to carbon-based electrodes, CPs can deliver higher specific capacitance by storing charge via ion adsorption as well as rapid faradaic redox reactions on the electrode surface or in the bulk near the surface. Conducting polymers can work well only within a suitable operating voltage window, beyond which they may degrade due to higher potential or may lose their conductivity at extremely lower potential [139]. Selecting a suitable electrolyte is also an important criterion for conducting polymers, for e.g., the performance of PAni is better in an acidic electrolyte due to the involvement of H^+ ions in the redox conversion of imine groups in PAni [140]. However, their repeated redox reactions cause mechanical stress (e.g., swelling and shrinkage) in the polymer structure, which degrades their performance with increasing number of cycles resulting in a short cycle life [24]. The cycle life of conducting polymers is therefore much lower than that of carbon-based electrodes, which is a major drawback in the development of CP based supercapacitors. Nanocomposites of CPs with carbon-based materials provides a promising approach to increase the cycle life, where the carbonaceous materials with high surface-area and flexibility can adapt to the volume change of CPs during redox reactions avoiding the cracks as well as can enhance the capacitive performance [138].

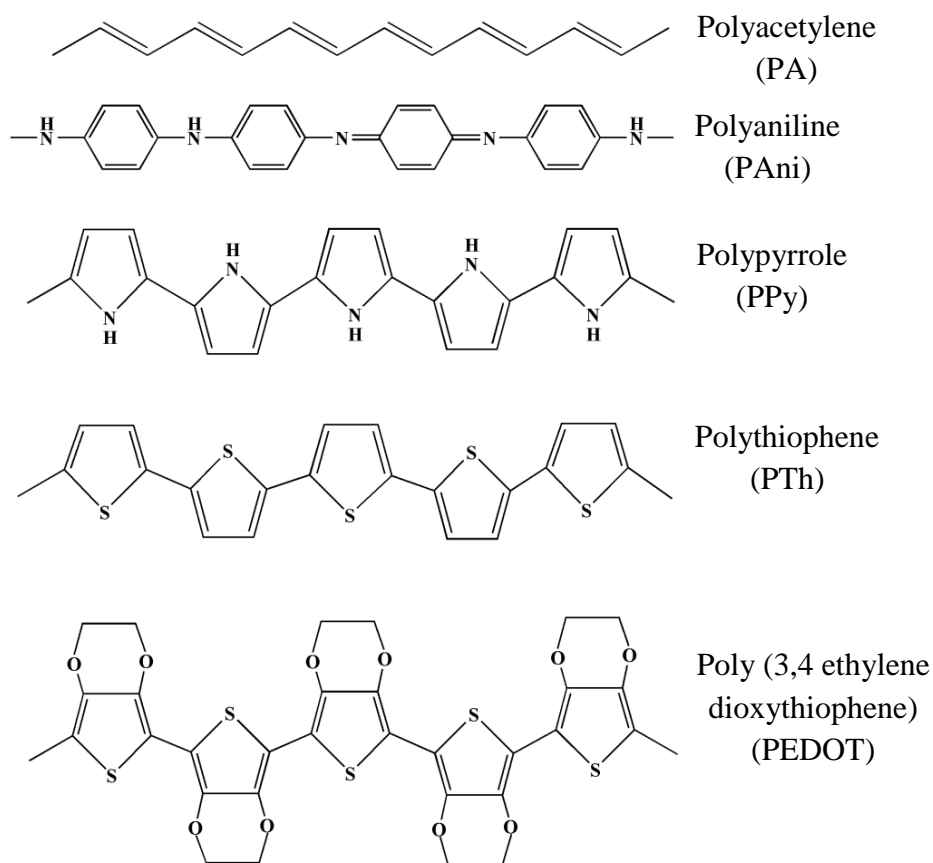
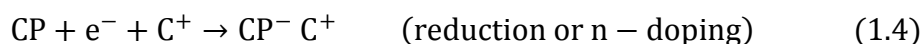
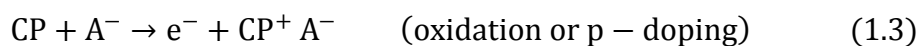


Figure 1.10: Chemical structures of some significant conducting polymers.

1.6.2.2.1 Electrochemical charge storage mechanism of conducting polymers

The redox reactions in conducting polymers imply the change in the number of electrons in its backbone with the simultaneous incorporation of cations and anions for charge neutrality, which is generally termed as doping and can be achieved either chemically or electrochemically. The redox reactions responsible for charge storage are described as electrochemical oxidation and electrochemical reduction and takes place in the presence of an electrolyte as depicted in equations (1.3) and (1.4), where A^- and C^+ are the electrolyte anion and cation, respectively [141].



When a positive potential is applied to CPs, the polymer chain loses an electron and an anion goes into the electrode from the electrolyte to neutralize it. Thus an anionic doping occurs and the polymer gets oxidized, which is referred to as p-doping.

Subsequent reduction of the polymer takes place by the addition of an electron and the release of the anion back into the electrolyte, which is termed as p-dedoping [142]. N-doping of CPs takes place by addition of an electron to the polymer chain and incorporation of a cation from the electrolyte for charge neutralization. The polymer gets reduced in the process. The oxidation process occurs by the reverse of this mechanism and is named as n-dedoping. All CPs are highly conducting in the doped states and exhibit fast and reversible redox processes [143]. The mechanisms of p-doping and n-doping of CPs are schematically shown in Figure 1.11.

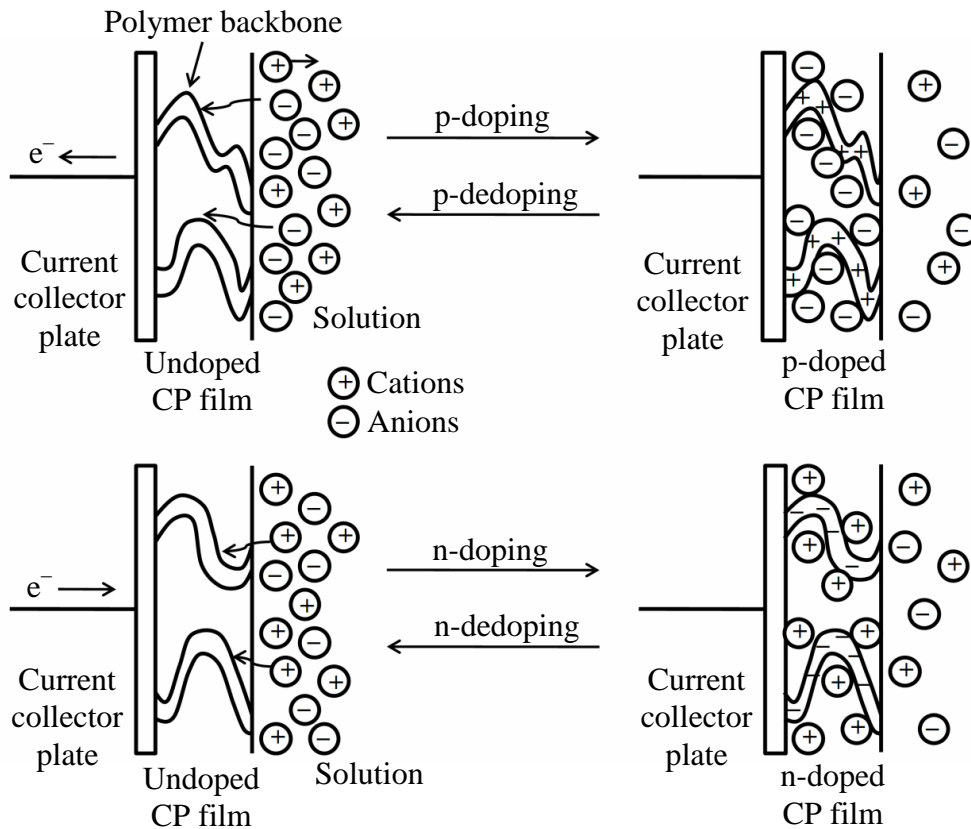


Figure 1.11: Schematic representation of p-doping and n-doping of conducting polymers.

Based on the two different types of doping, conducting polymers can be classified into p-type (positively charged) and n-type (negatively charged) polymers. Therefore, CP based pseudocapacitors can be fabricated in three different configurations on the basis of symmetric and asymmetric electrodes [144]:

- (i) Type I supercapacitor (symmetric): Here both the electrodes used are p-type CPs. Oxidation of the electrode will lead to a positively charged polymer

structure and reduction will neutralize the polymer chain. When fully charged, one electrode will be in fully p-doped state while the other will be in un-doped state. Upon discharge, the un-doped polymer will be oxidized to the doped state and the doped one will get reduced until both the electrodes are half doped such that the cell voltage becomes zero. Hence half of the fully doped charge is released on discharge.

- (ii) Type II supercapacitor (asymmetric): Here, both the electrodes used are p-type CPs, but of different materials with different ranges of oxidation and reduction potentials. A wide potential window is therefore achieved, which enhances the energy density of the supercapacitor.
- (iii) Type III supercapacitor (asymmetric): This type of supercapacitor is formed by using a p-type CP as the positive electrode and n-type CP as the negative electrode. When charged, one electrode will be fully p-doped and the other will be fully n-doped. On discharge, both the electrodes will return to their un-doped states. This configuration offers a wide range of operating voltages and high energy and power performance.

The energy density of type I and type II CP pseudocapacitors are not limited by the electrolyte concentration because the salt concentration of the electrolyte does not change during oxidation and reduction. Their maximum energy density is mainly limited by the specific capacitance and the operating voltage window. However, for type III CP pseudocapacitors, the salt concentration of the electrolyte changes during charging and discharging and therefore their energy density also depends on the electrolyte concentration. There are many CPs that can be p-doped and dedoped at electrode potentials within the range of stability of most aqueous electrolytes. However, n-dopable CPs are limited due to the low stability of aqueous electrolytes at highly negative reducing potentials. Therefore, considerable research has been focused on the use of p-dopable CPs as electrodes such as PPy, PANi etc [145].

1.6.2.2.2 Historical background and conduction mechanism

Polymers have long been known as heat sensitive, flexible and electrically insulating materials. A polymer also termed as macromolecule is a large molecule consisting of multiple repetitive units of low molecular masses known as monomers [146]. The concept of insulating behavior of conducting polymers was first shattered in 1977

with the unexpected discovery of a new class of polymers that can exhibit conducting properties. A breakthrough was established by Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa when they discovered an increase in conductivity of polyacetylene upto nine order by iodine doping [147]. This landmark discovery that changed the original idea of insulating π -conjugated polyacetylene earned Heeger, MacDiarmid and Shirakawa the Nobel Prize in Chemistry in the year 2000. It was all started with Shirakawa and co-workers in 1974 when they prepared polyacetylene from acetylene using Ziegler-Natta catalyst and obtained as a silver film instead of a black powder [148]. Though the film produced a metallic lustre, it did not conduct electricity. However, later in 1977, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered that the conductivity of polyacetylene films could be increased by 10^9 times than that of its original state by oxidizing with chlorine, bromine or iodine vapour, which provided the concept of doping conducting polymers to increase the conductivity for the first time. Though the doping effect of CPs was discovered lately, CPs such as PPy, PANi etc. were polymerized successfully by chemical and electrochemical routes in the early 19th century. PPy was first polymerized in 1963 by Weiss and co-workers by the pyrolysis of tetraiodopyrrole in an inert atmosphere at temperatures of 120-700 °C [149]. Similarly, PANi was synthesized for the first time by Dr. Henry Letheby in 1862 when he obtained a dark green precipitate upon electrochemical oxidation of aniline in H₂SO₄ solution [150]. The classification of PANi into four different redox states was reported for the first time at the start of the 20th century. The four redox states of PANi were designated as leucoemeraldine, emeraldine, nigraniline and pernigraniline, which are presented in Figure 1.12. However, it was in the mid of 1980s owing to the investigations of MacDiarmid et al. [151] that led to the discovery of electrical conductivity of PANi in its emeraldine salt form. Among the four states of PANi, leucoemeraldine is the completely reduced structure of PANi and pernigraniline is the completely oxidized form. The emeraldine form is the half oxidized or half reduced state and nigraniline is another intermediate state of PANi. Out of all the redox states of PANi, the emeraldine salt form is only electrically conducting while all other forms are insulating. Hence, a number of conducting polymers including PPy, PANi and PTh were reported soon after the discovery of polyacetylene.

Conventional polymers such as plastics are excellent insulators because of their saturated macromolecule consisting of sp^3 bonded carbon atoms where all the valence electrons are involved in σ (sigma) bonds. In contrast to ordinary polymers, the polymer backbone in conducting polymers has conjugated double bonds i.e. the carbon atoms are bonded alternately by single and double bonds. The carbon atoms throughout the backbone are sp^2 hybridized, where every bond contains a strong σ (sigma) bond and every double bond contains a delocalized pi bond [152]. This delocalization of pi bonded electrons along the polymer backbone is responsible for the special electrical properties of conducting polymers [153]. However, conjugation is not sufficient for making a polymer conducting and most polymers are insulating or semi-conducting in their pure form. Additional charge carriers in the form of electrons or holes need to be introduced within the polymer chain by doping to increase its conductivity [154].

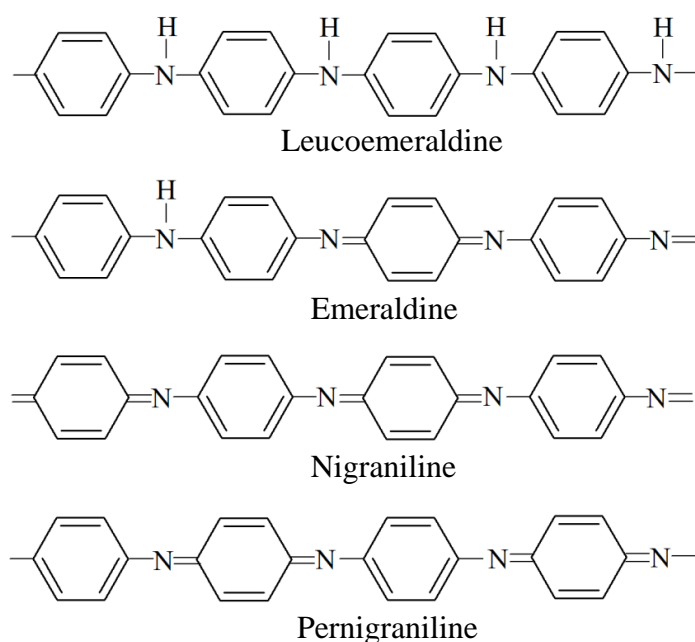


Figure 1.12: The four different redox states of polyaniline.

By doping, the conductivity of CPs can be raised to the metallic regime in the order of 10^5 S/cm. The band gap of conducting polymers is typically in the range of 1-3 eV. The doping process in CPs is reversible and the polymer chain can be made neutral by the reverse process of dedoping [155]. Unlike the doping process in semiconductors, the dopant here does not substitute the host atoms but occupy the interstitial positions within the polymer chain. Through the doping process, electrons

are injected into the polymer chain by reduction (n-doping) or removed by oxidation (p-doping). This generates charge carriers like polarons, bipolarons and solitons within the polymer chain, which promotes the electrical conductivity of CPs by several orders [156]. Upon oxidation of CP, an electron is removed from the polymer chain which produces a radical cation termed as polaron. The polaron has a spin of $\frac{1}{2}$ and is localized partly due to Coulomb attraction to its counterion. On further oxidation of the polymer chain, another polaron can be created or if the electron is removed from the same oxidized part of the chain, a bipolaron with a spin of zero is formed [157]. The mobility of polarons and bipolarons along the polymer chain could be very high in the presence of a high concentration of counterions, which offers high conductivity to CPs. Another charge carrier responsible for the conductivity of CPs is soliton, which is created in CPs having degenerate ground state structures. Solitons are isolated, non-interacting charged defects of two different phases having opposite orientation but identical energy that are separated by domain walls and have localized energy states that overlap at higher doping level to form soliton bands [158]. The formation of polaron, bipolaron and soliton in trans-polyacetylene is displayed in Figure 1.13.

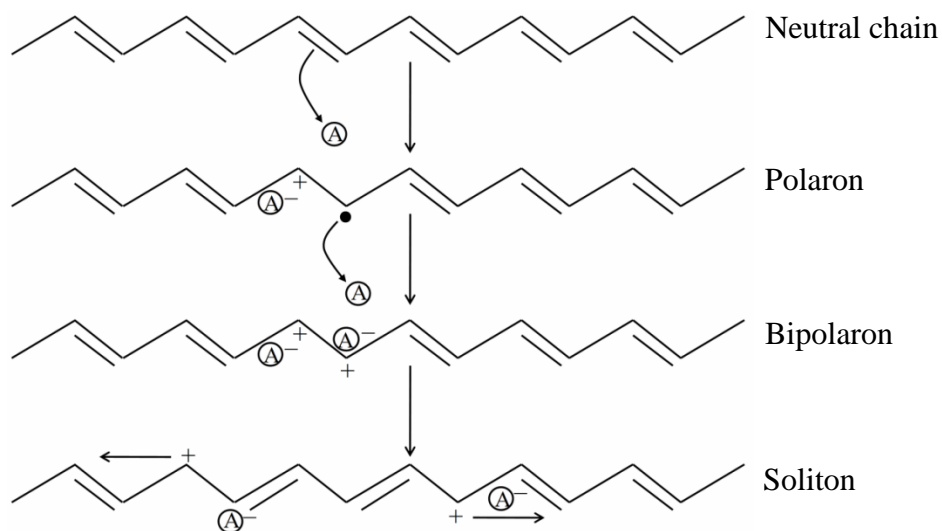


Figure 1.13: Formation of polaron, bipolaron and soliton in trans-polyacetylene.

1.6.2.2.3 Conducting polymer nanostructures

Since the discovery of conducting polymers, extensive research has been carried out on nanostructured conducting polymers for energy storage applications owing to

their high specific surface area, short pathlengths for charge transport, reduced weight, low toxicity, flexibility and excellent processability [159, 160]. Conducting polymer nanostructures of different morphologies such as nanoparticles, nanotubes, nanofibers, nanospheres etc. have been synthesized and investigated for supercapacitor electrode materials. The nanoscale design of CP electrodes offer advantageous properties like (i) increased electrochemical activity, (ii) shortened pathlengths for effective charge transport, and (iii) flexibility to adapt to the mechanical stress developed within electrodes by faradaic redox reactions [143]. Particularly, 1D CP nanostructures have received special attention for charge storage applications due to their high aspect ratio and efficient charge transport along one controllable direction. The well exposed surface of 1D CP nanostructures is beneficial for increased electrochemical activity and short and direct pathways for charge transportation and ion diffusion. A variety of 1D nanostructures (nanowires, nanorods, nanotubes) have been synthesized using different template assisted approaches like hard template method, soft template method, reactive self-degrade template method etc. and achieved with improved capacitive performance [161].

1.6.3 Nanocomposite electrodes for hybrid capacitors

The pseudocapacitive electrode materials including conducting polymers and transition metal oxides have the ability to store large amount of charges by faradaic redox reactions on the electrode surface and exhibit high capacitance and energy density. However, they suffer from the drawback of low conductivity and poor cyclic stability due to repeated redox reactions leading to easily damaged structure [24]. The EDLC electrodes based on carbon materials such as activated carbon, carbon nanotubes, graphene etc. have excellent cyclic stability and power performance since no chemical changes are involved in their charge-discharge processes. However, they are characterised by a low specific capacitance and energy density [162]. To improve the performance of supercapacitor electrodes, EDLC materials have been coupled with pseudocapacitive materials with an aim to combine both faradaic and non-faradaic charge storage mechanisms, which gives rise to hybrid capacitors [43]. The controlled incorporation of carbon materials within transition metal oxides or conducting polymers can produce a synergistic effect in the nanocomposite electrode, where charges are stored both by electrostatic charge separation and

faradaic charge transfer reactions. Therefore nanocomposite electrodes can offer much higher specific capacitance and energy density than that of the individual components. The carbon materials can provide efficient supporting backbone, high conductivity and improved cyclic stability, while pseudocapacitive materials can promote the capacitance and energy density through rapid and reversible redox reactions [40]. Recently, considerable efforts have been made to fabricate novel hybrid nanocomposite electrodes for supercapacitors to achieve improved electrochemical performance. The widely explored nanocomposites are carbon materials combined with transition metal oxides or conducting polymers.

1.6.3.1 Carbon based transition metal oxide nanocomposites

Carbon materials with high conductivity and mechanical strength have been used as a secondary component within transition metal oxides to obtain electrodes with improved conductivity, higher energy density, better cyclic stability and low cost. Therefore different carbonaceous materials incorporated into a variety of transition metal oxides such as MnO_2 , V_2O_5 , Co_3O_4 , RuO_2 , Fe_2O_3 , NiO etc. to form hybrid nanocomposite structures have been developed, where each component provides different properties such that a synergistic effect is achieved in the resulting nanocomposite and the electrochemical performance is enhanced. Wang et al. synthesized nanocomposites of MnO_2 nanoparticles and carbon nanotubes that exhibited an energy density of 16 Wh/kg at a high power density of 45 kW/kg [163]. A specific capacitance of 318 F/g with a cyclic stability of 81% over 2000 cycles was achieved, when RGO was combined with Fe_2O_3 nanoparticles [164]. Activated carbon incorporated NiO hybrid nanocomposites reported by Lee et al. resulted in a specific capacitance of 624 F/g, which was about 530% increase of the capacitance obtained from pure activated carbon [165]. Fabrication of nanocomposites of MnO_2 and porous carbon nanofibers demonstrated an improved specific capacitance of 313 F/g at a current density of 0.5 A/g than that of pure MnO_2 [166]. V_2O_5 -RGO hybrid nanostructures showed a higher specific capacitance of 484 F/g at a current density of 0.5 A/g as compared to that of pure V_2O_5 (314 F/g) and RGO (69 F/g) [167]. Incorporation of RGO into MnO_2 by Zhao et al. resulted in a specific capacitance of 326 F/g, which is higher than 201 F/g of that of pure MnO_2 at a current density of 0.2 A/g [168]. Hybrid nanocomposites of NiO and graphene have been prepared by

hydrothermal synthesis followed by microwave irradiation of the synthesis product, which showed a higher specific capacitance of 617 F/g as compared to 265 F/g of that of graphene at a current density of 1 A/g [169]. For carbon nanotubes combined with NiO, a maximum specific capacitance of 328 F/g is obtained at a current density of 0.33 A/g [170].

1.6.3.2 Carbon based conducting polymer nanocomposites

Significant research has been focused on integrating carbonaceous materials within conducting polymers as supercapacitor electrodes to improve their cyclability and power density. Till date, carbon materials of different forms such as activated carbon, carbon aerogels, carbon nanotubes, graphene etc. have been coupled with a variety of conducting polymers such as PPy, PANi, PEDOT to form nanocomposite electrodes. Carbon nanotube incorporated PPy nanowire nanocomposite electrodes have been fabricated by *in situ* polymerization and a specific capacitance of 183 F g⁻¹ have been achieved at a current density of 8 A g⁻¹ compared to 80 F/g of that of pristine PPy nanowire [171]. Activated carbons coated with PANi display a higher specific capacitance of 382 F/g than that of 121 F/g for pure activated carbons at a current density of 1 A/g [172]. Sun and co-workers synthesized graphene/PEDOT nanocomposites and characterized for supercapacitor electrodes, which showed a specific capacitance and energy density of 270 F/g and 34 Wh/kg at a current density of 1 A/g. Moreover, they achieved a power density of 25 kW/kg for the hybrid nanocomposite along with a capacitive retention of 93% after 10,000 cycles [173]. When tubular PPy was incorporated into activated carbon, a two-fold increase in the specific capacitance (82 F/g) of the nanocomposite was obtained as compared to that of pure AC (43 F/g) [174]. Similarly, a specific capacitance of 385 F/g was obtained for electrospun PANi/carbon nanotube electrodes at a current density of 0.5 A/g, whereas PANi showed a lower specific capacitance of 308 F/g. Moreover, the cyclic stability of the nanocomposite increased to 81% compared to 70% of that of PANi after 1000 cycles [175]. Supercapacitor electrodes based on PPy/carbon aerogel nanocomposites prepared by oxidative polymerization exhibited a specific capacitance of 433 F/g, while the capacitance of carbon aerogel obtained was only 174 F/g [176]. Incorporation of carbon nanoparticles into PANi by Wang et al. leads to a specific capacitance of 342 F/g at a current density of 0.5 A/g with an excellent

cyclic stability [177]. PPy/graphene hybrid aerogels have been fabricated by self-assembly of holey graphene nanosheets and PPy nanoparticles. The nanocomposite exhibited an improved specific capacitance of 418 F/g than that of the individual components and a cyclic stability of 74% over 2000 cycles [178]. Nanocomposites of tubular PANi and graphene oxide results in a specific capacitance of 475 F/g at a current density of 0.1 A/g, which is higher than that of pure PANi (438 F/g) and graphene oxide (388 F/g) [179]. Carbon quantum dots reinforced PPy nanowire reported by Jian et al. has reached a specific capacitance of 306 F/g at a current density of 0.5 A/g with 66% capacitance retention when the current density was increased to 40 A/g [180].

1.7 Electrolytes for supercapacitors

In addition to electrode materials, the electrolyte plays an important role in the performance of a supercapacitor electrode. An electrolyte is the media that provide ions for adsorption process or faradaic charge transfer processes across the electrode-electrolyte interface in supercapacitors. The mobility of ions between the electrodes during charge-discharge processes in a supercapacitor depends on the nature of the electrolyte. The ion-type and size, diffusion of electrolyte ions into the electrode and the electrode wettability by the electrolyte are important factors that determine the electrode-electrolyte interface resistance and affect the electrochemical performance [44]. The properties required for an ideal electrolyte are low resistivity, high ionic concentration, wide potential window, low viscosity, high electrochemical stability, low cost and toxicity [181]. The ionic conductivity of an electrolyte is highly dependent on the concentration of free charge carriers and the ionic mobility that is determined by the ability of the salt to dissociate into cations and anions in the solvent. A variety of electrolytes have been widely used in supercapacitors that include aqueous electrolytes, organic electrolytes, ionic liquid electrolytes and solid-state polymer based electrolytes.

1.7.1 Aqueous electrolytes

Aqueous electrolytes are grouped into alkaline, acid and neutral solutions where the most commonly used are KOH, Na₂SO₄, H₂SO₄, Li₂SO₄ and KCl electrolytes, respectively [182-185]. Aqueous electrolytes are advantageous in terms of high ionic

conductivity, low viscosity, safety, good compatibility and low cost. Due to their high ionic conductivity, a high power output could be obtained employing aqueous electrolytes in supercapacitors [123]. The ionic radii of aqueous electrolytes are generally smaller and therefore they have comparatively lower minimum pore size requirements than most electrolytes. Due to their high ionic concentration, low viscosity and small ionic radii, aqueous electrolytes can easily diffuse into the pores of less than 1 nm and can promote the capacitive performance by improving the electrode-electrolyte contact. Moreover, the preparation and application of aqueous electrolytes do not require specific conditions as is the case for organic or ionic liquid electrolytes. The only limitation with aqueous electrolytes is their small operating potential window of 1 V due to the thermodynamic decomposition of water [186]. Various efforts have been carried out to extend their voltage window and an increase of 1.8-2.2 V could be achieved [182-184]. There are numerous reports of obtaining high power densities along with good specific capacitance values using different aqueous electrolytes [182-185].

1.7.2 Organic electrolytes

Organic electrolytes have an advantage of wide potential window upto 2.7 V and higher, which allows supercapacitors to achieve high energy densities. Acetonitrile, propylene carbonate, dimethyl carbonate are some frequently used organic electrolytes for supercapacitors [187-189]. The melting points of most organic electrolytes are lower than room temperature, which allows their operation even at low temperatures. However, their high ionic resistance and viscosity lead to a low power output. Due to their high volatile and flammable nature, they are not suited for applications considering safety concerns. The industrial application of organic electrolytes is mainly limited by their expensive purification procedure from water, which is essential to achieve high voltage window without degrading the electrolyte. [28] Amongst the organic electrolytes, propylene carbonate is more environmentally safe with a wide operating voltage and temperature, and relatively good conductivity. In spite of their several advantages, a report by Kang et al/ has shown that the performance of organic electrolytes depends on temperature variations [190]. In case of electrodes with porous structure such as activated carbons, organic electrolytes are not beneficial as compared to that of aqueous electrolytes owing to

their large ionic size limiting their diffusion into the pores resulting in decreased electrochemical performance. Moreover, they undergo decomposition on the surface of activated carbons, which increases the equivalent series resistance as well as blocks the pores with decomposition products [191].

1.7.3 Ionic liquid electrolytes

Ionic liquids are pure organic salts with electrolyte properties such as high ionic conductivity, wide operating voltage, high thermal stability, low vapour pressure, non-volatile and poorly combustible [192]. These room temperature liquid solvent-free electrolytes comprise of a bulky asymmetric organic cation and a weakly coordinating inorganic/organic anion. They are considered as green solvents with a working potential window higher than 3 V, which is beneficial for obtaining high energy densities in supercapacitors [24]. The development of ionic liquids as supercapacitor electrolytes is still in the initial stage and further research is required to ensure their performance. Some of the reported ionic liquids for supercapacitors are pyrrolidinium and imidazolium based electrolytes [193, 194]. Due to their high thermal stability upto a wide temperature range, ionic liquid based electrolytes can be used for safe operation at higher temperatures. However, their low ionic conductivity and high viscosity at room temperature affect their performance [195]. The major challenges of ionic liquid based electrolytes for supercapacitor applications are maintaining its chemical stability, reducing the production cost and assuring proper wettability of the electrode by the ionic liquid.

1.7.4 Polymer electrolytes

Polymer electrolytes are solid-state electrolytes that have recently been studied in supercapacitors due to their low environmental hazards and less corrosion effects. They are a combination of an ionic conductor and a host polymer matrix and can serve both as an ionic conducting media and electrode separator. Polymer electrolytes are prepared by dispersing polymers such as polyethylene glycol, poly(methyl methacrylate), polyvinyl alcohol and polyvinyl pyrrolidone into a proton or lithium conducting medium like, H_3PO_4 , H_2SO_4 or LiCl solution [196]. These electrolytes allow the fabrication of flexible, compact solid-state structures free from leaks. Considerable efforts have been devoted to the development of all-

solid-state flexible supercapacitors in different structural forms like paper, fiber, cotton, film, fabrics etc. employing polymer electrolytes [197]. However, they exhibit some disadvantages such as low ionic conductivity and poor ion diffusion rate leading to low rate capability [198].

1.8 Swift heavy ion irradiation of conducting polymers and their nanocomposites

Swift heavy ion (SHI) irradiation is a novel technique to modify the properties of materials in a controlled way at the electronic and molecular level. A wide range of SHI with different energies and fluences has been utilized by researchers to selectively tailor the structural, morphological, optical, electrical and sensing properties of materials for a variety of applications [199-201]. Ion irradiation in polymers can induce irreversible modifications like formation of new chemical bonds, intermolecular cross linking, chain scissioning or bond-breaking, fragmentation of molecules and formation of unsaturated groups that give rise to macroscopic changes in their properties [202]. The modifications are brought about by the different processes of energy loss of the incident ions passing through the material. The energy deposited by the impinging ions per unit length of the target material is referred to as the “Energy loss” or “Stopping power” and is written as dE/dx , where E is the energy and x is the path length. When ions traverse through a solid material, it loses energy by two independent processes during their passage [203] as described below:

- (i) Nuclear energy loss (S_n): When the incident ions lose their energy by elastic collisions with the nuclei of the target material leading to atomic displacement, it is known as nuclear energy loss. The displacement occurs as soon as the energy transferred by the colliding particle is greater than certain displacement threshold energy (E_d) of the target atom. Ions with energy typically of few tens of keV/amu undergo nuclear energy loss [204]. It is derived by taking into consideration the momentum transferred from the incident ion to the target atom and the inner atomic potential between the charged ion and the target atom.
- (ii) Electronic energy loss (S_e): In electronic energy loss, the penetrating ions lose their energy by inelastic collisions with the atoms leading to electronic excitation and ionization. This energy loss is dominant at high energies of 1

MeV/nucleon or more, where the velocity of the impinging heavy ions becomes equal to or greater than the velocity of the Bohr electron [200]. Electronic energy loss takes place by two mechanisms. One mechanism is glancing collision, which arises by distant resonant collisions with small momentum transfer and low energy loss (< 100 eV) and the other one is knock-on collision where close collisions occur with large momentum transfer and high energy loss (> 100 eV) [205]. In both the collisions, the energy is transferred through excitation and ionization of the electronic subsystem. While glancing collisions are quite frequent, knock-on collisions are very infrequent. For films sufficiently thin than that of the stopping range of the incident ions, the electronic energy deposition is reasonably uniform throughout the film thickness.

The magnitudes of both the electronic and nuclear energy losses are decided by the incident ion mass and its energy. Heavy ions with energies so high that move at a velocity comparable to the Bohr velocity of the electron are referred to as swift heavy ions (SHI) [203]. For swift heavy ions, the electronic energy loss is dominant, where elastic collisions are insignificant and the energy is transferred mainly through excitation and ionization of atoms of the target material. Materials modification by low energy ions (tens of keV to a few MeV) occurs through ion beam assisted deposition, implantation, doping and new phase formation, where the incident ions get embedded in the material and cause modification due to the collision cascade produced by the elastic collisions. Whereas in SHI irradiation (few tens of MeV and higher), the ions do not get implanted and pass through the film owing to their large range (few tens of μm or more), where the modifications are caused by electronic energy deposition in the material during their passage [204].

Swift heavy ion irradiation of conducting polymers has been reported to undergo significant effects like chain scissioning, cross-linking, molecular fragmentation and formation of new chemical bonds with stimulated emission of gases that lead to different changes in their properties like density, conductivity, porosity, crystallinity, solubility etc. [206, 207]. These changes are governed by the parameters of ion beam like mass, energy and fluence and the target material parameters such as molecular weight, composition and melting temperature. Several works suggest the change in surface morphology of materials induced by SHI irradiation [199, 208]. With a high electronic energy loss of about $1\text{-}10$ keV/Å, SHI becomes a unique tool over other methods for producing exotic and diverse effects in

the target material such as defect annealing, cluster of point defects, carbonization and formation of ion tracks. PPy films irradiated with 100 MeV O^{7+} SHI showed improved crystallinity and reduced band gap [209]. 100 MeV oxygen ion irradiation on nanocomposites of PAni/single walled carbon nanotube has been reported to decrease the surface roughness of the nanocomposite films [210]. Madau et al. reported the formation of nanopores in graphene/polymer composite membranes upon irradiation with 1.1 GeV Au and 1.5 GeV U ions [211]. Nanochannels were created in poly(vinylidene fluoride-co-hexafluoro propylene) nanohybrid thin films by controlled variation of SHI fluence which improved its performance towards fuel cell applications [212]. In nanocomposites of PEDOT:PSS/nanographite, SHI irradiation results in homogeneous dispersion of nanographite fillers in PEDOT:PSS matrix giving rise to improved conductivity and sensing response of the irradiated nanocomposites [213]. For poly(methyl methacrylate) (PMMA) thin films, 2 MeV H ion irradiation leads to smoothening of the film surface, while development of porosity along with surface roughening was observed when the films were subjected to 2.1 GeV Bi and 17 MeV Au ions irradiation [207].

1.9 Scope of the thesis and statement of thesis problem

The supply of clean and sustainable energy is one of the most important scientific and technical challenges facing humanity in the 21st century. The growing demand for power generation, hybrid electric vehicles and portable electronic devices and the increasing threat of global warming due to extensive use of fossil fuels has raised unprecedented requirements for clean, sustainable and secured renewable energy sources. The reliable functioning of renewable energy sources needs efficient and low cost energy storage technologies that can deliver energy efficiently on demand. Supercapacitors are receiving increasing importance as energy storage devices over batteries owing to their high power performance, excellent cyclic stability and environmental benignity. However, their low energy density poses a significant challenge in their development and applications. Enormous research has been focused on synthesizing new electrode materials and tuning their properties to achieve improved specific capacitance and energy density. Conducting polymers are promising materials that can store charge by fast and reversible faradaic redox reactions between the electrode and the electrolyte, which is known as

pseudocapacitance. Particularly, 1D conducting polymer nanostructures with hollow tubular morphology are capable of storing greater amount of charge due to its high surface to volume ratio and can provide short charge transport pathways. Pseudocapacitive electrodes based on conducting polymers such as PPy, PANi, PEDOT etc. offer high specific capacitance and energy density, but they suffer from the drawback of low power density and lack of cycle life owing to the repeated volume changes of the electrode caused by faradaic redox reactions. Therefore the challenge is to improve the power density and cycle life of supercapacitor electrodes without sacrificing the specific capacitance and energy density. Apart from the conducting polymers, carbon materials are potential candidates for electrochemical supercapacitors due to their large specific surface areas and electronic conductivity. The mechanism of charge storage in carbon materials is by electrostatic separation and formation of an electric double layer between electrolyte ions and high surface area electrodes, which is termed as electric double layer capacitance (EDLC). The cycle life and power density obtained with EDL electrodes could be very high as the charges are stored by physical adsorption and no faradaic charge transfer processes across the electrode-electrolyte interface are involved. Amongst the carbon materials, graphene and its derivatives such as reduced graphene oxide (RGO) have gained immense attention as EDL capacitor electrodes owing to their unique mechanical and electrical properties, high aspect ratio and low density. However, inspite of their large specific surface areas, their specific capacitance is limited and the energy density of commercial carbon-based supercapacitors is not more than 10 Wh/kg, which is sufficiently low to meet the demand of high performance energy storage devices. To develop advanced electrode materials with high specific energy and power density, the overall performance of supercapacitor electrodes needs to be optimized, which could be achieved by combining EDL and pseudocapacitive materials to form nanocomposite electrodes. Incorporating graphene and its derivatives within conducting polymers is a promising approach to utilize the merits and overcome the shortcomings of both the individual components in the nanocomposite electrode. In such hybrid nanocomposite electrode, graphene can serve as an underlying conductive backbone with high rate capability and long cycle life, while conducting polymers can provide a high and stable electrochemical capacitance. Moreover, the tendency of graphene sheets to agglomerate due to their interlayer van der Waals interaction could be minimized by the presence of

conducting polymer nanostructures as spacers between them. The electrochemical performance of a supercapacitor is significantly controlled by the microstructure, porosity and specific surface area of the electrode. A developed surface area with well defined pores can promote the accessibility of the electrolyte ions to the electrode surface and can facilitate the charge transfer through interconnected network thereby improving the electrochemical performance. A novel route to modify the electrode surface in a controlled way is swift heavy ion irradiation. Irradiation with energetic ions can produce cylindrical disordered zones along each ion impact site, which provides a way to induce randomly distributed pores on the electrode surface that affects the electrochemical performance. However, the effects of swift heavy ion irradiation on RGO-conducting polymer nanocomposites have not yet been investigated.

Considering the above mentioned facts, the present thesis is devoted to the development of electrode materials based on conducting polymer nanotubes and their nanocomposites with RGO for improved electrochemical performance. Another prime focus of this thesis is to study the modifications of physico-chemical and electrochemical properties of RGO-conducting polymer nanocomposite electrodes upon swift heavy ion irradiation with different fluences. The main objective of the thesis is to improve the specific capacitance, energy density, power density and cyclic stability of conducting polymer electrodes by hybridizing with RGO and to investigate the effects of swift heavy ion irradiation on the electrochemical properties of the nanocomposite electrodes. To achieve these objectives, the following conducting polymer based systems have been investigated:

- 1) Polypyrrole nanotubes (PPyNTs) and polyaniline nanotubes (PAniNTs) have been synthesized by reactive self degrade template method and investigated for supercapacitor electrodes.
- 2) RGO-PPyNTs and RGO-PAniNTs nanocomposites have been synthesized by *in situ* reduction method for varying concentration of graphene oxide and their electrochemical properties have been investigated for supercapacitor electrodes.
- 3) RGO-PPyNTs and RGO-PAniNTs nanocomposite electrodes have been irradiated with 85 MeV C^{6+} swift heavy ions (SHI) of different fluences with an aim to modify their physico-chemical and electrochemical properties for supercapacitor electrodes.

The structural properties of the synthesized systems have been analyzed by X-ray diffraction. The morphology of the materials has been investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The molecular vibrations and defects in the materials have been investigated using Fourier Transform Infrared (FTIR) and Micro-Raman (μ R) spectroscopy. Thermogravimetric analysis has been carried out to investigate the thermal stability of the samples. The current-voltage (I-V) characteristics and conductivity of the fabricated electrodes have been measured with a view to study their charge transport characteristics and electrical properties. The specific surface area and porosity of the samples have been determined by N₂ adsorption-desorption measurements. The electrochemical performance parameters of the synthesized electrodes such as specific capacitance, energy density, power density and cycle life have been investigated by cyclic voltammetry and galvanostatic charge-discharge measurements using a three electrode configuration. The internal resistance of the electrode materials such as equivalent series resistance and charge transfer resistance have been estimated using electrochemical impedance spectroscopy.