CHAPTER 1

Introduction

1. Introduction

1.1. Necessity of energy storage devices

Global population expansion has boosted energy use in homes, cars, and factories over the past few decades. Energy is thus a necessity for human civilization to survive and flourish. There are many different types of energy; we convert and utilize it as desired [1]. The proportion of non-renewable forms of energy (crude oil, coal, natural gas, nuclear, etc.) is constrained. The main contributor to global warming and climate change is the excessive use of fossil fuels, which releases harmful greenhouse gases including methane, carbon dioxide, nitrous oxide, ozone, chlorofluorocarbon, etc. [2,3]. So, there needs to be a major shift toward clean, sustainable, and renewable energy sources including biomass, solar, wind, tidal, hydro, and geothermal energy. Due to their environmental acceptability and renewability, these renewable resources have a significant ability to replace fossil fuels. However, the volatile nature of solar, hydro, and wind energy makes it difficult to meet the demand. Taking the fickle nature and reliability into consideration, this has led to severe concerns about the need and availability of energy [4,5]. Also, the storage of these energies is a primary concern. To store energy and utilize it as needed, energy storage devices are required with properly designed storage devices on renewable sources of electricity in our homes, companies, and transportation systems that are feasible with zero or low emissions [6].

1.2. Kinds of energy storage devices

The widely used energy storage technologies fall into the following broad categories: electrical (supercapacitor, capacitor, battery, fuel cell, and superconducting magnetic energy storage), mechanical (pumped hydro, gravity storage, flywheel, and compressed air energy storage systems), thermal (thermochemical, latent-ice storage, hot bricks, cryogenic liquid air, and steam accumulator), biological (glycogen, glucose, and starch), and chemical (biofuels, liquid nitrogen, and hydrogen) [7]. However, there is not a perfect system for energy storage that could satisfy all the technological and financial requirements of a wide range of applications. The production of electricity in the electric power sector is roughly constant throughout a given period, while the sale and distribution of electricity change according to demand. The development of suitable and effective electrical energy storage technology has the potential to revolutionize the energy sector since it can perfectly balance supply and demand. It is important to note that power companies are unable to regulate the power output from renewable resources. The use of renewable energy sources rather than conventional fossil fuels for the production of electricity can be encouraged by these energy storage systems [8,9]. The modern world is moving toward electrochemical power systems (supercapacitors, capacitors, fuel cells, and batteries) that supply clean energy in consideration of the speedy depletion of fossil fuels and their effects on environmental pollution and climate change. Compared to fuel combustion systems, electrochemical systems are superior in a number of ways. In contrast to electrochemical systems, where energy storage is driven by reactions at the interfaces based on the surface shape, physical properties, and chemical makeup of the materials, heat-engine cycles depend on volume to carry out their activities [10,11].

The main energy storage technologies that have been industrialized include batteries, fuel cells, capacitors, and supercapacitors. They are all made up of a positive and a negative electrode, but they differ in terms of how they work. In all devices, the process of energy transmission takes place at the electrode/electrolyte interaction. In a conventional capacitor, a dielectric is used between two oppositely charged electrodes. In supercapacitors, fuel cells, and batteries, a separator is placed in between the electrodes and the electrolyte solution. The cathode and anode of fuel cells and batteries undergo redox processes, which transform chemical energy into electrical energy [12].

1.2.1. Battery

Battery components include a separator sandwiched in between two conducting electrodes submerged in an electrolyte (figure 1.1). Although allowing electrolyte ions through, the separator blocks the flow of electrons. The cathode, which is positive while discharging, and the anode, which is negative during discharging, are called electrodes. Positive ions migrate in the opposite direction to negative ions as they flow through the electrolyte from cathode to anode. Both the cathode and anode develop polarized charges, positively and negatively, respectively. The anode and the cathode are connected by negatively charged electrons moving through an external load. When the battery is being charged, a reverse process occurs and the voltage source pulls electrons from the anode (now the positive electrode) to the cathode (negative electrode) [13].

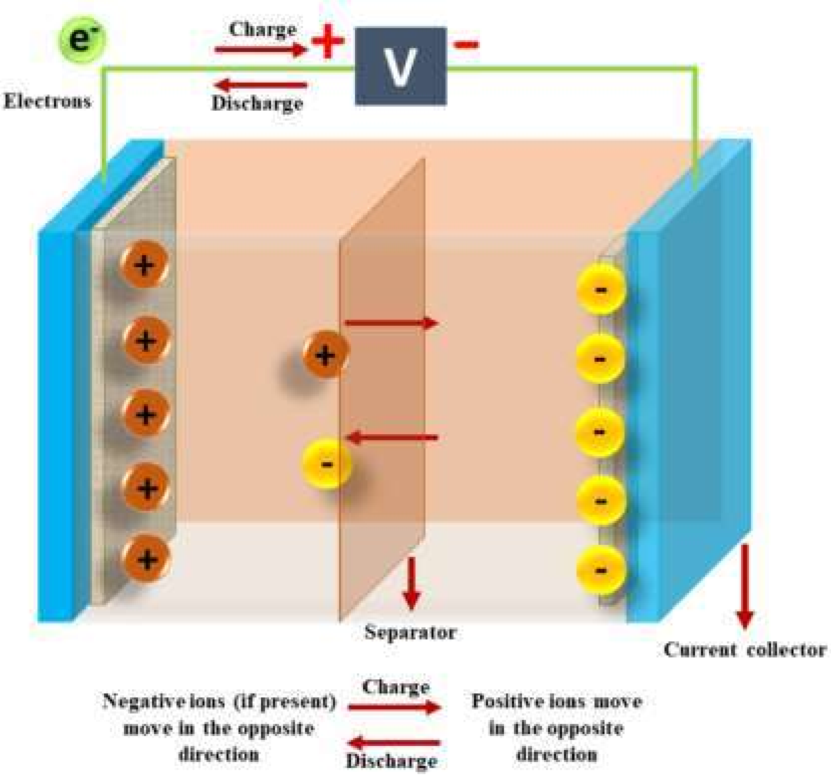

Figure 1.1: Charging and discharging mechanism in battery

1.2.2. Fuel cell

Fuel cells use electrochemical reactions, which are just reversed electrolysis reactions, to produce power and heat. Water is created when hydrogen and oxygen combine. Fuel cells come in a variety of designs, but they all function according to the same fundamental ideas. The chemical properties of the electrolyte are the one which differentiate different fuel cell designs from one another. The electrochemical reaction is shown in equation 1.1, and the schematic diagram of a fuel cell are shown in figure 1.2.

$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O + \text{Energy (electrical power + heat)}$

(1.1)

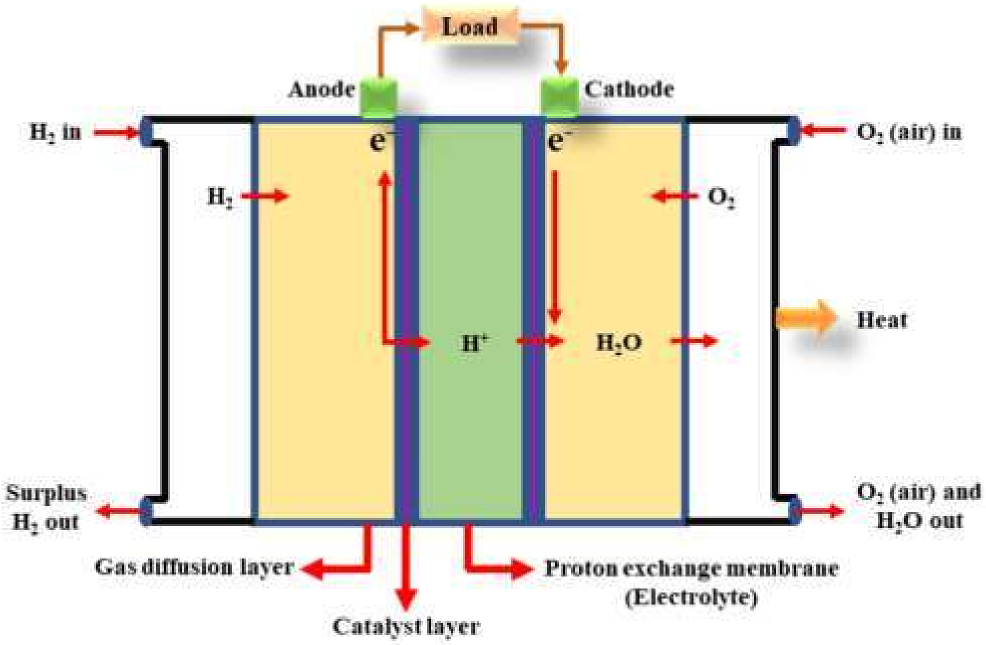

Figure 1.2: Proton exchange membrane fuel cell mechanism

1.2.3. Capacitor

Electric charge is stored electrostatically in conventional capacitors. The capacitor is linked to a source of voltage during the charging process. The positive and negative charges gravitate toward the electrodes with opposite polarizations as a result of the potential difference. If a load is connected to a fully charged capacitor in a circuit, the capacitor behaves as a voltage source at that point, and after the charge balance is attained, current flow ceases [14]. Equation 1.2 is used to compute the capacitor's capacitance based on the process of discharging.

$$C = \frac{Q}{V} \tag{1.2}$$

Q is the charge (in Coulombs), V is the voltage difference between the opposite charged plate (in Volt), and C is the capacitance (in Farads).

The capacitance of a capacitor changes inversely with the spacing between the electrodes and linearly with the surface area of the plates and permittivity, as shown in the equations 1.3 and 1.4.

$$C = \frac{\varepsilon_0 A}{d} \text{ (for vacuum free space between the plates)} \qquad (1.3)$$

$$C = \frac{\varepsilon\varepsilon_0 A}{d} \text{ (for dielectric material between the plates)} \qquad (1.4)$$

Here, ε_0 is the free space permittivity, ε is the permittivity of dielectric material (2 for polypropylene and 3 for polyester), A is the surface area of plates (in m^2), and d is the distance between the two plates (in m), respectively.

An illustration of a parallel plate capacitor with an insulating substance between the conducting plates is shown in figure 1.3. Charges and electrons cannot pass through a dielectric material. The physical form of static electricity is stored in capacitors as energy. In the beginning, both plates' positive and negative charges are equal. The positive terminal of the source begins pulling the electrons present in the electrode plate that is linked to it when an adjustable voltage supply is connected to the capacitor. The electrode plate attached to the negative end of the source receives electron deposition. In another way, both plates have accumulated charges (one is negative and another is positive). As long as the produced voltage does not match the supply voltage, electron movement continues. When a load is connected to circuit, electrons flow from the negatively to the positively charged plate through the circuit during discharging [15].

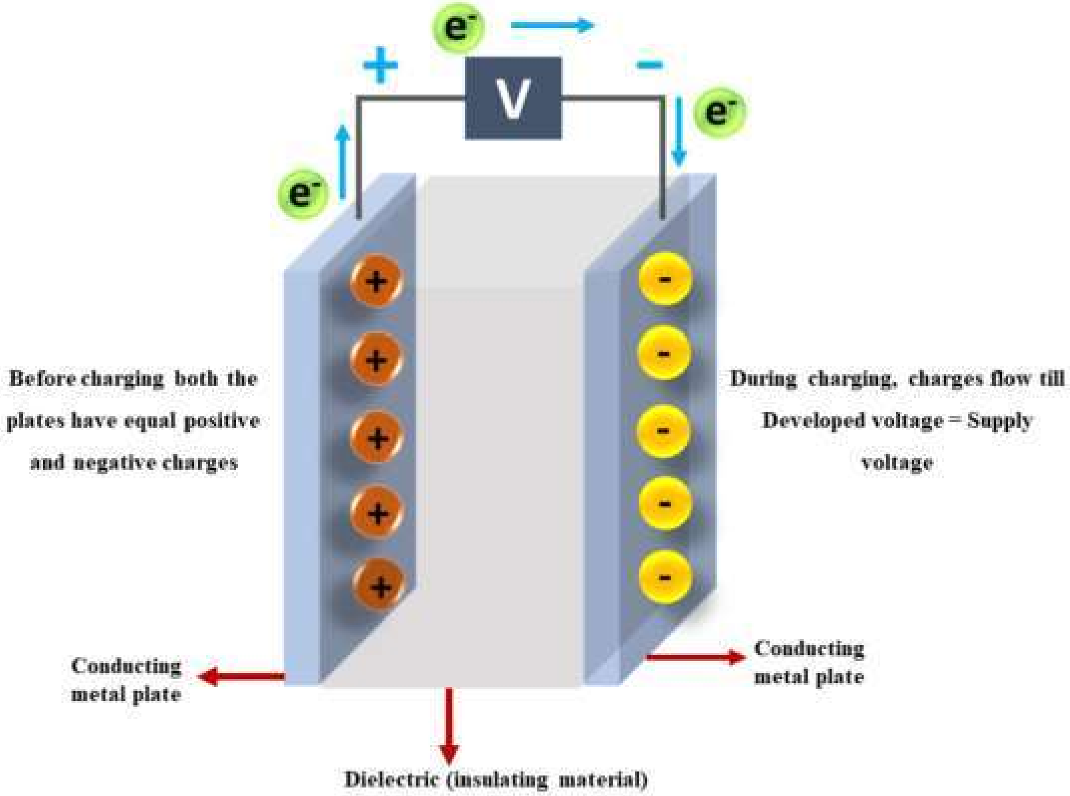

Figure 1.3: Capacitors charge-storage mechanism

Power and energy density are the two key components of a capacitor. A capacitor's capacitance directly correlates with the amount of energy it can store, which is known as energy density. Based on the rate of energy delivered per unit of time, a capacitor's power can be calculated. In some capacitors, the equivalent series resistance (ESR) produced by internal elements such as the electrode material, current collectors, and dielectrics is taken into consideration [16]. The energy density and maximum power are expressed by following the given equations 1.5 and 1.6.

$$E = \frac{1}{2} CV^2 \tag{1.5}$$

$$P_{\max} = \frac{V^2}{4ESR} \tag{1.6}$$

Where, C is the capacitance (in Farad), V is the voltage (in Volt), ESR is the equivalent series resistance (in Ohm), E is the stored energy (in Wh/kg), and Pmax is the maximum power of the capacitor (in W), respectively.

1.2.4. Supercapacitor

A supercapacitor, sometimes known as an ultracapacitor, is a high-capacity capacitor that fills the void between capacitors and rechargeable batteries. Its capacitance value is significantly higher than that of ordinary capacitors but has lower voltage boundaries [17]. It can take and deliver charge much faster than batteries, store 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, and withstand a great deal more charge and discharge cycles than rechargeable batteries Instead of long-term compact energy storage in vehicles such as cars, buses, trains, cranes, and elevators, SCs are employed in applications that call for a lot of quick charge/discharge cycles. They are also used in burst-mode power delivery in cranes, trains, and elevators [18].

1.3. Supercapacitors' fundamental working mechanism

The fundamental idea governing the charge storage process of supercapacitors must be understood. These unique energy storage devices store charges at the active sites of the electroactive materials as well as in the electrode-electrolyte interfaces. EDLC is a technique that explains how the charge is stored at interfaces. The process of storing charge at the electroactive sites is also described by a pseudocapacitive mechanism, which primarily involves redox transition and intercalation [19]. Conventional capacitors are perfect for applications requiring quick energy storage and discharge. Additionally, the charge is typically kept on plates with a limited surface area in conventional capacitors, rated in the milli (m) and micro (μ) farad ranges. Furthermore, SCs have many times more capacitance and energy than capacitors because their electrodes have bigger active surface areas and negligible dielectrics. In order to neutralize the surface charges, Helmholtz predicted that the layer of opposite ions would become immobilized on the charged electrode surface due to the electrostatic force of attraction. According to the Helmholtz model, the thickness of the layer made up of counter ions causes the electric potential of the surface (Ψo) to become zero in the bulk electrolyte solution [20].

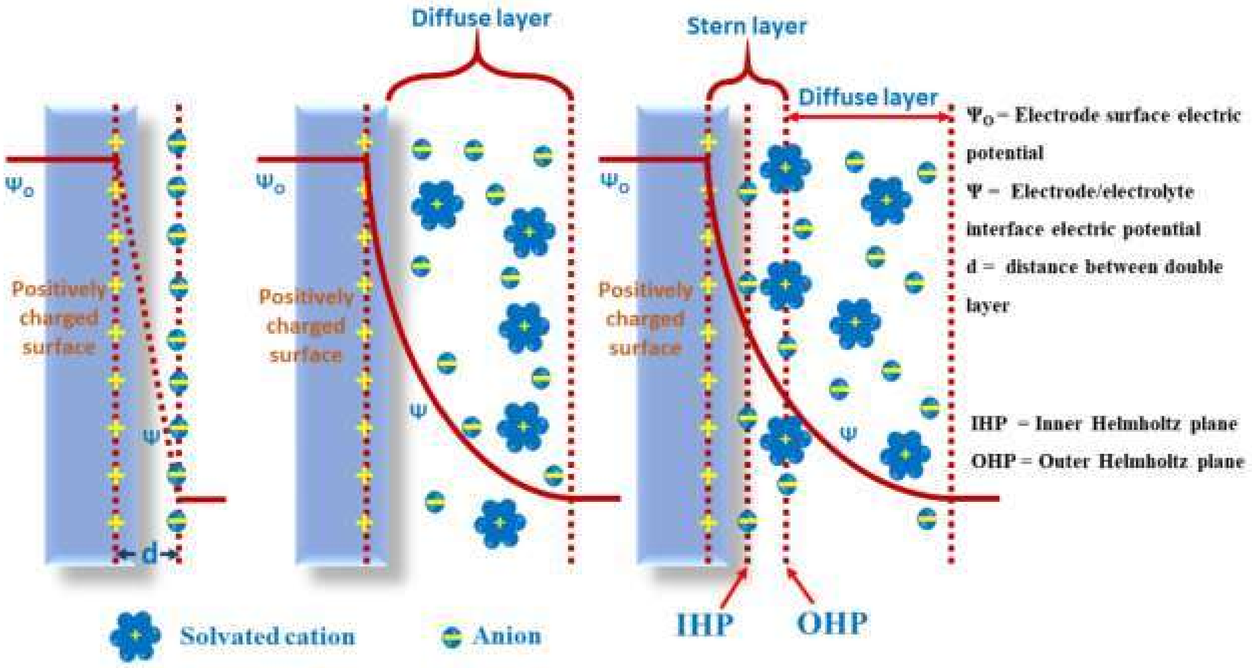

Figure 1.4: EDLC mechanisms suggested by Helmholtz, Gouy, and Chapman

The Helmholtz model was later updated by Gouy-Chapman. The electrolyte ions, in their model, have a continual, random thermal motion, making it impossible for them to become immobilized on the charged surface. In order to balance the charges on the electrode surface, electrolyte ions are dispersed throughout the solution and combined to form a diffused double layer. According to Gouy-Chapman, the potential in the bulk solution decreased gradually. EDLC was overestimated by the model. Point charge ions close to the charged electrode surface would result in an overstated capacitance since the capacitance value of two charged clouds varies inversely with their distance from one another [21].

Stern came to the conclusion in 1924 that the Helmholtz and Gouy-Chapman models together could effectively drive the Stern layer mechanism of the double layer [22]. He separated the ion distribution area into two parts. The stern layer or compact layer refers to the inner region that is closest to the charged surface, whereas the diffuse layer refers to the outer region (figure 1.4). Hydrated ions connect to the electrode in the compact layer. Ions that have been specifically and non-specifically adsorbed as well as counter ions make up the compact layer. Inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) are two categories for the adsorbed ions. The diffuse layer continues to exist as Gouy-Chapman described it.

Figure 1.5's Ragone plot demonstrates the variation of energy and power density available from electrochemical storage systems. Fuel cells clearly outperform lithium-ion batteries, capacitors, and supercapacitors in terms of specific energy and have a very low specific power. Capacitors have the highest specific power but the lowest specific energy. Compared to batteries and fuel cells, supercapacitors have a greater specific power. Table 1.1 details the various characteristics of supercapacitors, batteries, and capacitors.

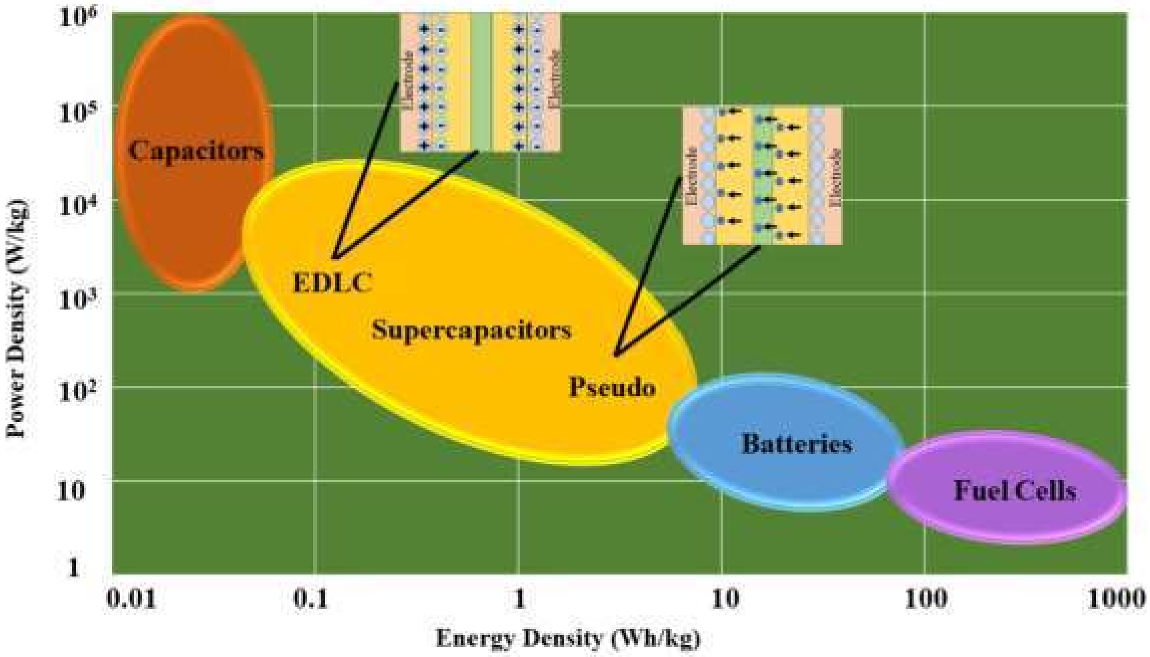

Figure 1.5: Ragone plot of different energy storage devices

According to the Ragone plot, an electric vehicle can travel a greater distance when powered by a battery (a high energy density device). A vehicle powered by a supercapacitor (a high power density device) may accelerate more quickly. The kinetic process in batteries alters the volume of the battery due to redox transitions in the materials that make up the battery. In comparison to supercapacitors, the batteries' durability is shortened by abrupt volume changes, which also restricts their ability to deliver power. The advantages of supercapacitors over other electrochemical devices are quick recharging (high power density), quick power supply, and long endurance (cycle life) [23].

Table 1.1: Comparison between supercapacitor, battery, and capacitor

Parameter	Supercapacitor	Battery	Capacitor

Electrochemical reactions	Moderately low activation polarization than battery	Need significantly high activation polarization	Require less activation polarization
Storage mechanism	Both, electrostatic and chemical	Chemical	Electrostatic (physical)
Charging time	1-30 sec	0.3-3 hours (hrs)	10^{-6}-10^{-3} sec
Discharging time	1-30 sec	1-8 hrs	10^{-6}-10^{-3} sec
Charging-discharging efficiency	90-95 %	70-85 %	100 %
Operating temperature (°C)	-40 to 85	-20 to 65	-20 to 100
Operating voltage (V)	2.5-3 per cell	1.25-4.2 per cell	6-800
Energy limitations	Electrode surface area	Electrode mass	Distance between parallel plates
Power limitations	Separator, ionic conductivity	Reaction kinetics and mass transport	No limitation (negligible)
Specific energy (Wh/kg)	1-10	10-100	<0.1
Specific power (W/kg)	1000-2000	<1000	>10000
Cycle life (cycles)	>100000	500-1000	>500000

1.4. Classification of Supercapacitors

On the basis of their charge storage techniques and kind of electrodes, supercapacitors are generally divided into three categories: EDLCs, pseudocapacitors, and hybrid supercapacitors [24].

1.4.1. EDLC

In order to permeate ions and prevent short circuits, the EDLC has two electrodes that are connected to the current collectors and submerged in an electrolyte with a separator in the middle. In such systems, the electrostatic force of attraction builds up charge at the electrode-electrolyte interface when a voltage is applied between the two electrodes (figure 1.6). By expanding the electrode surface area of EDLCs, the charge storage capacity can be increased. EDLCs have greater power densities, quick charging-discharging, and exceptional cycle stabilities since there is no Faradaic charge transfer and there is an ion adsorption (electrostatic process) mechanism.

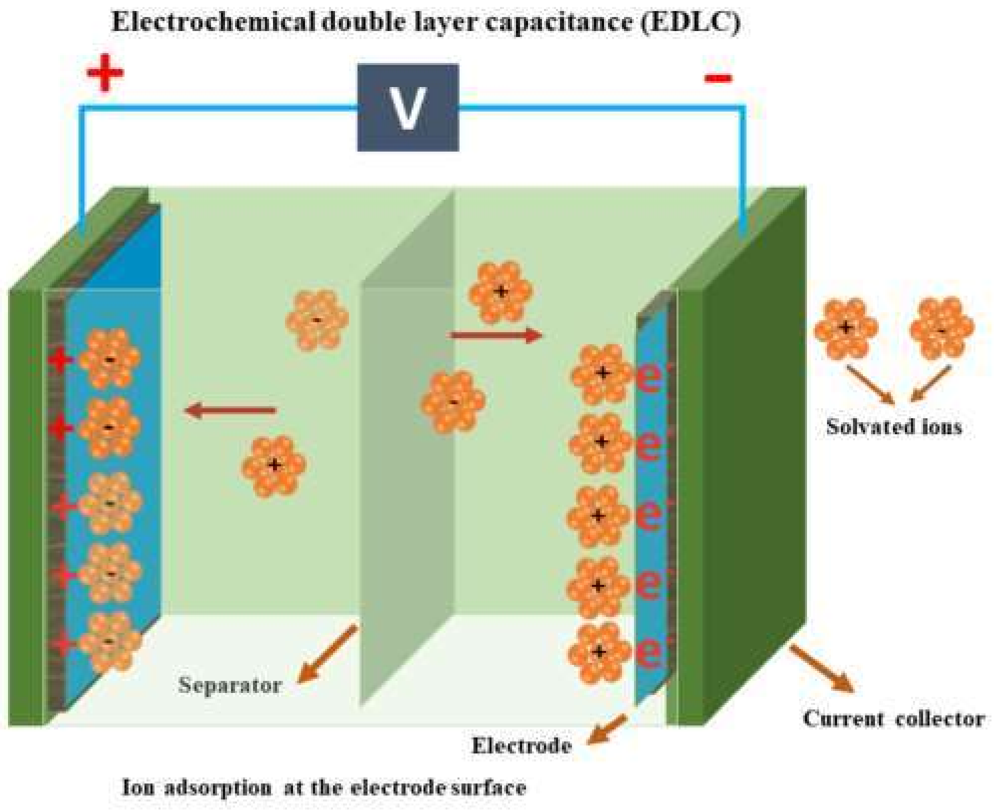

Figure 1.6: Schematic diagram of EDLC

The external voltage source acts as a conduit for the electrons as they pass from the positive electrode to the negative electrode of the EDLC during the charging process. Through the bulk electrolyte, cations and anions move in the direction of the negative and positive electrodes, respectively, forming double layers at the electrode-electrolyte interface. The opposite mechanism takes place when discharging. The capacitance of EDLC is dependent on the width of the binary layer formed at the electrode-electrolyte border (equation 1.3). Throughout the entire procedure, there is no net ion exchange between the electrode and electrolyte and no charge transfer across the electrode-electrolyte interface. As a result, throughout the entire charge-discharge cycle, the electrolyte concentration does not change [25,26].

1.4.2. Pseudocapacitor

The charge storage process of pseudocapacitors is based on reversible oxidation-reduction reactions (also known as faradaic transitions), which take place at or near the electrode surface (figure 1.7). As a result, these are more energy dense and have higher capacitance than EDLCs. The capacitance of a pseudocapacitor is roughly 10-100 times greater than that of an EDLC. The charge storage in a pseudocapacitor varies linearly with the charging potential. So, rather than relying on charge building up in the double layer, the charge storage mechanism relies on electron transport. It is important to note that the double layer capacitance coexists with the pseudocapacitance. Due to their distinctive physical processes, various types of materials display various faradaic mechanisms [27].

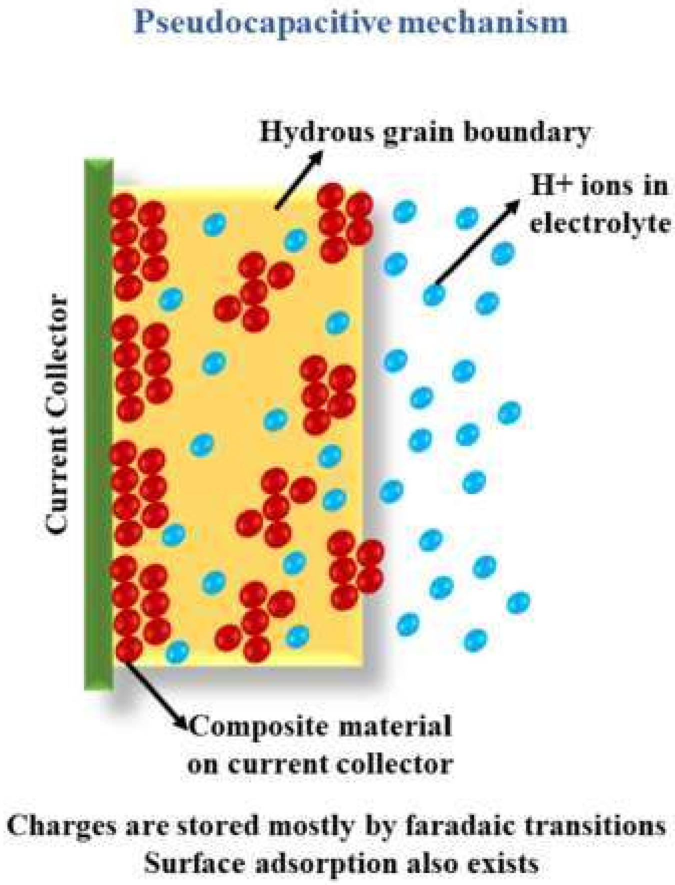

Figure 1.7: Charge storage mechanism of pseudocapacitor

1.4.3. Hybrid Supercapacitors

Hybrid supercapacitors are powered by both pseudocapacitive and electrostatic charge storage processes (figure 1.8). Pseudocapacitors have none of EDLC's drawbacks, and vice versa; as a result, their combined advantages transcend their individual drawbacks. In contrast to EDLCs, hybrid systems feature increased specific energy and high specific capacitance. The limiting factors of pseudocapacitors are great power density and cycle stability, which are demonstrated by hybrid systems [28]. Based on the materials employed in their construction, hybrid supercapacitors and the corresponding electrodes are divided into a number of kinds. One EDLC electrode and one pseudocapacitor electrode are used in asymmetric type hybrid supercapacitor electrodes. Asymmetric hybrids typically have negative and positive electrodes made of carbon-based and pseudocapacitive materials, respectively [29]. Electrodes for battery-type hybrid supercapacitors are composed of a battery electrode and a supercapacitor electrode. Due to the combination of a high energy density battery with a quick recharge time, an exceptional power density, and a supercapacitor with a better cycle life, the demand for high power batteries and high energy supercapacitors is repeated in battery-type hybrids. Composite electrodes are another form of hybrid electrodes used in supercapacitors. These electrodes are created by mixing conducting polymers, metal oxides, carbon-based materials, or any two of the three materials in a single electrode. The carbon-based materials offer an electrical double layer (capacitive charged layer) and a backbone with a large surface area, which improves the interaction between the electrolyte and the pseudocapacitive materials put on them. Additionally, the pseudocapacitive substances experience faradaic processes that aid in raising the capacitance of the corresponding composite electrode [30]. Operating potential windows, specific capacitance, corrosion stability, and cycle stability might all be improved by the synergistic mechanism of carbon-based and pseudocapacitive materials. Based on their arrangements, hybrid supercapacitors can be either symmetric or asymmetric. Two comparable pseudocapacitive and EDLC materials make up the electrodes of the symmetric hybrid supercapacitors. Asymmetric hybrid supercapacitors have two electrodes constructed from different materials. In comparison to symmetric supercapacitors, asymmetric supercapacitors enable higher energy and power densities. However, asymmetric supercapacitors are inexpensive and simple to make. By focusing on a single electrode, it is possible to determine the properties of a symmetric supercapacitor. Each electrode significantly affects the overall properties of the supercapacitors since asymmetric systems are made of materials that are different from one another. The operational voltage of each electrode determines how the device behaves in such systems, which limits how well their unique qualities may be reflected. The electrochemical properties of an asymmetric design apply to the supercapacitor as a whole rather than to each electrode separately [31,32].

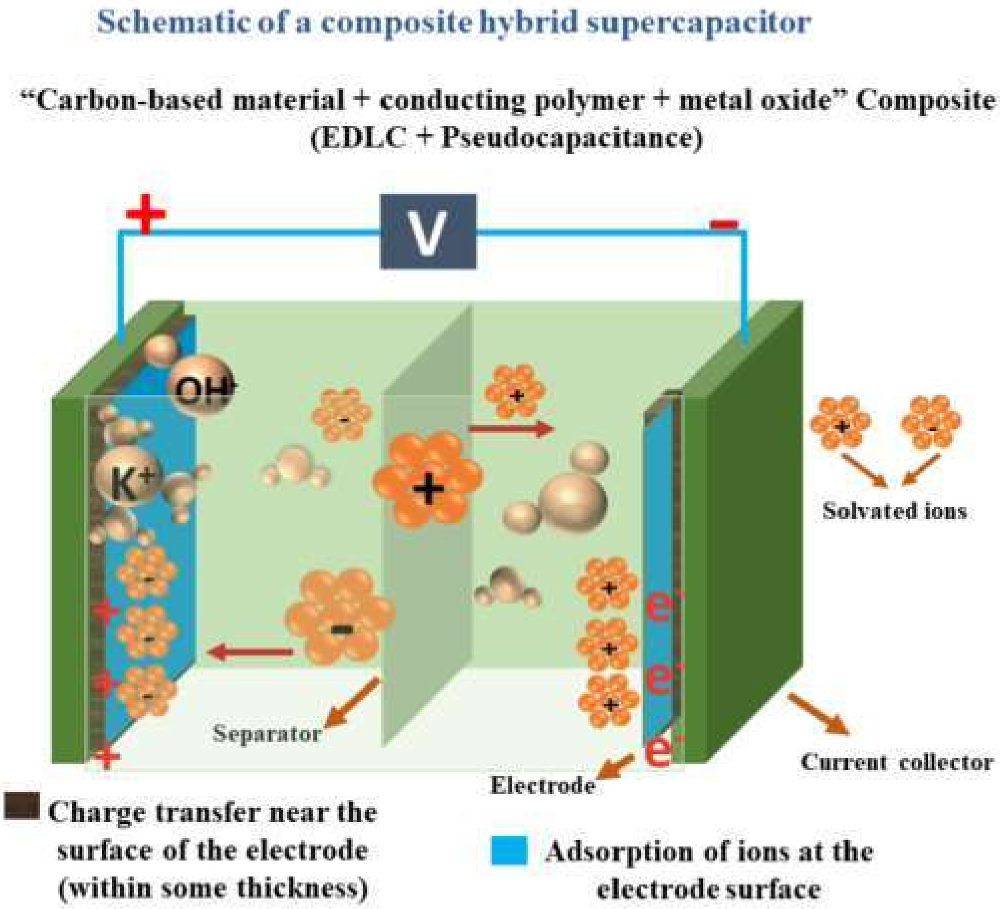

Figure 1.8: Mechanism of hybrid systems

1.5. Components of supercapacitors

Supercapacitors are made from many different components. These include sealants, separators, current collectors, electrodes, electrolytes, and electrodes. The effectiveness of supercapacitors in practical applications is greatly influenced by these components.

1.5.1. Electrode

The accompanying electrodes for each energy storage system and conversion device should have greater conductivity, chemical stability, thermal stability, corrosion resistance, and surface area, as well as being affordable and environmentally friendly. Different types of materials, such as carbon-based, conducting polymers, and metal oxides are processed to make electrodes [33].

1.5.1.1. Carbon based

Carbon-based materials like graphene, activated carbon, carbon nanofibers, and carbon nanotubes have a high surface area, large corrosion resistance, and enormous electric conductivity. These have outstanding characteristics for developing high power density in devices like supercapacitors. Because of these outstanding properties of pure carbon-based materials, many scientists are exploring new dimensions of such materials in this area. Among the various kinds of carbon-based materials, graphene and its sub-classes are promising candidates in the area of supercapacitors. Due to its excellent properties like large electrochemical activity, many binding sites, wide potential window, and large surface area. The most suitable sub-class of graphene is graphene oxide as it presents active functional groups like carboxyl, hydroxyl, and carbonyl [34,35].

1.5.1.2. Conducting polymer based

Conjugated polymers have electrical conductivities of about 104 S/cm, making them effective conductors of electricity. In supercapacitor electrodes, a variety of conducting polymers including polyaniline, polypyrrole, polythiophene, etc. are employed. These store and deliver energy by redox reactions. Ions are transported to the conducting polymer's backbone during oxidation (doping). A reduction (de-doping) process causes the ions to return to the main electrolyte solution. As a result, charging takes place in the conducting polymer-based electrode's bulk material as well as on its surface. Due to this, such electrodes exhibit high specific capacitance values. Polyaniline is frequently utilized in energy storage devices, particularly supercapacitors, because of its high theoretical capacitance, simplicity in synthesis, and inexpensive cost [36].

1.5.1.3. Metal oxide based

The electrodes for supercapacitors are made from a variety of transition metal oxides, including Fe_2O_3, MoO_3, Co_2O_3, MnO_2, RuO_2, NiO, V_2O_5, and CuO. Because they may undergo reversible redox reactions and have numerous valence states, they are excellent for electrochemical applications [37]. However, due to their low conductivities, they show lower electrochemical potentials. As a result of their superior electrochemical capabilities, binary and ternary metal oxides have gained popularity recently. Binary transition metal oxides are commonly written as $A_XB_{3-X}O_4$, where "A" and "B" stand for any transition metal, such as Mn, Cu, Fe, Co, Ni, Zn, etc [38]. Compared to single transition metal oxides, they have higher electrical conductivities and redox potential. Binary transition metal oxides contain at least one transition metal species and one or more electrochemically active or inactive ions. Together, they have a synergistic impact that increases the capacitance and contributes to a large stability potential window, more electroactive sites, and strong stability. Due to the redox activities that occur during electrochemical reactions, all metal oxides exhibit pseudocapacitive properties [5].

1.5.2. Electrolyte, separator, current collector, and sealants

In electrochemical supercapacitors the electrolyte is another essential component. There are several other types of electrolytes that can be used, including redox-type, aqueous, ionic liquid, and organic electrolytes. Solid or semi-solid electrolytes, redox-type, and organic electrolytes are just a few of the categories of electrolytes that are accessible [39].

Supercapacitor electrolyte requirements [40]:

(a) Wide potential window.

(b) Should provide ionic conductivity.

(c) High electrochemical stability.

(d) Low resistivity/volatility/toxicity.

(e) Availability with high purity and low cost.

A supercapacitor's separator is the wall separating its two electrodes. It encourages ionic flow through the main electrolyte and prevents short circuits [41]. Separators may be made of paper, glass, ceramics, polymers, etc.

Separator needs:

(a) The electrolytes must easily wet the separators.

(b) Separators should be non-conductive.

(c) In order to prevent swelling, they must compensate for pressure and volume changes occurring inside the system.

(d) They must have a lower ionic resistance and be permeable to electrolyte ions.

A link is made between the active material on the substrate and the current source by means of current collectors, which are electronic conducting components. They support the transfer of electric current from the current source to the working electrode during charging and from the working electrode to the external load during discharging. Current collector materials include copper, aluminum, stainless steel, iron, and alloys. High resistance is produced in supercapacitors as a result of the distortion of the active material, the degradation of the electrode, and the degradation of the current collector, as the number of cycles increases. Along with the cycle life, this lowers the specific capacitance also. Active materials are combined with polymeric binding materials such as Nafion, polyvinylidene fluoride, polytetrafluoroethylene, etc. to ensure that they will hold up to the current collector for an extended period of time [42].

Sealants support the prevention of impurities introduced by external elements such as chemicals, air, water, etc. The impurities may cause electrolyte degeneration and an unintended oxidation reaction on the electrode surface. The supercapacitors must therefore be properly sealed. Shunt resistance in the supercapacitor assembly could result from improper sealing. Shunt resistance can impair the supercapacitor's overall performance by mandating alternative current routes. Polymeric materials are typically utilized as sealants because of their flexibility, high moisture resistance, etc. [43,44].

1.6. Challenges with supercapacitors

Supercapacitors have several advantages over fuel cells and batteries, however, they have some challenges in some areas [45].

(a) Low energy density

Compared to batteries (> 50 Wh/kg), supercapacitors have a specific energy of around 5 Wh/kg. For applications that demand significant energy capacities, a big supercapacitor or numerous supercapacitors are needed, which will increase the cost.

(b) High self-discharging rate

The self-discharging rate of supercapacitors is quite high. Efficient electrode materials must be discovered to beat the challenges coming in the path of real applications of supercapacitors in various fields.

To overcome the obstacles standing in the way of genuine applications of supercapacitors in many fields, effective electrode materials must be found.

1.7. Applications

Every day, more people are looking for portable energy storage systems. Due to their high energy densities, batteries and fuel cells now hold a monopoly on the market for energy storage devices. Because of their high power density and long cycle life, supercapacitors have quickly entered this market by displacing these conventional energy sources in a few applications. Supercapacitors are chosen over other energy storage technologies in applications where high power delivery rates are necessary [46]. Listed below is a short list of applications.

(a) In regenerative braking systems, supercapacitors are widely utilized. They swiftly store the braking energy they have recovered.

(b) Supercapacitors are used by electrical cars that need to be charged quickly and at very high current levels.

(c) When a sudden power outage occurs, supercapacitors provide a backup source of power for PC cards, RAM, SRAM, and other components, protecting them from damage and data loss. They have been widely utilized in solid-state discs together with conventional capacitors.

(d) Supercapacitors are used in applications that require high power and extended cycle times, such as communication devices, navigational aids, sensors, radar systems, torpedoes, electromagnetic pulse weapons, radar antennae, missiles, and GPS.

(e) Supercapacitors are employed in security applications where a quick power supply is needed.

(f) Sam Beck's (Blueshift) portable speakers use supercapacitors, which enable them to playback audio for up to 6 hours after just 5 minutes of charging.