CHAPTER 1

Introduction

Introduction

Energy serves as a fundamental input in numerous manufacturing and consumption activities, making it a key driver for economic growth. It is one of the most critical components of economic development. Energy is vital for the operation of any modern economy, fueling industrial development and enhancing productivity. It is argued that, increases in energy consumption are directly linked to rises in gross domestic product (GDP) [1]. The energy crises of the 1970s and soaring energy costs significantly impeded economic progress [2]. Since the late 1970s, there had been considerable research in finding the relationship between energy consumption and economic growth [1, 2, 3]. Energy systems play a pivotal role in collecting energy from various sources and converting it into the forms necessary for diverse industries and sectors, including transportation, manufacturing, construction, and utilities. Fossil fuels and other energy sources can be readily stored to meet consumer demand when needed. In contrast, energy derived from renewable sources including wind and solar requires captures during peak availability and storage for subsequent use. Thus, energy storage systems are essential for functions including load leveling, power quality and reliability [1-3].

1.1 Importance of energy storage

Storing energy for future use is the most basic form of energy storage. This capability reduces the need for fuel dependent backup power sources like generators. In recent times, there has been a constant demand for sustainable, economical, and efficient energy sources to meet the world's rising energy needs as technology advances. The new energy economy is redefining the need for a global shift in energy dependence from conventional fossil fuel based resources to renewable sources [5]. As a result, renewable energy sources are being prioritized to provide clean energy. Many initiatives are being made to harness energy for renewable clean energy sources, such as solar, wind, and tidal energy which can reduces reliance on fossil fuels and enable zero carbon emissions in the environment [6, 7]. In general, multiple kinds of energy storage systems exhibited, which fall into different categories. Among these, electrochemical energy storage technologies, like rechargeable batteries and supercapacitors stand out as highly efficient and promising because of their impressive energy and power density, durability, small size as well as simple assembly process. [6-8]. Electrochemical energy storage devices have revolutionized the world of portable electronics, and are also used in electric vehicles. A "Ragone plot" [8, 9] is frequently used to display the relationship between specific energy as well as specific power storage characteristics of various electrochemical energy storage types (Figure 1.1). This plot highlights the advantages and disadvantages of each storage type for applications requiring different energy storage capacities and on demand energy extraction rates. Additionally, it helps to determine which energy storage option is best suited for a given application or set of requirements. Here, specific power density or power density is defined as the rate of energy transfer per unit volume or mass, and specific energy or energy density is defined as the amount of energy accumulated per unit volume or mass [8]. As a result, a device that offers high energy and power density is always preferable.

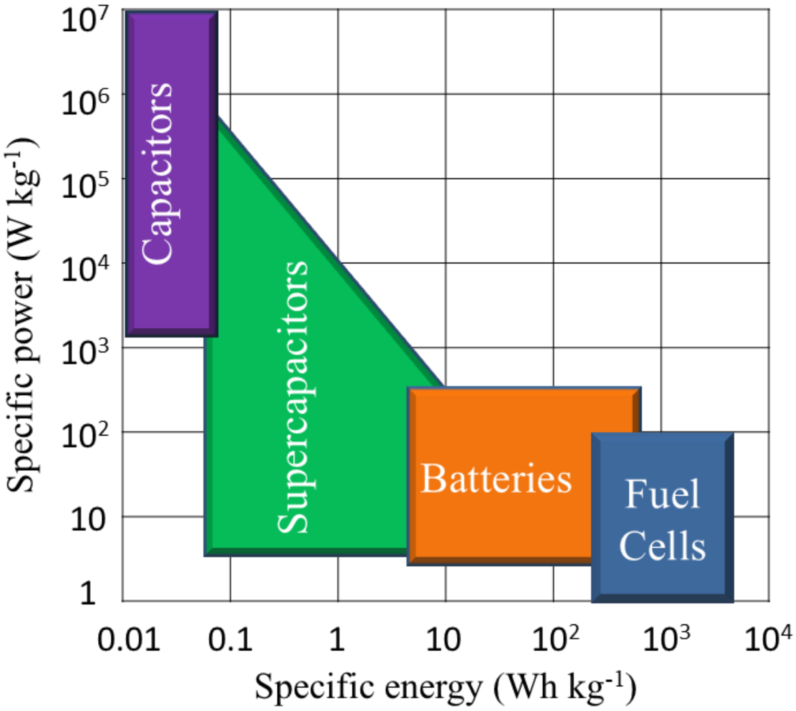

Figure 1.1: Ragone plot of various electrochemical devices.

1.2 Electrochemical ways to store energy

1.2.1 Battery

Batteries are the form of energy storage device that can be broadly classified into two categories viz primary batteries and secondary batteries. The redox reactions that occur in primary batteries are irreversible, meaning they cannot be electrically recharged. Secondary batteries, on the other hand, undergo reversible Faradic redox processes. Rechargeable batteries are another common name for secondary batteries. Batteries have comparatively high energy storage capacity than electrochemical capacitors. The outcome of a battery is a lower power density but higher energy density. Therefore, the development of electrode as well as electrolyte materials that can provide high energy and power density at a reasonable cost is one of the main goals in rechargeable battery research [10]. Over the past thirty years, research on rechargeable batteries such as lithium ion (LIBs) and lead acid batteries (LEAs) has received the highest priority in electrochemical energy storage technologies [5-7]. Despite the fact that, lead acid batteries have been available for a while, the invention of rechargeable Li-ion batteries, which debuted in 1991, significantly altered humankind's modern way of life. $LiCoO_2$ was used as the cathode and graphitic carbon as anode in the first Li-ion battery [11, 12]. Most portable electronic devices, including laptops and cell phones, are powered by Li ion batteries. However, due to the scarcity and rising expense of Li resources, there are now rising doubts about the sustainability of Li based batteries [13]. Therefore, cost effective and sustainable electrochemical energy storage technologies must be developed using resources that are mostly found on the Earth’s crust and, if possible, locally accessible over a wide range of geographic locations. As a result, there has been a surge in research on battery chemistries that utilize ions other than Li ion, like Na^+, Mg^{2+}, K^+, Zn^{2+}, and Al^{3+} ions etc.

1.2.2 Electrochemical capacitor/Supercapacitor

Energy storage technologies, such as lead acid and metal ion batteries, deliver high energy densities but are hindered by their poor power densities and short operational life time. A conventional capacitor works as an energy storage device by isolating the opposite charges through the application of electric field. The energy stored is released as electrical power. Yet, the specific capacitance of a conventional capacitor is restricted to the microfarad range as only the electrode’s surface area is used for charge storage. To address this limitation, supercapacitors (or ultracapacitors/electrochemical capacitors) have been developed because of their high power density [14]. Similar to conventional capacitor, supercapacitors also composed of two electrodes having electroactive materials of high surface area. The electrodes are called cathode and anode, and they are separated by an electrolyte. The last twenty years have seen a great deal of research on supercapacitors because of their capacity to withstand millions of rapid charge/discharge cycles and instantaneous power supply [14-18]. Supercapacitors employ a range of electrolytes and high surface area electrodes to achieve optimal electrochemical performances [19]. Typically, the maximum voltage that a supercapacitor can withstand with water based electrolytes is approximately 1.23 V. However, with non aqueous electrolytes such as organic or ionic liquid electrolytes, the voltage can surpass 3 V [20-22]. Depending on charge storage processes, supercapacitors are classified as either electrochemical double layer capacitors (EDLCs) or pseudocapacitors [23, 24]. In EDLC, charges are accumulated at the electrode-electrolyte interface through the formation of electrochemical double layers. In contrast, in pseudocapacitors, rapid redox reactions occur in the electrodes [24, 25]. Additionally, there is a type of supercapacitor known as hybrid supercapacitor. It is the improved version of EDLC and pseudocapacitors designed to address the shortcomings of their individual charge storage mechanisms. It stores charges using a combination of chemical and physical processes [14]. The electrochemical performance of supercapacitors is significantly enhanced by the developments in nanoscience and nanotechnology. This is because extremely high surface electrode materials could be achieved in nanostructured materials and the electrolyte can access more area in these materials resulting in higher ion flux. The electrodes used in EDLCs are typically carbon nanomaterials like graphene and carbon nanotubes [26]. Pseudocapacitor electrodes can be made from various materials such as transition metal hydroxides and oxides, electrically conducting polymers, MXenes, transition metal dichalcogenides (TMDs) and metal-organic frameworks [27-33].

Supercapacitors are also categorized as symmetric, asymmetric, or battery type depending on the arrangement of the electrodes within the cell [14]. Symmetric supercapacitor uses two similar electrodes, whereas asymmetric supercapacitors employ two different electrode materials. Since the supercapacitor electrode do not have higher energy density than the battery electrodes, therefore, a third form of supercapacitor known as battery type hybrid supercapacitor exists where one of the electrodes is battery type [14]. Metal ions, such sodium and lithium ions, are incorporated into the electrode nanostructure for charge storage, which results in the high energy density [34]. A block diagram classifying the supercapacitors is shown in figure 1.2.

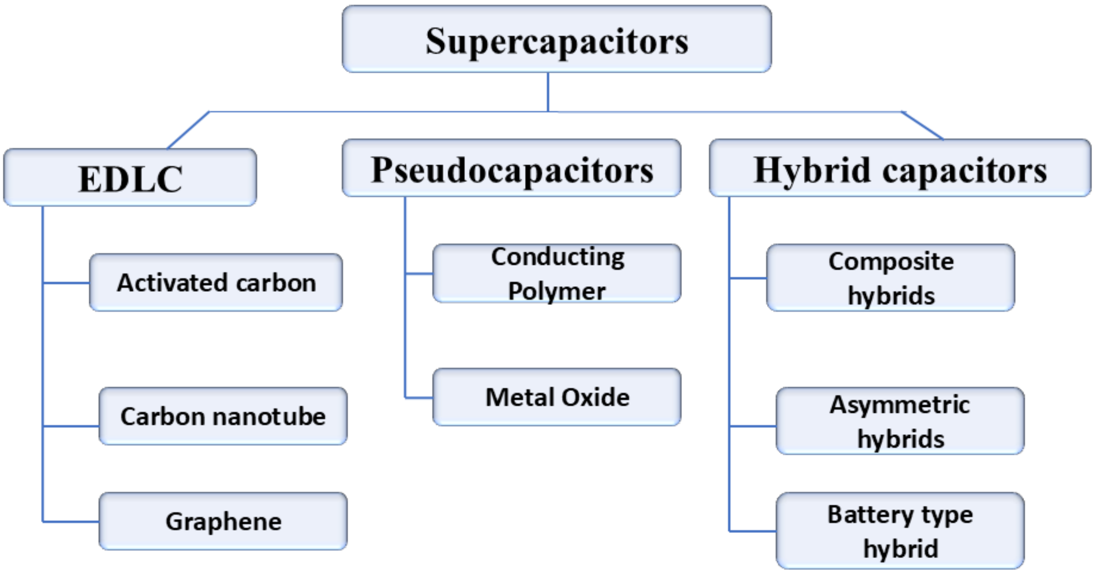

Figure 1.2: Block diagram of different classes of supercapacitors

1.2.2.1 Electric double layer capacitor (EDLC)

Becker was the first person who introduced the idea of EDL capacitance in 1957 using an aqueous electrolyte and a porous carbon substance [35]. Later, Helmholtz proposed the double layer charge storage process [36]. It states that, depending on the size of the ions in the electrolyte, oppositely charged ions are adsorbed at the electrode/electrolyte interfaces. Through Coulombic contact, the ions with opposite charges form in the electrolyte near the electrode, keeping the system's charge neutrality intact. Figure 1.3 shows the EDL formation between the electrode and electrolyte. The double layer formation is somewhat close to that of a traditional capacitor, where the double layer capacitance can be derived as:

$$C = \frac{\varepsilon A}{d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1.1)$$

where "C" represents the capacitance, "ε" represents the permittivity of dielectric medium, "A" represents the surface area of the electrode and "d" represents the distance between the electrode and electrolytic ions [37]. This kind of charge storage is generally found in carbon-based materials such as graphene, carbon nanofibers, graphene derived carbons, carbon nanotubes [38-40].

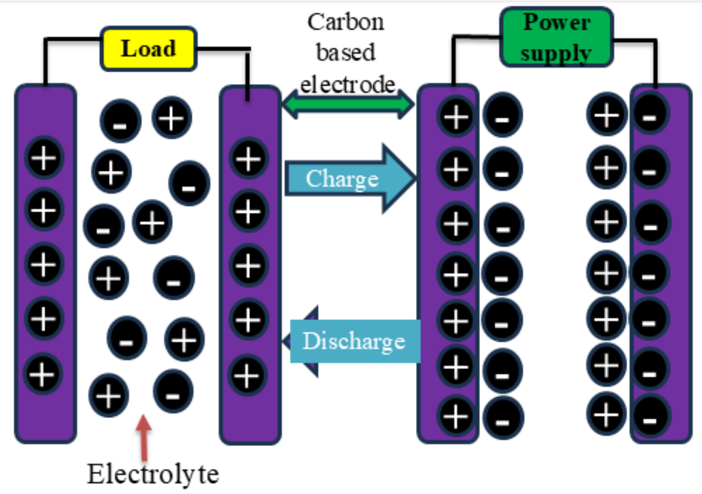

Figure 1.3: Mechanism of EDLC type electrochemical capacitors (supercapacitors)

Additionally, EDLC stores charges electrostatically, therefore, any changes in potential cause them to react instantly. Moreover since, there is no faradic reaction, they have a high power density but a low energy density. Because the physical adsorption of electrolytic ions inhibits their energy density, which creates a barrier to their practical applicability [41, 42]. Gouy and Chapman, proposed a different model for double layer formation, who took into account the thermal motion of ions and treated them as point charges. This concept states that the solution's temperature fluctuation causes the "diffuse layers" of oppositely polarized ions to balance the electrode's surface charge. By taking into account the ions' finite size, Stern [43-44] altered Gouy and Chapman's model where the overall capacitance of the double layer was estimated by considering both the Helmholtz/diffusion layers. Then, Grahame improved Stern's model by taking into account the fact that anions and cations have various sizes, as a result, the anions and cations have varying distances from the electrode [43-44]. Several factors affect the EDLC component of the double layer, including the solvent for the electrolyte, the size and concentration of ions, their specific absorption, and the interaction between the ions and solvent. The electrodes in EDLC systems, composed of thin EDL and porous carbon material with an extremely high specific surface area (approximately 2000 m^2g^{-1}), result in high capacitance value [45]. Besides, the pores in the carbon materials also significantly impact the dynamics of electrolytic ions and, hence, the specific capacitance value. If the two electrode surfaces are denoted by ES(1) and ES(2), the cations and anions are represented by C^+ and A^-, respectively, and the EDL is represented by //. Thus the reversible charging-discharging process of EDLC may be stated as follows:

Anodic reaction: $ES(1)+A^- \leftrightarrows ES(1)^+//A^- + e^-$

Cathodic reaction: $ES(2)+e^- + C^+ \leftrightarrows ES(2)^-//C^+$

As charging occurs, the cations in the electrolyte are attracted to the cathode and the anions travel towards the anode under the influence of an external power supply. While preventing short circuit between the cathode and anode, the membrane selectively permits the passage of electrolyte ions from one side to the other. As a result, the device stores the energy. This stored energy is used when electrons move from cathode to anode during discharge. However, electrodes do not alter their structure and, hence, the electrodes have an exceptionally long cycle life (~10^5 cycles) [46]. Therefore, due to the quick reversible charge storage and release at the electrode and electrolyte interfaces, supercapacitors utilizing the EDLC process exhibit high power density (greater than 500 W kg^{-1}) [46]. But while comparing to battery energy densities, EDLC supercapacitors have a lower energy density since these physical charge transfer phenomena are limited to the electrode’s surface. This disadvantage can be improved by employing pseudocapacitive mechanism.

1.2.2.2 Pseudocapacitor

In 1997, Conway described that pseudocapacitors have comparable electrochemical properties to EDLCs, but their charge storage process differs greatly from that of typical EDLCs because extremely reversible faradic redox processes occur at the surface and subsurface regions of the electrode materials [47, 48]. The pseudocapacitors are divided in three different subcategories according to the charge storage mechanism: (i) surface redox reaction or intrinsic pseudocapacitors (ii) intercalation type reaction or intercalation pseudocapacitors and (iii) battery type faradic reaction or extrinsic pseudocapacitors (Figure 1.4).

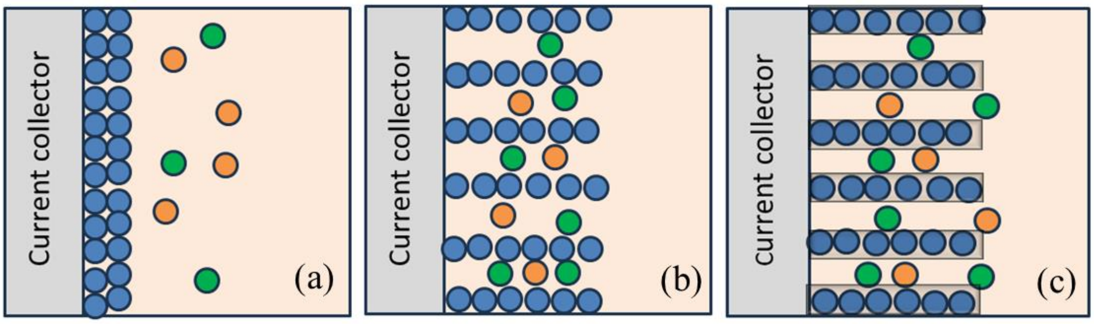

Figure 1.4: Three different pseudocapacitors: (a) Intrinsic pseudocapacitor, (b) Intercalation pseudocapacitor and (c) Extrinsic pseudocapacitor.

Typically, the specific capacitance of pseudocapacitors is 10-10^2 times higher than EDLC [49]. However, their cyclic stability is generally lower due to the degradation of the electrode materials from the electrolyte ions penetration and redox reactions within the electrode [49]. Thus, higher specific capacitance is achieved by pseudocapacitors at the expense of cycle life. The main challenge facing the field of supercapacitors is extending the cycle life of pseudocapacitive materials.

1.2.2.3 Hybrid Supercapacitor

A hybrid supercapacitor is special type of electrochemical capacitor that integrates multiple energy storage mechanisms to enhance the performance. Supercapacitors based on EDLC have long cycle life and high power densities, but poor energy density remains a barrier for long term use. Conversely, pseudocapacitors are better because of their high energy densities, but they are not very good at producing high power and have a short cycle life. Therefore, a method for creating a hybrid supercapacitor that combines a battery type electrode and a supercapacitor (EDLC) electrode may be able to address the energy and power issues related to each of its separate counterparts. As a result, a single device can achieve great energy and power densities [14]. Depending on the electrode configurations, hybrid capacitor can be in three different forms: first one is composite hybrid supercapacitor. It combines the properties of both carbon and metal oxides in a single electrode. It exhibits synergistic advantages such as improved specific capacitance, better cycling stability and superior conductivity. Second one is asymmetric hybrid supercapacitors, which uses two different electrodes. One electrode is made of carbon based materials that act capacitively and are usually cathode, whereas the other electrode is composed of metal or metal oxides or conducting polymers, which operate via Faradic reactions and are typically anode. Through this arrangement, a hybrid capacitor can achieve both high energy as well as power density simultaneously. Thirdly, the hybrid capacitor is battery type hybrid capacitor. It again consists of two completely different electrodes (battery electrode and supercapacitor electrode), thereby having two different storage mechanisms in the same device. The energy density and power density can be improved by either increasing the power density of the battery electrode or energy density of the supercapacitor electrode [50].

1.3 Importance of aluminum-ion based energy storage devices

Aluminum (Al) ion batteries have garnered lot of interest lately. There are tremendous advantages such as high abundance in the Earth's crust (~8 %) and small ionic radius (0.54 Å) [51] Moreover, Al has the highest volumetric capacity (8046 mAhcm^{-3}) compared to Na (1050 mAhcm^{-3}), Mg (3868 mAhcm^{-3}), K (609 mAhcm^{-3}), Zn (5857 mAhcm^{-3}), and Ca (2061 mAhcm^{-3}). The large volumetric capacity of aluminum indicates that the energy storage per unit volume is also higher which subsequently aids in the batteries total size reduction. Additionally, metallic Al is easy to handle at ambient atmosphere, resources for Al are less expensive, and its three electron electrochemistry is an attractive trait. A comparison of the volumetric capacities, ionic radius, and abundance of some selected ions is provided in below (Table 1.1) [51].

Table 1.1: Comparison of abundance, ionic radius and volumetric capacities of some selective metal ions

Ion	Ionic radius (Å)	Volumetric capacity (mAhcm^{-3})	Abundance (wt %)	E Vs SHE
Lithium (Li^+)	0.76	2042	0.002	-3.04
Zinc (Zn^{2+})	0.74	5857	0.007	-0.76
Magnesium(Mg^{2+})	0.72	3868	2.33	-2.37
Calcium (Ca^{2+})	1	2061	4.15	-2.87
Aluminum (Al^{3+})	0.54	8046	8.23	-1.66

There are substantial studies on Al ion chemistry. For example, Holleck et al. explored an Al-ion battery using a vitreous carbon based electrodes with an $AlCl_3$-KCl-NaCl molten salt as non-aqueous electrolyte [52, 53]. Archer et al. studied an Al-ion battery incorporating V_2O_5 nanowires using $AlCl_3$ and 1-methyl-3-ethylimidazolium chloride (MEICl) ionic liquid as the electrolyte, which exhibits discharge capacity around 273 $mAhg^{-1}$ after 20 discharge cycles [54]. Similarly, Lin. et al. investigated an Al-ion chemistry through pyrolytic graphite/porous graphitic foam cathode, utilizing $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride ionic liquid as the electrolyte [55]. This Al/graphite cell demonstrated high power density of about 3000 W kg^{-1} and operated for 7500 cycles without capacity loss. Xu et al. reported Al ion battery with Aluminium as anode and graphite as cathode in $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride based ionic liquid, which delivered a cathodic capacity 112 $mAhg^{-1}$ and high capacity retention (97.3 %) after 30,000 discharge cycles [56].

1.4 Al-ion supercapacitor

Recently, the concept of electrochemical capacitors focused solely on Al^{3+} ion storage has garnered significant attention [57]. There are several studies explored in the area of Al-ion supercapacitors. For examples, Thalji et al. studied the performance of an asymmetric supercapacitor utilizing $W_{18}O_{49}$ nanowires and reduced graphene oxide for Al^{3+} ion storage, achieving specific capacitance about 350 Fg^{-1} at current density of 1 Ag^{-1} up to 12,000 cycles [58]. Likewise, Li et al. investigated an asymmetric capacitor with $W_{18}O_{49}$/SCNT and polyaniline/SCNT electrodes, exhibited energy density about 19 mWh cm^{-3} at power density around 295 $mWcm^{-3}$ [59]. Ma et al. described an Al^{3+} ion capacitor employing graphene and MXene as electrode materials in the operating potential up to 2 V, delivering a high energy density 112 Wh L^{-1} and power density about 30000 W L^{-1}, and long lifespan over 10000 cycles [60]. Tian et al. presented an Al^{3+} ion symmetric capacitor based on a V_2O_5 mesoporous carbon composite electrode, which delivered an energy density 18 Wh-kg^{-1} and power density 147 W kg^{-1} over 10,000 discharge cycles [61]. Ai et al. illustrated the Al^{3+} ion storage capabilities of PEDOT conducting polymer, showing that an asymmetric electrochemical capacitor based on PEDOT and activated carbon could achieve energy and power densities about 41 Wh kg^{-1} and 0.24 kW kg^{-1}, respectively [62]. However, significant challenges remain in the intercalation of Al^{3+} ion due to the strong electrostatic repulsion between the cations and intercalation framework. Additionally, there a lack of suitable materials with advanced nanostructures that would facilitate the efficient insertion and extraction of Al^{3+} ions [59].

1.5 Aqueous electrolytes

Although, the non aqueous (organic solvent) Li-ion batteries are available in the market but there are many safety risks such as flammable, harmful leakage, toxic, and low ionic conductivity, and high costs due to the low abundance of lithium. Therefore, non volatile aqueous electrolyte based batteries are gaining interest which can mitigate the risk of thermal runway and minimize the costs by using low cost salt in the electrolyte [63]. It has also some other advantages such as environmentally friendly and high ionic conductivity (10^{-1} S cm^{-1}) compared to organic electrolytes (10^{-3}-10^{-2} S cm^{-1}), polymer electrolytes (10^{-7}-10^{-3} S cm^{-1}) and inorganic solid electrolytes (10^{-7}-10^{-2} S cm^{-1}) [63]. These properties enhance the power density as well as the rate capability, and easy to assemble in an ambient atmosphere. Dahn et al. were the first in 1994, reported the Li-ion cell ($LiMn_2O_4$ as cathode and VO_2 as anode) with 5 M $LiNO_3$ and 1 M LiOH aqueous electrolytes which exhibited the potential window about 1.5 V and energy density of 175 Wh kg^{-1}, which is larger than lead acid batteries [64, 65]. But its cycle life was limited to only 25 cycles. There are some other reports where Li-ion based aqueous electrolytes were utilized in $LiFePO_4$ $LiMnPO_4$ and $LiNiPO_4$ cathode materials [66-69]. Liu and coworker investigated the Al ion behavior in anatase TiO_2 using $Al_2(SO_4)_3$ aqueous electrolyte [70]. Lahan et al. studied Al^{3+} ion intercalation and deintercalation in MoO_3 using various Al-based aqueous electrolytes like 1 M $AlCl_3$, 0.5 M $Al_2(SO_4)_3$ and 1 M $Al(NO_3)_3$, where they observed that MoO_3 exhibited better stability as well as storage performance in 1 M $AlCl_3$ as compared with other two electrolytes [71]. Kumar and his coworkers demonstrated the Al-ion storage performance in $FeVO_4$ (about 350 $mAhg^{-1}$) using aqueous electrolyte [72]

Additionally, potential window of different electrolytes plays an important role in case of electrochemical capacitor. In general, energy density as well as power density are proportional to the square of the potential window. Therefore, wider potential window is always beneficial for electrochemical capacitors. Theoretically, aqueous electrolyte provides a narrow potential of 1.2 V [73-76]. However, there are examples of aqueous electrochemical capacitors working beyond 2 V with the strategy of water in-salt concept [77, 78]. But again, the high concentration of salts can limit the use to a large scale. Moreover, self discharge is a frequent issue encountered in aqueous batteries. This phenomenon involves the gradual depletion of battery's charge, even when it's idle, due to internal chemical processes [63]. Therefore, it is a challenge to increase the stable potential window in low cost as well as to obstruct the high self discharge rate.

1.6 Gel electrolytes

Although aqueous electrolytes are being used in electrochemical energy storage because of their high ionic conductivity (~10^{-1} S cm^{-1}) but there are certain issues such as electrolyte leakage, instability in the internal interfaces and functionality of the separator [79]. Therefore, gel polymer electrolytes (GPEs) are gaining attention. These are mainly a viscous solution in which a host polymer matrix is mixed with an electrolytic salt and solvent. GPEs are also called to as hydrogel, when aqueous solvent is used. In general, the polymer matrices in gel are linked by either physical forces, such as electrostatic interactions, hydrogen bonding, chain entanglements, or chemically via covalent bonds, making them thermoset and irreversible [80]. The polymers in gel electrolyte, encapsulate the liquid to prevent its escape. GPEs can be used both as electrolyte and as separator [79, 81-83]. Due to the workable property of polymers, GPEs can be arranged in different shapes with high flexibility [84-86]. Moreover, flexibility or the elasticity in GPEs are favorable with the volume change of the active electrode materials during charge and discharge process [87-92]. In case the Li ion battery, gel electrolyte help prevent dendrite growth on anode as well as minimize the reactivity between anode and liquid electrolyte, and hence can improve the safety and manufacturing integrity [92]. To achieve a high performance GPE, there are several criteria for choosing the host polymer such as speedy segmental mobility of the polymer chain, special groups for the easy dissolution of salts, relatively low glass transition temperature, high molecular weight, wide electrochemical window and enhanced degradation temperature [93-94]. Polyvinyl alcohol (PVA) is the most commonly used host polymer for forming GPE. It has many advantages including low cost, easy processing, easy film formation [64, 95]. In 1988, Petty et al. reported the development of polyvinyl alcohol based proton conductive (PVA/H_3PO_4) gel electrolyte with high ionic conductivity [96]. Later, Karthika et al. fabricated a flexible paper-based supercapacitor using carbon nanotube covered electrodes and PVA/H_2SO_4 gel electrolyte, which exhibited a remarkable specific capacitance of 270 Fg^{-1} and energy density of 37 Wh kg^{-1} [97]. There are many reports, where, researchers focused on various gel electrolytes, such as: PVA/H_2SO_4 [97-104], PVA/KOH [98-106], PVA/LiOH [107], PVA/Na_2SO_4 [108], PVA/KNO_3 [109], PVA/KCl [110], PVA/LiCl [111, 112]. Yu et al. demonstrated a Et_3/NH_4Cl based gel polymer electrolyte in a wider potential window (~0-2.96 V) for a quasi state Al ion battery [113]. Ge et al. highlighted the reduction of self discharge voltage in solid state supercapacitor using PVA [114]. Lu et al. introduced silica in 2 M Li_2SO_4 and 1 M $ZnSO_4$ and prepared gel electrolyte which could increase the rate capability (~10-12 %) and decrease the self discharge voltage (up to 15 % after 24 hours) compared to aqueous electrolyte [115]. Poly(ethylene oxide) (PEO) based gel electrolytes are also getting interest because of their higher ionic conductivity (~10^{-3} S cm^{-1}) [116]. Li et al. studied the Li-ion storage capacity in $LiFePO_4$ using PEO based gel electrolyte and found 81 % retention after 500 cycles [116]. Xantham gum or polysaccharide, frequently used as food additives has recently been incorporated in liquid electrolyte to form gel electrolyte by Yu groups, as it is non toxic and low cost. They assembled a symmetric supercapacitor based on MnO_2/CNT as electrodes and Na_2SO_4/xantham gum gel electrolyte, which exhibited a specific capacitance of 347 Fg^{-1} with a capacity retention of 82 % over 5000 cycles [117].

1.7 Molybdenum Oxide

Electrodes play a crucial role in the high performance of electrochemical capacitors. Among various types of materials, transition metal oxides (TMDs) are very promising electrode materials due to their multiple oxidation states which is responsible for high pseudocapacitance contribution. MoO_3 is one of the most commonly used transition metal oxides, utilized in different fields including catalysts, gas sensors, batteries, supercapacitors and lubricants [118]. It is a n-type semiconductor having band gap of ~3.2 eV [118, 119]. Besides, it is non toxic, eco-friendly and has the valance states (-2 to +6), enabling high electrochemical activity for pseudocapacitance through the facilitation of Faradic redox reaction in between the layers or tunnels [119, 120]. Notably, MoO_3 is highly stable thermally as well as chemically, provides high carrier mobility. Moreover, MoO_3 can be nanostructured in different morphologies such as nanorods, nanofibers, nanosheets, nanotubes, nanoflakes, nanobelts, nanoplates, nanospheres etc. [120]. It has three different phases: $\alpha-$ MoO_3 (thermodynamically stable), $\beta-$ MoO_3 (metastable) and $h-$ MoO_3 [119]. One of the great advantages of MoO_3 is that it can be synthesized via different easy procedures such as thermal evaporation method, sputtering process, hydrothermal synthesis, chemical vapour deposition and electrospinning [121-124]. N. G. Prakash et al. fabricated $\alpha-$ MoO_3 by solution combustion method and measured its Na^+ ion storage capacity (176 Fg^{-1} at current density of 1 mAg^{-1}) with good cycling stability [125]. Elkholy et al. prepared $\alpha-$ MoO_3 by electrochemical deposition method and used as an electrode for electrochemical capacitor, achieving energy density of 22 Wh kg^{-1} at power density of 301 W kg^{-1} in a 1 M Na_2SO_4 aqueous electrolyte, over a wide potential window 0-2.2 V [126]. Cui et al. prepared $\alpha-$ MoO_3 using facile hydrothermal method in different morphologies (microsphere, nanobelt and nanorod) and evaluated their pseudocapacitive charge storage. They demonstrated that nanorod morphology of $\alpha-$ MoO_3 exhibited the highest charge storage capacity [127]. In another study, Noby et al. fabricated $\alpha-$ MoO_3 and treated under different atmospheric conditions (vacuum, H_2 and N_2). They observed that the vacuum treated $\alpha-$ MoO_3 electrode delivered the highest specific capacitance of ~39 mF cm^{-1}, with a capacity retention of ~76 % after 10,000 cycles [119]. Kundu et al. compared the electrochemical performance of both $\alpha-$ MoO_3 and $h-$ MoO_3, finding that $\alpha-$ MoO_3 delivered greater specific capacitance of 829 Fg^{-1} compared to 452 Fg^{-1} for $h-$ MoO_3. They also assembled a solid state asymmetric supercapacitor, which exhibited an energy density of 36.3 Wh kg^{-1} at power density of 50 W kg^{-1} [128].

1.8 Conducting polymers

From 1960s, as a promising supercapacitor electrode material, conducting polymers are widely used due to their impressive storage capacity, excellent conductivity, large potential window, high energy density (compared to metal oxides), and environmentally friendly nature [129]. These polymers are also cost effective and can be easily synthesized. Additionally, they exhibit fast doping and de-doping behavior during the Faradic charge transfer process, with oxidation and reduction reactions of the polymer backbone resulting in the formation of delocalized π

electrons [130, 131]. Numerous studies have reported the use of various conducting polymers including polyaniline, polypyrrole, polythiophene etc. in the energy storage application [129, 132, 133]. Among these, polyaniline (PANI) stands out as a commonly used conducting polymer for supercapacitor electrodes because of its high electrochemical performances (due to multi redox reactions) in acidic environments, high electrochemical durability, exceptional wave absorption distinctive doping mechanism and strongly conducting matrix [132, 134]. It also exhibits excellent electronic properties upon protonation and superior thermal stability as compared with other conducting polymers [132]. At the very beginning, it was known as "aniline black", with further research but it was reclassified as a conducting polymer [130]. PANI has a theoretical specific capacitance of ~1200 Fg^{-1} and its performance can vary depending on the synthesis method which influences its morphology (such as nanotubes, nanofibers, nanorods, nanospheres, nanoflowers) and film thickness [134, 135-139]. Electrochemically deposited PANI generally exhibits better specific capacitance compared to chemically generated PANI due to more uniform dispersion during polymerization. PANI exits in three different states: leucoemeraldine base, pernigraniline base, and emeraldine base depending on the degree of doping in the molecular chain [135-139]. Luo. et al. reported the use of PANI in lithium ion batteries, lithium sulfur batteries as well as in supercapacitors [140]. Liu et al. reported that PANI exhibited a specific capacitance of 243 Fg^{-1} at a current density of 0.3 Ag^{-1} in 2 M H_2SO_4 aqueous electrolyte [141]. Vujkovic et al. studied the Al^{3+} storage capacity of PANI in $Al(NO_3)_3$ solution, achieving specific capacitance of about 269 Fg^{-1} at high current density (=10 Ag^{-1}) [142]. Additionally, numerous studies have explored PANI based composites supercapacitor application. For examples, Zhao et al. demonstrated a PANI/CNT symmetric supercapacitor in 1 M H_2SO_4, which exhibited a high specific capacitance of 455 Fg^{-1} at a current density of 10 Ag^{-1} [143]. Chang et al. studied PANI/GO composite in 6 M KOH, obtaining a specific capacitance of 475 Fg^{-1} with 90 % capacity after 2000 cycles [144].

1.9 Graphene

Graphene is a sp^2 hybridized monolayer of graphite, known for it excellent electrical conductivity, mechanical strength, making it a widely used in supercapacitor application. It has high surface area ($\approx$ 2675 m^2g^{-1}), and is light weight [145, 146]. Ruoff et al. modified graphene chemically and demonstrated as a supercapacitor that achieving a specific capacitance 135 Fg^1 in aqueous electrolyte and 99 Fg^{-1} in non aqueous electrolytes [147]. Liu et al. reported graphene's performance in electrochemical capacitors, showing an energy density of 85.6 Wh kg^{-1} at room temperature and 136 Wh kg^{-1} at 80^o C [148].

Graphene can be used as conducting network in composite materials with transition metal oxides and sulfides to increase the electrochemical performance by increasing the surface area as well as the electrical conductivity of the composites [146]. Yan et al. synthesized MnO_2/Graphene composite using $KMnO_4$ which achieved a specific capacitance of 310 Fg^{-1} with ~95 % capacity retention after 15,000 cycles in 1 M Na_2SO_4 aqueous electrolyte [149]. Zhang et al. fabricated graphene/Mn_3O_4 composite for supercapacitors obtaining a specific capacitance of 326.9 Fg^{-1} with 94.6 % capacity retention over 1000 cycles [150]. Graphene can be functionalized with various groups such as epoxy, hydroxyl and carboxyl, to form graphene oxide (GO) [151]. Down and his colleagues fabricated GO and assembled it into symmetric supercapacitor, which delivered an energy density ~ 11.6 Wh kg^{-1} at power density ~ 13.9 kW kg^{-1} [152]. GO is highly hydrophilic, making it easily dispersible in water and other solvents. By reducing the functional groups GO, reduced graphene oxide (rGO) can be obtained, which has an excellent electrical conductivity and easily dispersible in solvents [153, 154]. Zhang et al. used rGO as supercapacitor and obtained a specific capacitance of 194 Fg^{-1} at current density 1 Ag^{-1} [155]. Mishra et al. demonstrated a symmetric supercapacitor using rGO and nitrogen doped rGO in the potential window 0-2.2 V and achieved high energy density ~106.3 Wh kg^{-1} and power density around 15184 W kg^{-1}, with 95.5 % retention after 10000 discharge cycles [156]. Pandey et al. prepared hybrids of rGO/V_2O_5 and demonstrated as an electrochemical capacitor exhibiting high specific capacitance about 466 Fg^{-1} [157].

1.10 Vanadium based materials

Vanadium based materials are also important in energy storage due to their wide range of valence states (from +2 to +5), enabling them to transfer multiple electrons and offer high theoretical capacity. Additionally, these materials are naturally abundant in the earth's crust, making them cost effective [158-160]. For instance, as a lithium battery cathode, V_2O_5 can accommodate two Li^+ ions proving a high specific capacity 294 $mAhg^{-1}$, and a specific capacity ~ 437 $mAhg^{-1}$, when accommodate three Li^+ ions [161, 162]. Recently, De et al. studied Al^{3+} chemistry with V_2O_5, exhibiting a specific capacity about 140 $mAhg^{-1}$with remarkable capacity retention ~ 96 % after 5000 cycles [160]. Similarly, V_2O_5 has been explored as an electrode material for supercapacitor, delivering an impressive areal specific capacitance of ~417 $mFcm^{-2}$ along with excellent rate capability and cycling stability [162]. VO_2 has been investigated both as battery and supercapacitor electrode material [162]. Feng et al. exfoliated bulk VS_2 into VS_2 nanosheets and demonstrated its potential as a supercapacitor, achieving a high specific capacitance of 4760 Fcm^{-1} with outstanding capacity retention [163]. Wang et al. reported organic vanadium oxy acetylacetonate as an anode material for Li-ion batteries and obtained specific capacity of 620 $mAhg^{-1}$ at current density (=100 mAg^{-1}) with excellent coulombic efficiency. Their cells also exhibited a ultralong cycling stability of about 508.5 $mAhg^{-1}$ over 1000 cycles [164]. Wein et al.were the first to study the Li-ion insertion in vanadyl acetate which exhibited highly reversible specific capacity of 1065 $mAhg^{-1}$ at current density of 200 mAg^{-1}. They also achieved an attractive rate capability about 1012 $mAhg^{-1}$after reverting current density to 200 mAg^{-1} [165]. Later, they extended their research to Zn ion batteries, where vanadyl acetate demonstrated a reversible specific capacity about 239 $mAhg^{-1}$ at current density of 500 $mAg^{-1}$with only 0.027 % capacity fading after 1000 cycles [166]. In current research, a promising strategy to improve cycling stability involves incorporating water molecules between the layers of vanadium oxides. These water molecule act as a pillar, improving structural stability by expanding the layers of vanadium oxides. Additionally, the water reduces the interaction between the cations and makes the ions to move through it. Again, to further improve the performances of hydrated vanadate various cations are inserted between the layers to expand the interlayer spacing. Larger cations in particular, expand the energy band gap, which accelerate the ion movements [166, 167]. Liu et al.

studied the hydrated vanadate for Zn ion storage behavior with aqueous medium, achieving a specific capacity of 400 $mAhg^{-1}$. They also chemically inserted Mn(II) ion, expanding the interlayer spacing of pentavalent vanadium to 12.9 Å. As a result, manganese expanded hydrated vanadate (MnVO) exhibited a higher specific capacity about 415 $mAhg^{-1}$ with 90 % capacity over 2000 cycles [167]. They further inserted Al ion into the pure hydrated vanadate (VOH) and studied the Zn^{2+} diffusion, which resulted a specific capacity around 380 $mAhg^{-1}$ at current density of (=50 mAg^{-1}) [168].

1.11 Objectives of the thesis

The main objectives of the thesis are as follows:

1) To explore and identify high performance electrode materials for Al^{3+} ion storage in aqueous and gel based electrolytes for electrochemical capacitor.
2) Pursuing detailed structural and electrochemical studies on electrode materials synthesized via electrospinning, hydrothermal and sol-gel procedures.
3) Develop and adopt strategies to enhance the electrochemical performance of certain identified electrode materials.
4) Understanding the electrochemical mechanisms of the electrochemical capacitors.

While exploring the thesis objectives, the Al^{3+} ion storage behaviours in transition metal oxide (such as MoO_3), conducting polymer (such as polyaniline (PANI) and various vanadiumbased materials (including vanadium oxy acetylacetonate, vanadyl acetate, and hydrated vanadate)are investigated and demonstrated their potential use electrochemical capacitors.

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