CHAPTER 1

Introduction

1.1 Introduction

The enormous consumption of fossil fuels (oil, gas, and coal) as a readily accessible carbon source has been integral to a country's social and economic prosperity since the industrial revolution [1,2]. Natural resource depletion and uneven distribution have already led to economic challenges (such as price swings and unbalanced supply chains), which negatively impact many areas, including energy production and storage, industrial operations, and transportation [1,3–5]. Moreover, the massive worldwide consumption of fossil fuels has caused carbon accumulation in the natural cycle. Further, with the rising energy demands, the exploitation of non-renewable energy sources is increasing daily, resulting in high pollution and the generation of greenhouse gases [6–8]. As science and the economy advance, so does the world's demand for energy. However, the earth's fossil fuel sources are running out.

Pollution caused by fossil fuels is having a detrimental effect on the environment, including climate change and ecosystem disruption. Countries worldwide are exploring renewable energy technologies like solar, wind, biomass, tidal, hydro, and geothermal energy to mitigate these issues. Because they are environmentally friendly and endless, these renewable resources have a huge potential to replace fossil fuels. However, one of the challenges with renewable energy is their intermittent nature. For example, solar and wind energy generation completely rely on weather conditions. This intermittency creates difficulties in meeting the energy demand consistently. Thus, the role of energy storage systems becomes crucial. Energy storage devices allow excess energy generated during peak production periods to be stored and make them available when and where needed. This would make the usage of renewable energy sources smooth, making them more reliable and ensuring a continuous supply of energy. By doing so, we can switch from internal combustion engines to vehicles with zero or low emissions and energy storage devices, relying on renewable energy sources in our homes, businesses, and industries [9,10].

1.2 Importance of energy storage

Energy storage is essential to the energy security of the existing energy networks. Hydrocarbons, whether in the form of coal piles, oil and gas reserves, or other refined or unrefined forms, are used to store a lot of energy today. Power precursors are stored instead of electricity since energy storage is significantly more effective, and demand for generation fluctuates. The only exception is a pumped hydroelectric plant, which can increase energy output quickly. The function and nature of energy storage are anticipated to alter significantly as energy systems adopt low-carbon technology. Two significant trends might drive this development. Firstly, it will get harder and harder to match the supply of electricity with demand due to intermittent nuclear power and fixed production, and imbalances will eventually take over and dominate. With the exception of flexible gas generation, most power suppliers cannot be stored like hydrocarbons as we move away from fossil fuel production.

Furthermore, if low-carbon power replaces oil and gas for transportation and heat supply, where there is a huge need, the structure of the electricity demand will shift dramatically. Electricity is stored in energy storage systems to meet demand during periods of excess energy supply. By storing excess electricity as heat or hydrogen for use in other industries, such storage systems could, for instance, serve the energy system in other areas. The utilization of energy storage will revolutionize the transition to a low-carbon civilization. Condenser energy is a common example of low-quality energy; in contrast to batteries, whose output capacity is often stable, condenser energy's supplied voltage strongly depends on the discharge state. Fuel cells use liquid fuels such as methanol allow for high energy storage, but they have a low power output, Low power and high energy density are both possible for lithium-oxygen batteries. Consequently, they are operating at their best. Therefore, utilization of energy storage will fundamentally alter the process of moving towards a low-carbon society.

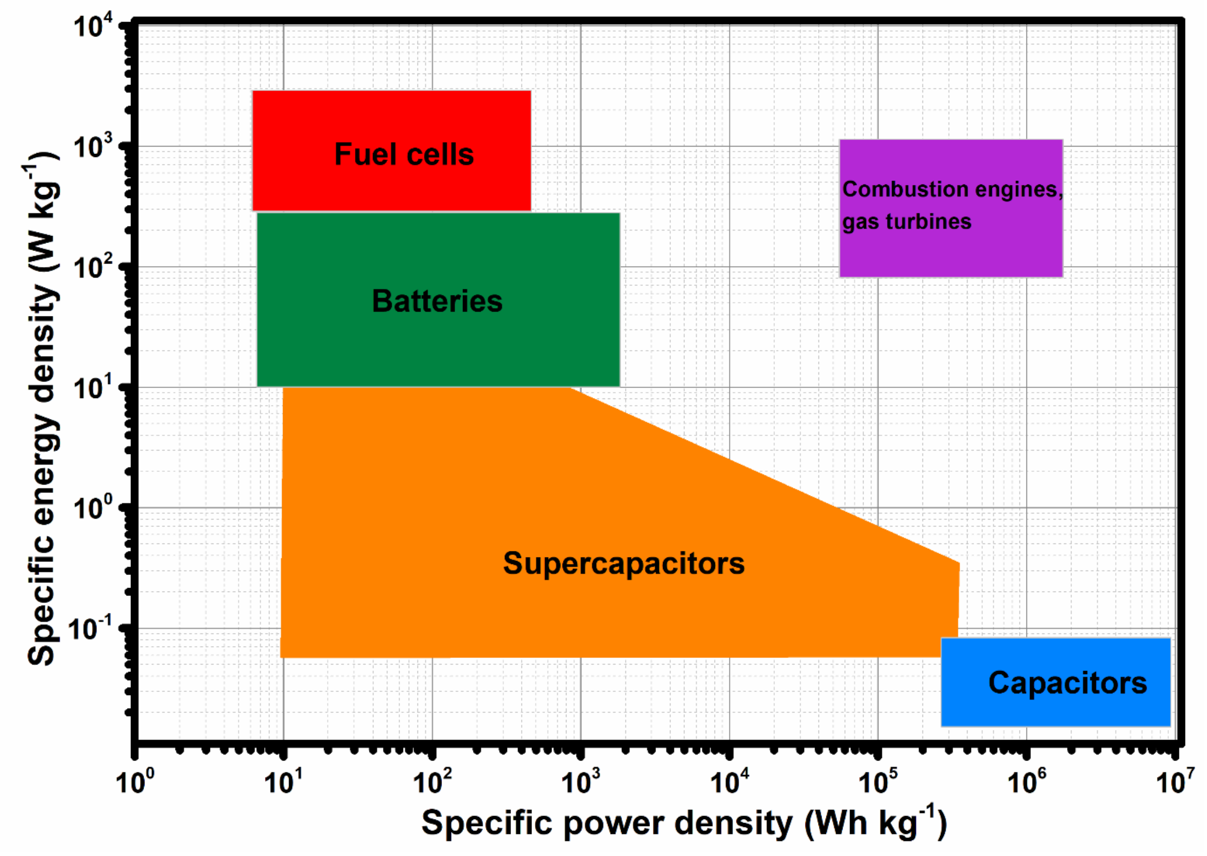

Fig 1.1: Ragone plots for various energy storage devices

Ragone plot (Figure 1.1) shows the relation between specific energy density and specific power density for various energy storage devices. It could be observed that fuel-cells possess the highest specific energy density and lower specific-power density, implying that they store a relatively large amount of energy per unit mass, but the delivery of power would be at a lower rate compared to lithium-ion batteries, capacitors, and supercapacitors. Additionally, capacitors show highest specific power density among the mentioned devices; however, lesser specific energy density. Supercapacitors show better specific power density than lithium-ion batteries and fuel cells as well as better energy density than conventional capacitors.

1.3 Various electrochemical energy storage and conversion devices

Electrical energy storage systems include capacitors, supercapacitors, batteries, fuel cells, and superconducting magnetic storage devices. Each of these systems has its characteristics, advantages, and limitations. Mechanical energy storage systems like hydroelectric, flywheels, and compressed air storage systems offer the ability to store large amounts of energy but have limitations in terms of efficiency or site-specific requirements. Chemical energy storage systems include hydrogen, liquid nitrogen, and biofuels. They can provide high energy density and a longer duration of storage but may face challenges in terms of infrastructure and safety. Thermal energy storage systems include steam accumulators, cryogenic liquid air, ice storage, and hot bricks [11]. They possess the advantage of storing heat, but the efficiency and scalability of these systems vary depending on technology and applications. However, there isn't a perfect energy storage system that could satisfy all the technological and financial requirements of various applications. The electricity production in the electric power sector is roughly constant throughout a given period, and changes are made during the sale and distribution of electricity according to demand. A breakthrough in the energy sector may result from developing suitable and effective technology for electrical energy storage, which can perfectly balance supply and demand. It is important to note that grid managers are unable to regulate the amount of power generated by renewable energy sources. These energy storage technologies could encourage the use of renewable energy sources rather than conventional fossil fuels to generate electricity [12]. Modern society is moving towards electrochemical power systems (supercapacitors, fuel cells, and batteries), which produce clean energy, in light of the quick depletion of fossil fuels and their effects on environmental pollution and global warming. In many ways, electrochemical systems are superior to fuel combustion systems. While energy storage in electrochemical systems is driven by reactions at the interfaces based on the materials' surface shape, physical and chemical properties, the processes involved in heat-engine cycles are volume dependent.

Supercapacitors, batteries, fuel cells, and capacitors are the leading energy storage technologies that are available commercially. Each of these energy storage devices consists of a positive and a negative electrode; however, the operating mechanism differs. In all devices, the process of energy transmission takes place at the electrode/electrolyte contact. A dielectric is placed between two charged electrodes in the case of a conventional capacitor. In supercapacitors, fuel cells, and batteries, a separator is placed between the electrodes and the electrolyte solution. Redox processes occur at the cathode and anode of fuel cells and batteries, converting chemical energy into electrical energy.

1.3.1 Conventional electric capacitor

A conventional capacitor is designed to store electrostatic charges. It consists of two parallel electrodes (plates) separated by a dielectric layer. When a potential difference (voltage) is applied across the electrodes, the positive and negative charges move in opposite directions and accumulate on the surfaces of the electrodes. This charging process leads to the capacitor storing electrical energy. A capacitor that is attached to a circuit and charged will temporarily work as a voltage source. The capacitance (C), measured in Farads (F), is the product of the potential difference (V) between each electrode and the electric charge (q) on each electrode. Figure 1.2 represents a conventional capacitor with two conducting plates and a dielectric medium between them.

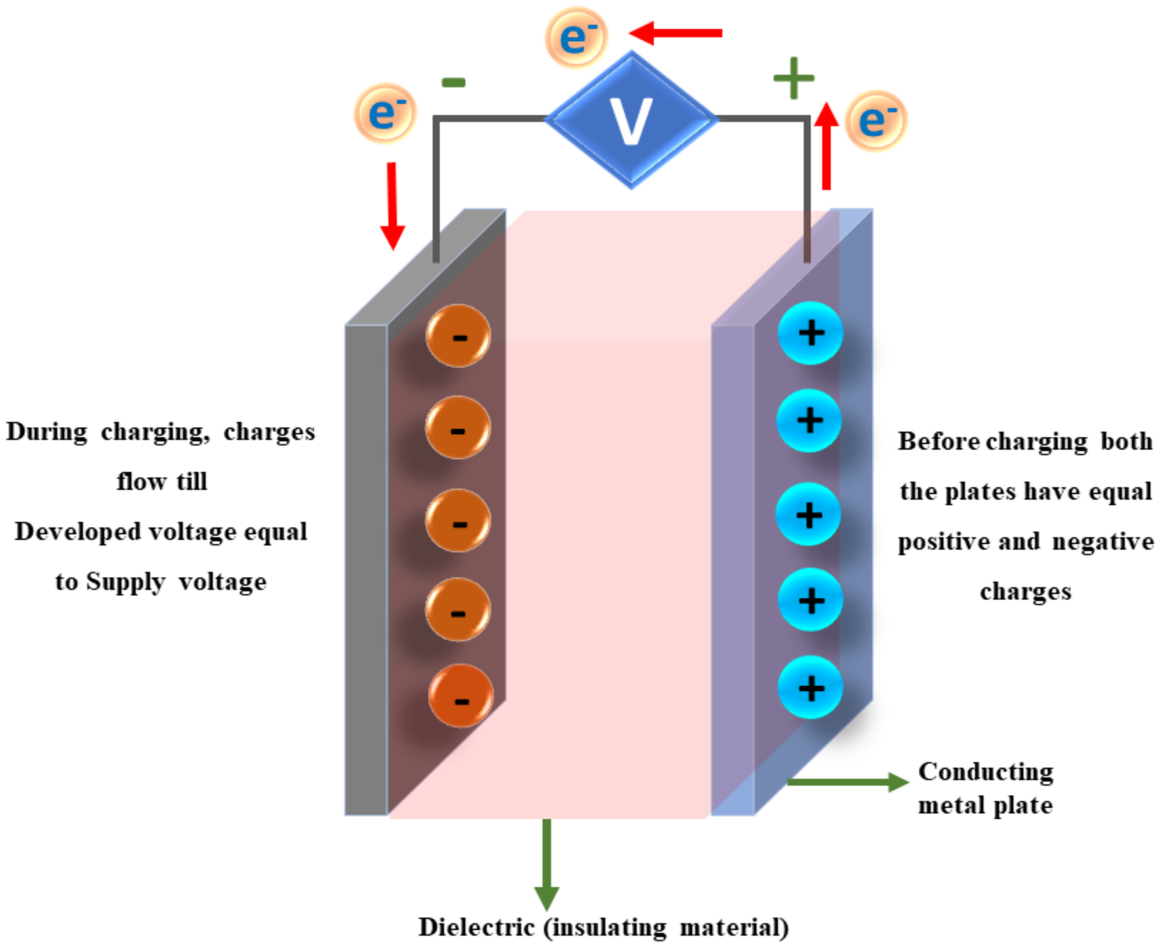

Fig 1.2: Charge storage mechanism in conventional capacitors

For a conventional parallel plate capacitor,

$$C = \frac{q}{V} \qquad 1.1$$

The capacitance, C, is inversely proportional to the distance (d) between the electrodes and directly proportional to the area (A) of each electrode and the permittivity of the dielectric medium. Which means:

$$C = \frac{\varepsilon\varepsilon_0 A}{d} \qquad 1.2$$

where ε_0 is the permittivity of free space, and ε is the dielectric constant (or relative permittivity) of the material between the plates. Therefore, the three main factors that determine the capacitance of a capacitor are plate area, electrode separation, and the characteristics of the employed dielectric (inductor). Its energy and power density, which can both be described as a quantity per unit weight (specific energy or power) or per unit volume, are two of a capacitor's key characteristics. The capacitance at each interface and potential difference are related to the energy stored in a capacitor as per equation 1.3:

$$E = \frac{1}{2} CV^2 \qquad 1.3$$

When V reaches its maximum, which is typically constrained by the breakdown strength of the dielectric, maximum energy is attained. Power is typically defined as the rate of energy supply per unit of time. In order to determine the output power, various factors like materials, properties of dielectric/electrolyte, and separators need to be considered. The resistance of these parts is typically calculated as a whole and is known as the equivalent series resistance (ESR). The ESR restricts the maximum energy and power that a capacitor may be produced by introducing a voltage drop that defines the capacitor's maximum voltage during discharge. Since the resistance of the load is believed to be the same as the capacitor ESR, power measurements for capacitors are frequently conducted at matched impedance, which corresponds to the maximum power Pmax.

$$P_{max} = \frac{V^2}{4ESR} \qquad 1.4$$

Due to the electrostatic method of charge storage, conventional capacitors offer an exceptional power density despite having very little energy density.

1.3.2 Fuel Cells

Fuel cells are galvanic open circuits that produce electricity through chemical reactions involving an oxidant source immersed in an electrolyte and an external fuel [10]. Fuel cells constantly consume reactants that need to be replaced, as opposed to batteries, which electrochemically store energy in a closed system. Unlike battery electrodes, which react with electrolytes and go through irreversible changes during charge/discharge processes, fuel cell electrodes are catalytic and electrochemically stable. Different fuels (such as hydrogen) and oxidants (such as oxygen) are combined to create various kinds of fuel cells. Figure 1.3 demonstrates a typical proton exchange membrane fuel cell.

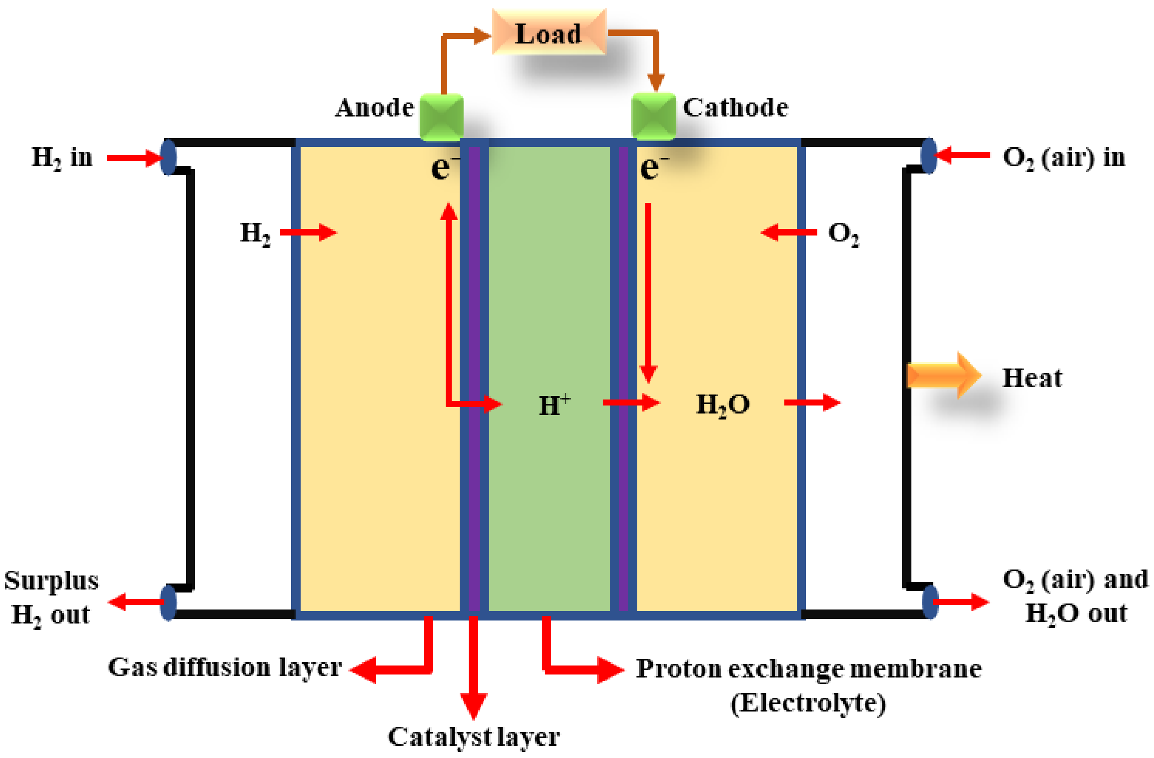

Fig 1.3: Proton exchange membrane fuel cell

Hydrogen is oxidized at the anode, and protons enter the electrolyte,

$H_2 \rightarrow 2H^+ + 2e^-$ 1.5

At the cathode, oxygen gas reacts according to

$O_2 + 4e^- \rightarrow 2O^{2-}$ 1.6

In the external circuit, electrons move from the anode to the cathode and can be used to power a device. The fuel cell's overall reaction is provided by,

$H_2 + \frac{1}{2} O_2 \leftrightarrow H_2O$ 1.7

1.3.3 Batteries

Batteries are designed to transform chemical energy from solid electrode components into electrical energy, generating an electric current between two electrodes that are not similar and have different values of electrochemical potential (positive and negative terminals). During discharging, the positive electrode is the cathode, and the negative electrode is the anode. Negative ions move from the cathode to the anode through the electrolyte, and positive ions travel in the opposite direction. The anode and cathode become negatively and positively charged, respectively. Negatively charged electrons travel from the anode to the cathode through the external circuit. The reverse process takes place during charging, and electrons are pulled away by the voltage source from the anode (now positive electrode) to the cathode (negative electrode). Figure 1.4 shows the illustration of the working mechanism of a battery.

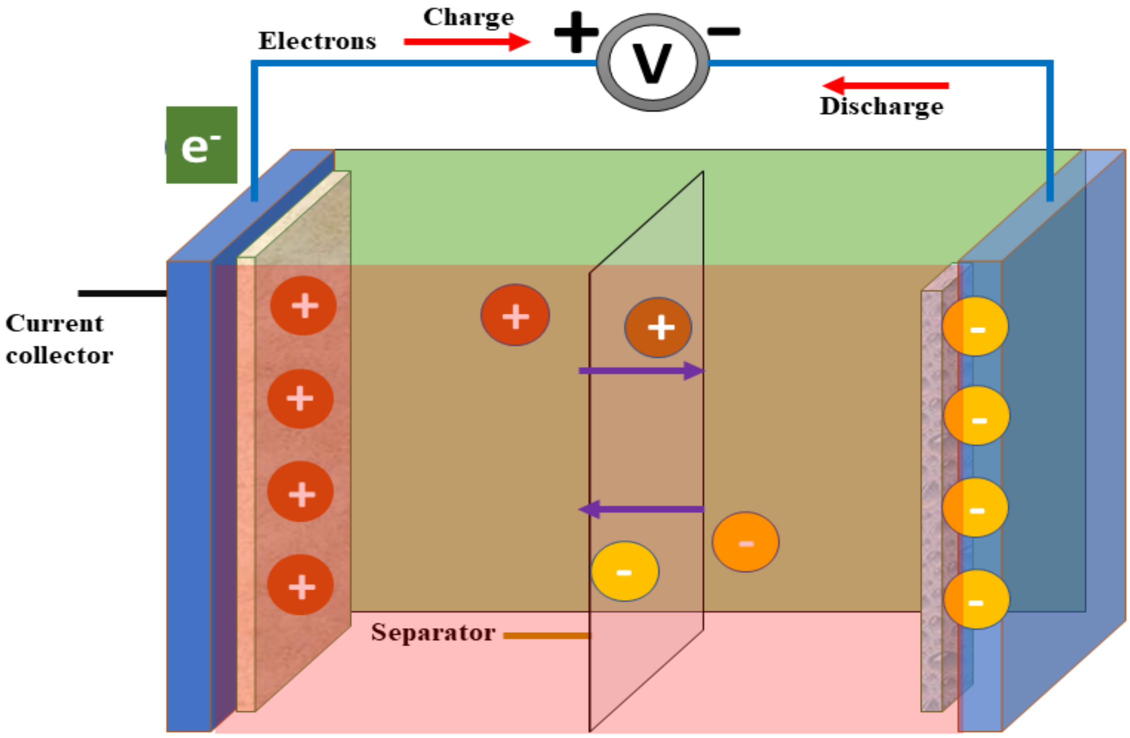

Fig. 1.4: Illustration of the working mechanism of a battery

1.3.4 Supercapacitor

Supercapacitors are energy storage devices that bridge the gap between battery and fuel cells with their high-power density and fairly good energy densities. Electric double-layer capacitors (EDLCs), electrochemical capacitors, electrochemical supercapacitors, and ultracapacitors are other names for supercapacitors. The term "supercapacitor" originates from standard electrolytic capacitors, which consist of two electrically conducting plates that are separated by a dielectric such as air, glass, or ceramic. When the plates are equally and oppositely charged, the dielectric material creates an electric field. If an electrochemical capacitor with a rated capacitance of 1 F is charged at a potential of 1 V, it discharges with the current of 1 A for 1 second theoretically. The term ‘super’ is used due to its capacitance of order the order of Farads, compared to conventional capacitors with capacitance in the range of microFarads. Supercapacitors are suitable for applications where energy is required to be delivered at a lower rate over an extended period. Supercapacitors, which have a very high-power density and a moderate level of energy density, are the best option under these circumstances and are therefore preferred to conventional electrochemical devices when quick energy delivery is required. The primary challenge in the advancement of supercapacitors is to enhance their energy density with a reduction in fabrication costs without sacrificing power density, cycling capability, and safety.

Typically, the energy density of a supercapacitor falls in the range of a few Wh/kg, which is insufficient for applications like hybrid vehicles. Consequently, supercapacitors are often used alongside battery systems as auxiliary components providing short power bursts when needed [13].

In order to address this issue, tremendous efforts have been made to develop innovative electrode materials, electrolytes, and designs. These advancements aim to bridge the gap between the energy storage capabilities of batteries and the high-power performance of supercapacitors. Table 1.1 shows important features and limitations of batteries, supercapacitors, and conventional capacitors [14].

Table 1.1 Important features and limitations of batteries, supercapacitors, and conventional capacitors.

Property	Battery	Supercapacitor	capacitor
Operational voltage (V)	1.25-4.2	2.3-2.75	6-800
Charge-discharge efficiency	0.7-0.85	0.85-0.98	>0.95
Energy density (Wh/kg)	10-100	1-20	<0.1
Power density (W/kg)	<1000	32000	$>10^6$
Charging temperature (°C)	0-45	-40 – 70	-20 - 125
Cycle life	500-2000	10^6	10^6
Charging-discharging time	1-10 h	ms to s	ps to ms
Weight	1 g to >10 kg	1 g to 230 g	1 g to 10 kg
Pulse load	Upto 5A	Upto 100 A	Upto 1000A

1.3.5 Other energy storage systems

Several other electrochemical energy storage methods have been utilized in practical applications, such as closed batteries (lead acid, sodium-sulfur, sodium nickel chloride, and nickel-cadmium), flow batteries, vanadium redox batteries, and zinc-bromine batteries. Among these systems, redox flow batteries have gained significant attention in both academic and industrial spheres. Flow cells have the ability to independently adjust their power output and storage capacity [15]. Unlike other battery technologies, this one has a reduced incremental cost per additional unit of capacity because increasing storage capacity only requires adding more electrolytes. Flow batteries have the potential to be used in a wide variety of electrochemical energy storage applications due to these qualities.

1.4 Mechanism of operation of supercapacitors

Understanding the fundamental principle of operation and charge storage mechanism of supercapacitors (SCs) is crucial. SCs belong to a distinct category of energy storage devices in which charges are stored at the electrode-electrolyte interface and in the active sites of the electroactive species. The charge storage at the electrode-electrolyte interface through surface adsorption is termed electric double-layer capacitance (EDLC); on the other hand, the charge storage mechanism at the electroactive sites involving redox transition and intercalation is known as pseudocapacitance [16]. In conventional capacitors, charges are stored mainly by surface adsorption of ions on plates with relatively smaller surface areas making them suitable for fast charging/discharging applications. As a result, conventional capacitors are rated in milli to microFarad range. However, supercapacitors earn the designation ‘super’ due to the high surface area of the electrodes and the extremely small distance of separation between them. This unique configuration results in several thousand times more energy and capacitance compared to conventional capacitors [17].

The formation of electric double-layer in supercapacitors can be explained by various theories. It was initially proposed by Hermann von Helmholtz and further developed by Guoy-Chapman, Grahame, and Stern. Electric double-layer theory served as the foundation of electrochemistry and later served as a base for the development of many electrochemical theories and technologies, such as supercapacitors, batteries, and fuel cells [18].

If a charged electrode is immersed in an electrolyte, it attracts oppositely charged ions and repels the similarly charged ions, which creates a cloud of charges in the proximity of both electrodes. Due to Coulomb's forces, an accumulation of positive charges on the positive electrode draws an equivalent number of negative charges from the electrolyte side of the electrode. However, due to thermal fluctuations in the electrolyte, a scattering distribution of charges of ions occur, leading to a net presence of negative charges in the electrolyte region close to the electrode. The charge balance between the electrode represents an electric-double layers the electrolyte, as two charged and parallel layers are formed, separated by a distance 'd'[19]. It was initially assumed that the electrostatic forces of attraction would immobilize the layer of counter ions on the charged electrode surface, neutralizing the surface charges as suggested by Helmholtz. He also proposed that the electric potential at the electrode surface becomes zero in the bulk solution over the thickness of the layer formed by the counter ions, as shown in figure 1.5 [20].

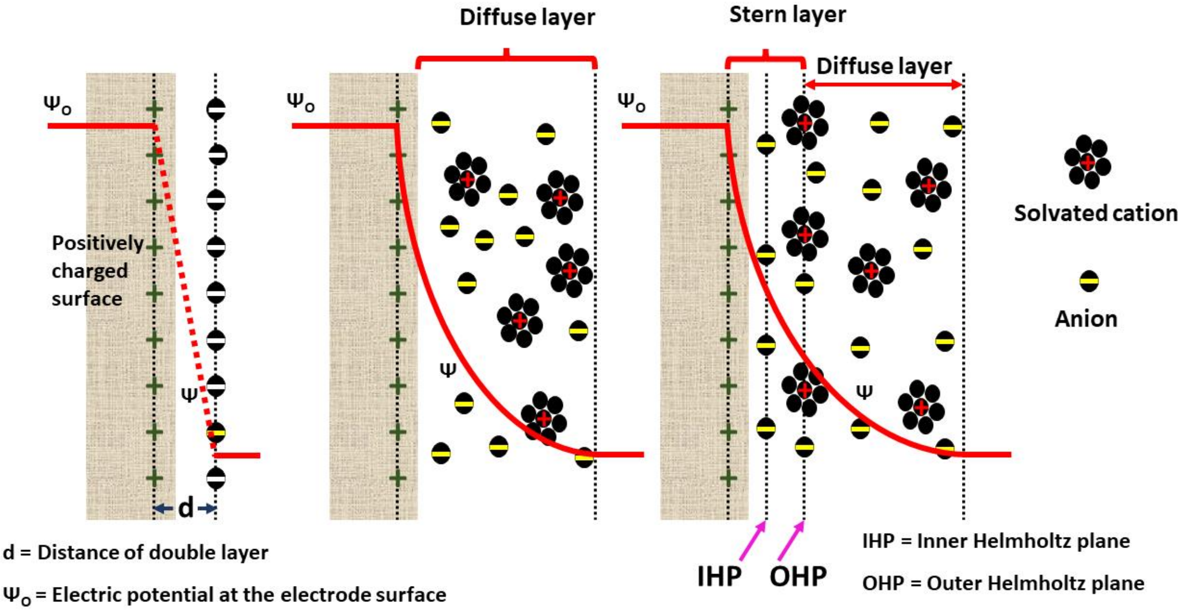

Fig 1.5: Double layer models proposed by Helmholtz, Gouy-Chapman, and Stern

Later, Guoy and Chapman modified the Helmholtz theory and proposed that electrolyte ions possess a continuous and random thermal motion and cannot be immobilized on the charged surface. These electrolyte ions neutralizing the charges on the charged surface are distributed in the solution and form a diffused double layer such that the rate of fall of electric potential is lower in the bulk solution. However, this model overestimated the value of electric double-layer capacitance [21]. Stern, in the year 1924, concluded that the Helmholtz and Guoy-Chapman models might be used effectively to drive the Stern layer mechanism of a double layer. He separated the ion distribution layer into two parts. The inner region, closer to the charged surface, is referred to as the Stern layer or compact layer, and the outer layer as the diffuse layer. Hydrated ions get adsorbed in the compact layer, and it consists of specifically and non-specifically adsorbed and counter ions. The layer of adsorbed ions is classified into the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP), whereas the diffuse layer remains the same, as described by Guoy and Chapman [22]. Under these circumstances, the electric double layer capacitance (C_{dl}) can be computed with the help of the capacitance contributions of diffuse layer (C_{diff}) and Stern layer (C_H) as given in eqn. 1.8 below:

$$\frac{1}{\mathrm{Cdl}} = \frac{1}{\mathrm{Cdiff}} + \frac{1}{\mathrm{CH}} \qquad 1.8$$

Various factors like the kind of electroactive material, electrode surface, electrode conductivity, electrolyte ions conductivity towards active sites inside electrodes, and chemical affinity among adsorbed ions play a role towards C_{dl}.

1.5 Types of supercapacitors

Generally, supercapacitors are classified as electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors on the bases of their charge storage mechanisms and type of electrodes.

1.5.1 Electric double layer capacitors (EDLCs)

The EDLCs consist of two electrodes connected to the current collectors and immersed in electrolyte along with a separator in between to allow permeation of ions. In these systems, charges are accumulated at the electrode-electrolyte interface through electrostatic forces of attraction when a potential difference is applied across the electrodes. The charge storage capacity of these electrodes can be increased by enhancing their specific surface area as only surface adsorption of ions occurs. Therefore, the EDLCs demonstrate excellent power densities (> 500 W kg^{-1}), quicker charging-discharging, and magnificent cycling stabilities [23]. The process of charging and discharging in the case of EDLCs can be represented as follows:

On positive electrode

$E_{S1} + A^- \leftarrow \rightarrow E_{S1}+ //A^- + e^-$

On negative electrode

$E_{S2} + e^- + C^+ \leftarrow \rightarrow E_{S2}^- // C^+$

The overall process of charging and discharging

$E_{S1} + E_{S2} + A^- + C^+ \leftarrow\rightarrow E_{S1}+ // A^- + E_{S2}^-//C^+$

Where E_{S1} and E_{S2} represent the surface of two electrodes, // is the electric double layer where charges are accumulated, and A^- and C^+ are anions and cations present in the electrolyte.

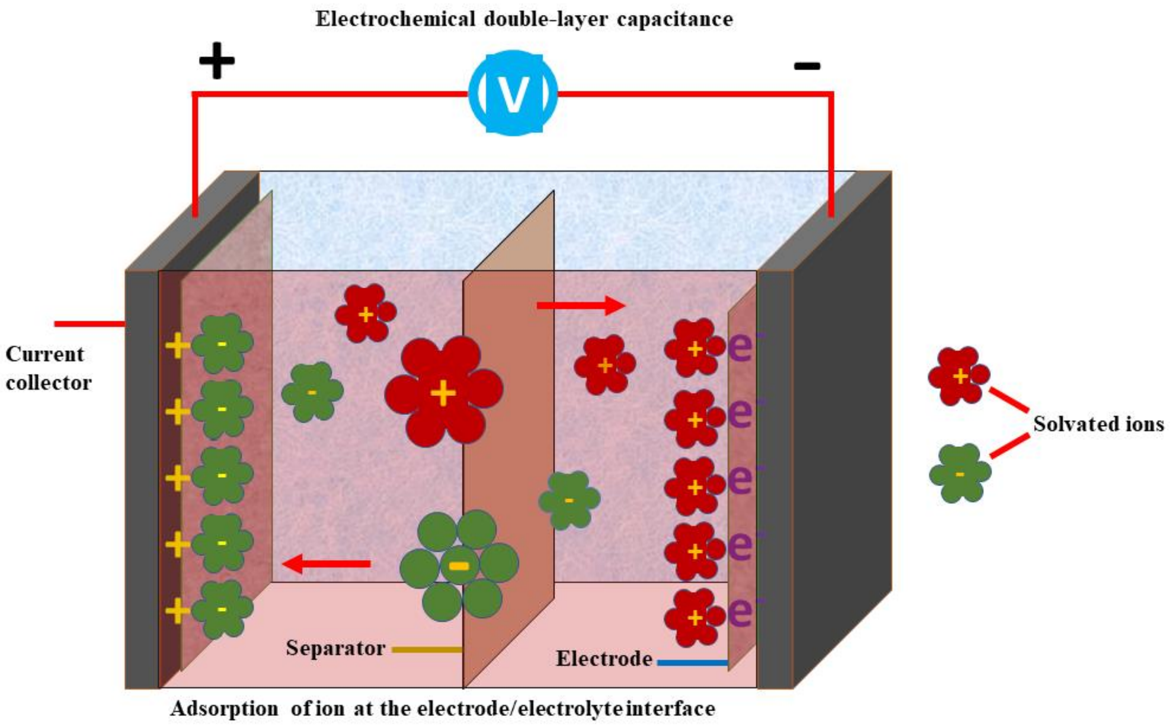

Fig 1.6: Illustration of an electrical double-layer capacitance

Figure 1.6 illustrates the mechanism of electrical double-layer capacitance. During the charging process, the electrons flow from the positive electrode to the negative electrode through an external voltage source. Simultaneously, positive ions (cations) and negative ions (anions) migrate toward the negative and positive electrodes, respectively. This movement results in the formation of as electric double layer at the electrode-electrolyte interface, with the width of the double layer determining the double layer capacitance. During the charging and discharging cycle, there is no transfer of charges across the electrode-electrolyte interface, and no net ions are exchanged, due to which negligible volumetric and structural changes occur in the electrode materials. This unique characteristic enables, the EDLCs to have tremendously long cycle lives of charging and discharging (usually upto 10^6 cycles) [24].

1.5.2 Pseudocapacitors

In the case of pseudocapacitors, the charge storage mechanism is based on the reversible and fast redox reactions occurring on the electrode surface or in the vicinity. Thus, pseudocapacitors exhibit higher energy density and capacitance compared to EDLCs. The capacitance in pseudocapacitors is usually 10-100 folds greater than that of EDLCs. In pseudocapacitors, the small change in charge (dQ) during a faradaic reaction is directly proportional to the change in electrode potential (dV), resulting in a measurable capacitance ($C = dQ/dV$) [25]. The term 'pseudo' originates as the capacitance, in this case, is not solely derived from the traditional double layer mechanism. It should be noted that double-layer capacitance coexists with pseudocapacitance, but because of the distinctive physical processes involved, different materials display different faradaic mechanisms. Figure 1.7 illustrates the various types of redox mechanisms that generate pseudocapacitance, as elaborated below:

1.5.2.1 Underpotential deposition

This phenomenon occurs when metal ions form a monolayer of adsorbed species on the surface of different metal, typically above their redox potential. The protons or the metal ions get adsorbed to the surface from the bulk electrolyte [26]. The underpotential deposition of Pb monolayer on the Au electrode is an example of underpotential deposition.

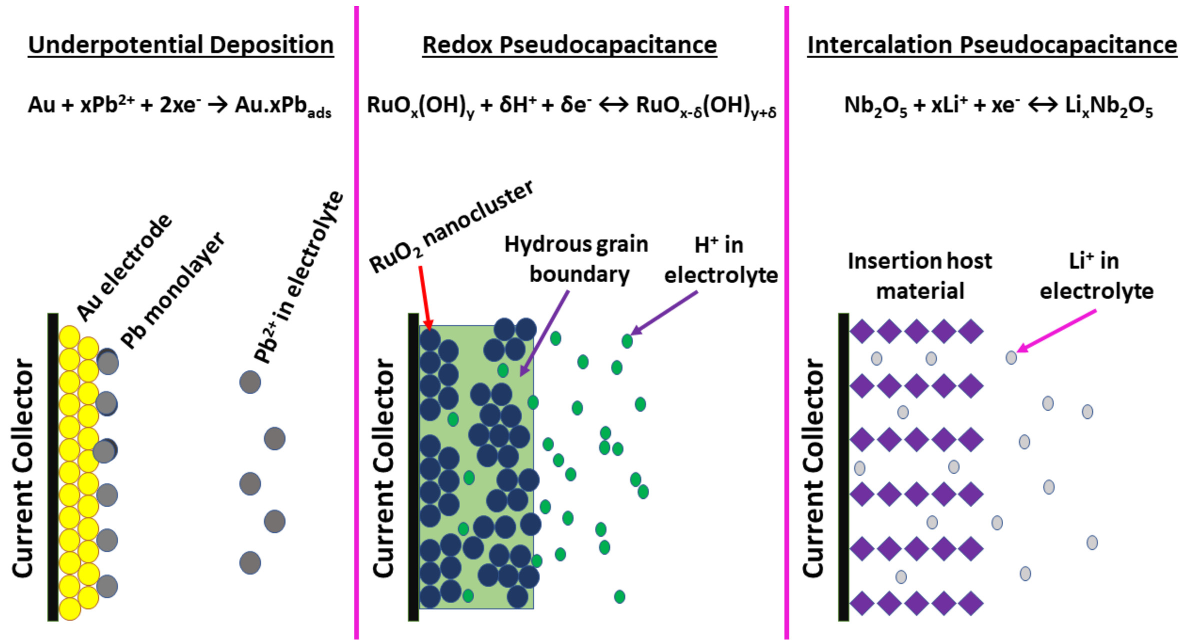

Fig 1.7: Different types of redox mechanisms for pseudocapacitance

1.5.2.2 Redox transitions

Pseudocapacitors are driven by redox transitions when electrochemical adsorption of ions takes place on or near the electrode surface, followed by redox reactions. The redox reactions on some electroactive materials, such as metal oxides and hydroxides, are the source of this pseudocapacitance. RuO_2 has been recognized as one of the most extensively studied redox-type pseudocapacitive materials, primarily due to its high specific capacitance. In its hydrous form, it exhibits capacitance values ranging from 200-1000 F/g. Additionally, conducting polymers exhibit electrochemical doping-dedoping and reversible redox transitions [27].

1.5.2.3 Intercalation

The intercalation of electrolyte ions, such as Li+, into the tunnels, van der Waals gaps, or lattice of redox-active electrode materials, such as MoO_3, coupled with a faradaic charge transfer, can also result in pseudocapacitance. It is important to note that the electrode only displays pseudocapacitive activity when the intercalation process is quick enough. If not, it will act like an electrode similar to that of a battery. Nb_2O_5 in lithium electrolytes demonstrates this kind of behavior.

1.5.3 Hybrid supercapacitors

The hybrid supercapacitors capitalize on the merits of both EDLC and pseudocapacitors as the limitations of one are absent in the other and vice versa. Consequently, the two together outweigh their respective limitations, and hybrid supercapacitors exhibit better specific capacitance as well as specific energy density. The hybrid systems demonstrate excellent power density and cyclic stability, which are the major barriers in pseudocapacitors. Hybrid supercapacitors can be classified into three types. Asymmetric type of hybrid supercapacitor uses one electric double-layer type electrode (such as carbon materials) and one pseudocapacitive electrode (such as metal oxides or conducting polymers). The second type uses one rechargeable battery-type electrode and one pseudocapacitive electrode. The third and last one employs composite materials derived from both pseudocapacitive and electric double-layer materials. The composite hybrid electrode used in supercapacitors can be made from conducting polymer, metal oxide, carbon-based material, or a combination of any of the three materials. The capacitive charged layer (electric double layer) and the backbone of the large surface area provided by the carbon-based materials improve the interaction between the electrolyte and the pseudocapacitive materials deposited on them [28]. Additionally, due to faradaic processes, the pseudocapacitive materials contribute to raising the capacitance of the corresponding composite electrode. The potential operating window, specific capacitance, corrosion stability, and cycle stability could all be augmented by the synergistic mechanism of carbon-based and pseudocapacitive materials. Asymmetric supercapacitors comprise two electrodes with different materials and help attain better energy and power densities than symmetric supercapacitors but are difficult to fabricate. Each electrode substantially impacts the overall characteristics of the supercapacitors in asymmetric systems since they are constructed from materials that are distinct from one another. In these systems, the performance of the device is restricted by the operational voltage window of each electrode, and electrochemical characteristics embrace the supercapacitor as a whole rather than the individual electrodes.

1.6 Components of a supercapacitor

Supercapacitors are fabricated with the help of a wide a range of components. They include electrodes, electrolytes, separators, sealants, and current collectors. Each element plays a crucial role in the performance of supercapacitors in practical applications as discusses below:

1.6.1 Electrode

To ensure optimal performance, the electrodes used in energy storage systems and conversion devices must possess excellent conductivity, chemical stability, corrosion resistance, and a substantial surface area. Additionally, they should be cost-effective and environmentally friendly. Electrodes are classified into different categories, such as conducting polymers, perovskites, metal oxides, and carbon-based materials [29].

1.6.1.1 Based on conducting polymers

Organic polymers that conduct electricity are referred to as conducting polymers. The valence electrons in conventional polymers like polyethylenes are bonded in sp^3 hybridized covalent bonds (σ bonds) which possess low mobility. Conducting polymers feature an alternating single and double-bond conjugated -system that is created by the overlap of carbon p_z orbitals. This results in a continuous backbone of sp^2-hybridized carbon centres. Conjugated polymers are effective electrical conductors with conductivities of about 10^4 S/cm.

Supercapacitor electrodes are made of various conducting polymers, including polyaniline (PANI), polypyrrole, polythiophene, and others which utilize redox reactions for storage and release of energy. During oxidation (doping), ions migrate into the core of conducting polymer while they return back to the bulk electrolyte solution during reduction (de-doping). As a result, charging takes place in the conducting polymer-based electrode's bulk material and on its surface; these electrodes exhibit high specific capacitance values. Polyaniline in particular, stands out as a conductive polymer with a theoretical specific capacitance of 2000 Fg^{-1} apart from being low cost, and it can be easily synthesized [16]. Due to these advantages, polyaniline (PANI) is widely employed in energy storage devices, especially supercapacitor applications.

However, it is noteworthy that only limited data is available on PANI-based devices that have been cycled more than 10,000 times. It has been reported that extended cycling of the polymer leads to mechanical breakdown due to the repetitive volume changes of the polymer electrode brought on by the doping and de-doping of counterions during the charge/discharge process. Additionally, PANI is vulnerable to oxidative deterioration with minor overcharging, which can negatively impact its performance [30].

1.6.1.2 Based on carbon

Currently, activated carbons are the most commonly used active materials in commercial EDLCs. This is mainly due to their unique combination of high surface area and conductivity. The are also preferred for their well-defined processing techniques and consistent availability. Apart from activated carbon, carbon nanotubes (single-walled or multiwalled), carbon fibres, graphene, and reduced graphene oxide etc., have also been investigated for supercapacitor applications. These carbon-based materials predominantly exhibit double-layer capacitance owing to the surface adsorption of ions on the electrode-electrolyte interface. Carbon-based materials do not take part in the redox transitions and therefore demonstrate better cycling stability than their pseudocapacitive counterparts [31].

1.6.1.3 Based on transition metal oxides

Certain metal oxides, such as CuO, ZnO, MnO_2, TiO_2, $NiCo_2O_4$, Co_3O_4, $CoFe_2O_4$, $CuFe_2O_4$, $CuCo_2O_4$ participate in quick reversible redox reactions at their surface, demonstrating strong pseudocapacitive behavior. These oxides have attracted significant research attention as they surpass that obtained from double-layer carbon materials. In order to boost the specific energy of conventional EDLCs while maintaining high power capabilities and long-term cyclability, pseudocapacitors have been developed. These materials may experience poor long-term stability and cycle life since the redox mechanisms that underlie their charge storage mechanism are the same as those found in batteries. Recent advancements have focussed on binary and ternary metal oxides compared to single ones. Binary transition metal oxides consist of at least one transition metal species and one or more electrochemically active or inactive ions. The synergistic effect of these components enhances the capacitance and expands the stable potential window, provides more electroactive sites, and improves stability. Due to the redox activities that occur during electrochemical reactions, all metal oxides exhibit pseudocapacitive properties [32].

1.6.1.4 Based on perovskite

Usually, perovskites are represented as MNX_3, where M, N are cations, and X is an anion. The X position is held by oxide and halide ions. The cations occupying the M site are generally bigger and more electropositive than the N site cation. The charge storage in these kinds of materials is due to the insertion of anions. $SrRuO_3$, $GdInO_3$, $SrTiO_3$, and $LaNiO_3$ are some examples of perovskite that have been reported as electrode materials.

1.6.2 Electrolyte

Electrolytes play a crucial role in electrochemical energy storage devices and supercapacitors. They are responsible for maintaining ionic conductivity, facilitating the formation of electrical double layer in EDLCs, and participating in reversible redox reactions in the case of pseudocapacitors. Consequently, the choice of electrolyte has a significant impact on the performance of supercapacitors. There are several different types of electrolytes that can be used, including ionic liquids, aqueous electrolytes, solid or semi-solid electrolytes, and organic electrolytes [33]. The classification of electrolytes has been illustrated in figure 1.8. Each type of electrolyte has its own set of characteristics and suitability for specific applications in electrochemical energy storage systems.

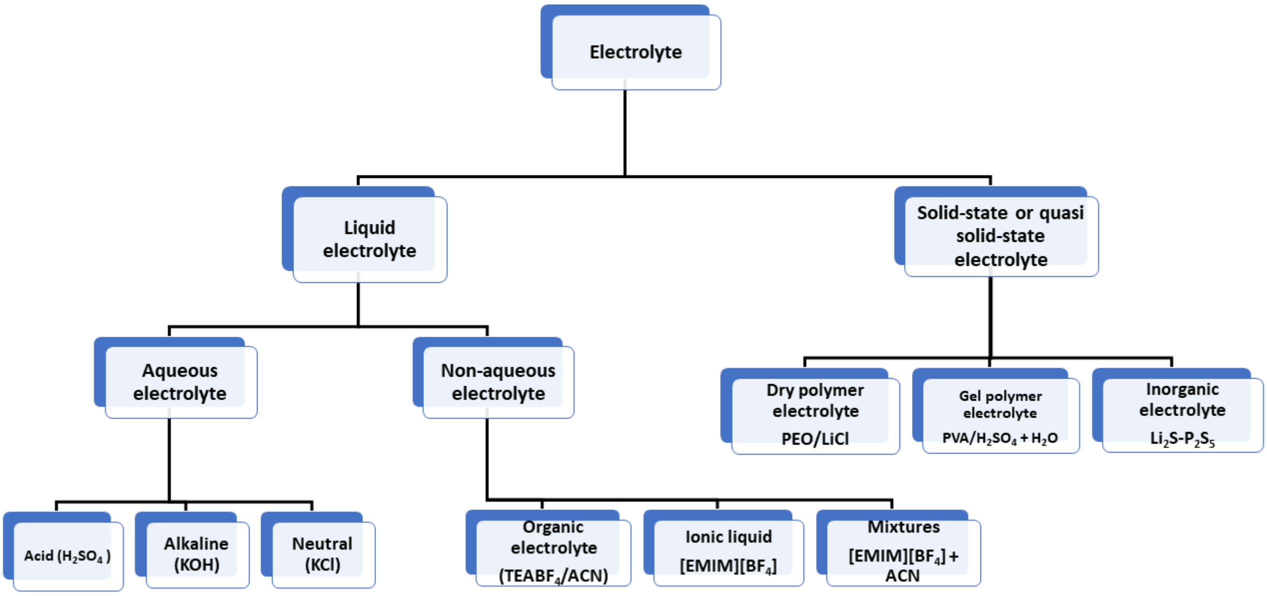

Fig 1.8: Classification of electrolytes for supercapacitors

The following are the key requirements for electrolytes in supercapacitors [34]:

(a) Wide potential window
(b) Electrochemically stable
(c) Low ionic radius
(d) Should provide ionic conductivity
(e) Low resistivity

(f) Non-toxic

(g) Non-volatile

(h) Availability in desired purity

(i) Low cost

As of yet, there isn't an ideal electrolyte that satisfies every requirement, and however, every electrolyte has merits and demerits. For instance, supercapacitors based on aqueous electrolytes have high conductivity and capacitance, but the electrolytes' low decomposition voltage restricts their working voltage. Acidic and neutral electrolytes corrode the electrodes rapidly in comparison to alkaline electrolytes [35]. Organic electrolytes can support higher voltages, but they have substantially lower ionic conductivity, and are more toxic, flammable, volatile, and costlier than aqueous electrolytes. Ionic liquids, on the other hand, provide a wider working potential window but offer high viscosity and lower ionic conductivity. Therefore, significant efforts have been devoted to enhancing the overall functionality of electrolytes. Solid or quasi-solid electrolytes help prevent electrolyte leakage but suffer from reduced ionic conductivity and energy density. Therefore, compared to electrochemical supercapacitors containing other electrolytes, aqueous electrochemical supercapacitors have better specific capacitance, energy density, and power density. This might be due to the narrow ionic radius and high ion concentration of aqueous electrolytes [36].

1.6.3 Separator

The separator located between the two electrodes serves to facilitate the flow of ions through the bulk electrolyte while preventing short circuit [36]. By meeting these requirements, a well-designed separator contributes to the optimal performance and safety of a supercapacitor.

1.6.4 Current collector

Electronically conductive components known as current collectors connect the active material on the substrate and the current source. During the charging or discharging process, they assist in transferring electric current from the current source to the working electrode. Commonly used materials for current collectors are copper, aluminium, stainless steel, iron, and various alloys. However, overtime and with an increasing number of cycles, supercapacitors experience higher resistance due to degradation in the active materials, deterioration of electrodes, and current collectors. As a result, the specific capacitance gradually decreases. Thus, active materials are blended with polymeric-binding substances such as Nafion, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and others. This blending helps to ensure the integrity of the active material with the current collector over an extended period of time [37]

1.6.5 Sealants

An essential part of cell assembly is proper sealing. With time, surface oxidation of the electrode, gas evolution from the electrolyte, packing, and corrosion poses challenges. Sealants also assist in preventing contaminants that are carried in by external elements like chemicals, air, water, etc. These contaminants have the potential to degrade the electrolyte and trigger undesired oxidation reactions on the electrode surface. If not properly sealed, the supercapacitor assembly may experience shunt resistance, thereby mandating alternative current routes, which may harm their overall performance. Mostly, polymeric materials are used as sealants as they offer better flexibility and moisture resistance [38,39].

1.7 Advantages of supercapacitors

Supercapacitors offer several advantages over other energy storage devices, which are outlined below:

(a) High specific power density: The specific power density of supercapacitors (1-10 kW kg^{-1}) is much high higher than lithium-ion batteries (about 150 W kg^{-1}). The charging-discharging rates are higher in supercapacitors, making them suitable for high-power delivery applications [40].

(b) Longer cycle life: Typically, the electrode materials undergo irreversible phase changes and interconversion during faradic transitions in batteries, whereas in the case of supercapacitors, the reactions are reversible in nature. The life expectancy of electrochemical supercapacitors is nearly 30 years or 50000 to 1000000 charge-discharge cycles. The lithium-ion batteries exhibit a life cycle of 5 to 10 years with about 1000 to 10000 charge-discharge cycles.

(c) High efficiency: The operation of supercapacitors is reversible throughout the potential window over a charge-discharge process, and the losses due to heat dissipation are relative to smaller magnitude. The cycle efficiency of supercapacitors is high (upto 95%) even at 1 kW kg^{-1} [41].

(d) Longer shelf life: Rechargeable batteries corrode and self-discharge if left unused for extended periods, rendering them useless. On the other hand, Supercapacitors maintain their capacitance and can thus be recharged to their initial condition [42].

(e) Wide operating temperature: Supercapacitors are designed to operate reliably in a wide range of temperatures with capabilities ranging from as low as 40°C to as high as 70°C. Such dependable energy sources are employed in military applications to maintain under challenging circumstances [43].

(f) Safety: Supercapacitors are safer than batteries, especially lithium-ion batteries, which sometimes explode due to heat dissipation that create a thermal runaway condition

(g) Environmental friendliness: Supercapacitors typically use non-toxic materials, and the waste by-products are easy to dispose of.

1.8 Challenges for supercapacitors

Supercapacitors have several advantages over fuel cells and batteries, but they do face certain difficulties in specific areas [44]. These include:

(a) Low energy density: The specific energy density in the case of supercapacitors (~5 Wh/kg) is much lower than batteries (upto 150 Wh/kg). This requires stacking multiple supercapacitors in applications demanding higher energy densities, which eventually raises the cost.

(b) High cost: Individual components such as electrode materials, electrolytes, current collector, separator etc., add to the total cost of fabrication. Expensive transition metal oxides like RuO_2 and high surface area carbon materials are used in commercial supercapacitors. Further, the use of organic electrolytes instead of aqueous electrolytes may also increase the cost.

(c) High rate of self-discharging: The rate of self-discharging in the case of supercapacitors is quite high, which is a significant drawback. To overcome this, innovative and highly efficient electrode materials need to be developed. Only then devices for various real-world applications can be fabricated.

(d) Complex electronic control and switching equipment: Unlike practical batteries, complex electronic control and switching equipment is required for effective energy storage and recovery, which may increase costs and, subsequently, its adaptability.

(e) Risk of spark hazard: Due to the very low internal resistance of the supercapacitors, there is always a risk of extremely rapid discharge, which may also lead to spark hazards.

(f) Power availability duration: In the case of supercapacitors, power is available only for a very short duration as opposed to batteries.

1.7 Various applications of supercapacitors

The demand for portable energy storage technology is growing day by day. Due to its high-power density and long cycle life, the supercapacitor has surged into this market by replacing these conventional energy devices in certain applications. Supercapacitors are preferable for applications where a fast rate power supply is required [45,46]. Some notable applications of supercapacitors have been listed below:

(i) Memory backup: Supercapacitors can serve as power backup to PC cards, RAM, SRAM, and other components ensuring data preservation during unexpected power outages. In solid-state discs, they have been widely utilized alongside conventional capacitors.

(ii) Defence and military applications: Supercapacitors can be 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 antenna, missiles, and GPS.

(iii) Automobile applications: Supercapacitors can be used in electric vehicles charging and regenerative braking systems. They contribute to efficient energy storage and retrieval during vehicle operation.

(iv) Medical applications: Supercapacitors can be utilized in the healthcare industry as a power backup system to run various pieces of medical equipment and prevent catastrophic failure.

(v) Miscellaneous applications: Supercapacitors can also be employed in portable consumer electronics and security applications to provide power in case of a power outage.

1.8 Motivation and scope of work:

As the global consumption of fossil fuels continues to rise, leading to environmental issues like greenhouse gas emissions and air pollution, the need for sustainable, renewable, and clean energy sources such as solar, wind, and tidal power has become increasingly urgent. Given that these renewable energy sources are often intermittent and dependent on factors like time of day and location, it is crucial to develop effective energy storage devices to fully utilize them. Electrochemical energy storage devices, including batteries and supercapacitors, are expected to play a vital role in enabling the widespread and sustainable use of energy from these renewable sources, particularly in addressing challenges related to the scarcity of sustainable energy sources. Beyond conventional batteries and capacitors, there is a significant need for high-performance supercapacitors to bridge the gap in efficient energy storage solutions with lower environmental impact. Supercapacitors offer significant advantages, including high power density, rapid charge-discharge rates, and long cycle life. However, their practical use is limited by relatively low energy density, as previously mentioned. One of the most effective strategies to enhance energy density is augmenting the specific capacitance of their electrode materials and consequently the specific energy density. Additionally, the growing market for electronic devices demands energy storage solutions that not only deliver high energy and quick charging but longer cycle lives. In addition to achieving high specific capacitance, other critical properties for supercapacitors include energy density, power density, capacitance retention, and low internal resistance must be taken into account. These characteristics, including specific capacitance, depend heavily not only on the electrode material but also on the electrolyte and the overall energy storage system. In this discussion, we primarily focus on the electrode materials. A review of recent research on available electrode materials reveals that no single material meets all the requirements for supercapacitor electrodes, with each having specific drawbacks that need to be addressed. Therefore, the strategy of developing hybrid composite materials by combining different species uses their advantageous characteristics might prove to be promising. Considering the strengths and limitations of the existing electrode materials, the scope of work for current study has been structured as follows:

(i) To identify the best individual low cost materials for ternary composite materials based on their individual characteristics of electrochemical performance and environmental impact.

(ii) To synthesize the preliminary ternary composite materials with reasonable trade-offs for various properties and to evaluate their electrochemical performance for supercapacitor applications.

(iii) To optimize the constituents of these composite materials for best performance.