Chapter-1

Introduction and Literature Review

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1.1 Global Energy Dependence and the Role of Renewables

Fossil fuels have been reliable source of energy throughout the past centuries. Reserves of fossil fuels are depleting and their pricing is being inflated. In addition, exploitation of fossil fuels leads to environmental pollution by emitting CO_2 as end product. This summarily leads to global warming and climate change.

The world is now looking at alternative energy sources for the ever increasing energy demands of modern civilization. [1, 2] In 2013, 86.7% of the global energy came from fossil fuels, such as crude oil, coal, and natural gas (Fig. 1.1). Additionally, the global primary energy consumption is rising by 2.5% annually and is expected to climb by 56% by 2040, with oil as the primary energy source. [3, 4]

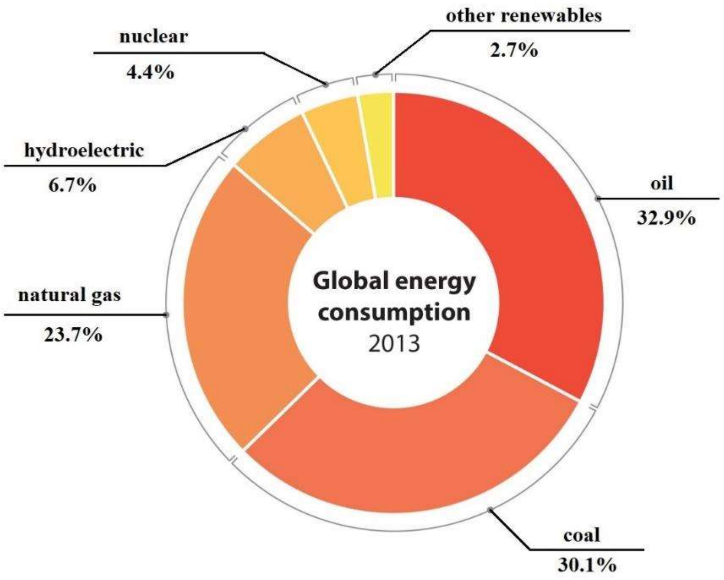

Figure 1.1 The global energy usage in 2013 as a percentage of energy sources [4]

There has never been a greater demand for reliable and efficient energy storage technologies as the world increasingly depends on like wind, thermal, and solar. The ever-demanding energy crisis is prompting the need for novel and innovative technologies for the discovery and development of renewable energy sources and modern energy-stowing system. [2, 5] Advanced electronic and optoelectronic devices have recently been subject to a large demand for highly dependable energy sources with greater energy density and a longer lifespan. Technological advancements in recent years have resulted in the development of a variety of energy storage technologies that have the potential to revolutionize the way we power our businesses, houses, and industries. In recent years, significant efforts have been made to create an integrated, sustainable self-power system for innovative electronics with enhanced energy harvesting and storage device architecture. The efficient use and management of energy resources, made possible by energy storage devices (ESDs) are essential to the modern energy system. A comprehensive comparative analysis of ESDs has shown that different technologies have different power and energy density characteristics, and the choice of technology depends on the specific application. [6-8] Electrical, mechanical, chemical, or thermal energy can be stored using ESDs, transforming it into usable energy when needed. ESDs are critical for integrating renewable energy sources, balancing the supply and demand of electrical energy, and ensuring grid stability. Further in developing portable gadgets, electric cars, and the internet, high-performance energy storage devices with additional features like flexibility, lightweight, cost-effective, renewable, and eco-friendly qualities have been extensively demanded. [9, 10]

The importance of renewable energy is rising as world seek to lower their dependence on fossil fuels. The United Nations estimates that over 80% of the global energy output still comes from fossil fuels, although renewable energy sources continue to catch up. [11] To ensure continuous growth, new policies must be implemented rapidly. The International Energy Agency (IEA) also points out that over the next five years, renewable energy sources are expected to surpass coal and account for over 90% of the growth in global electrical power. [12] Several types of renewable energy sources are available (Fig. 1.2) and each type has advantages and limitations.

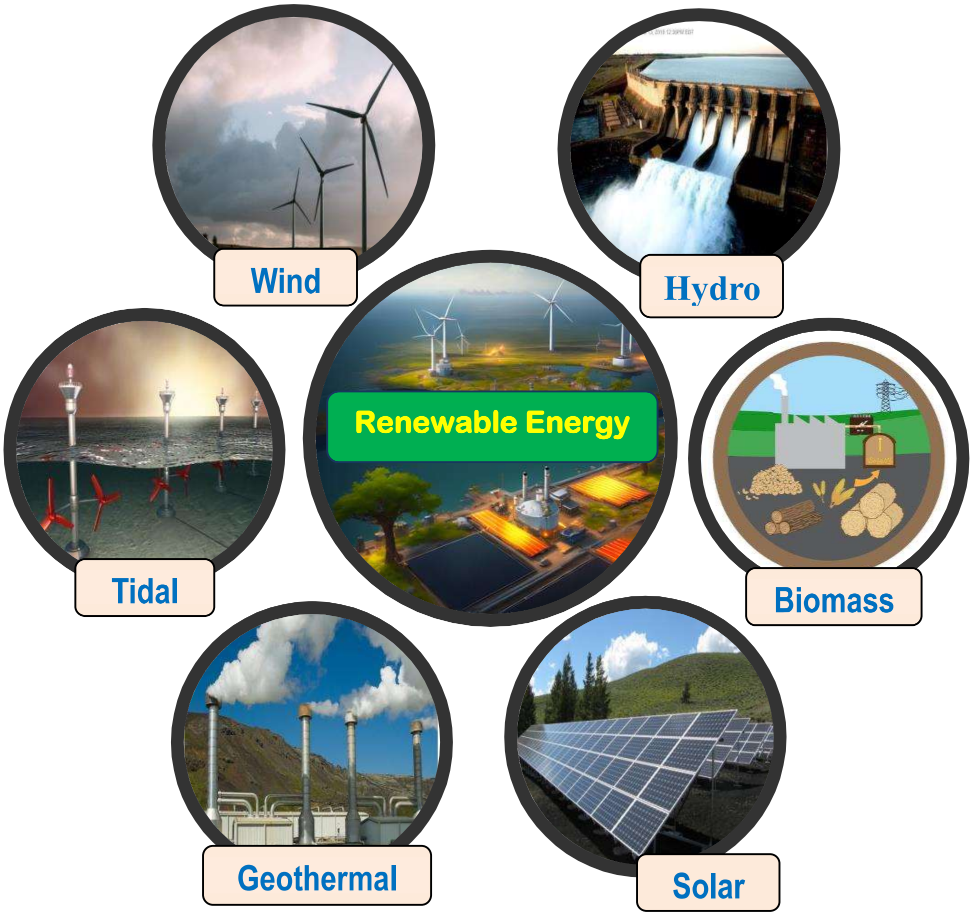

Figure 1.2 Renewable energy sources

1.2 Problems/Limitations with Renewable Energy Sources

Renewable energy sources like solar, wind, hydro, tidal energy, natural gas, etc., can produce electricity. There are numerous limitations to using renewable energy sources like the sun and wind. These limitations include-

- Power and current fluctuations
- They are intermittent and dispersed since the energy supply depends on the time and the weather
- Due to production uncertainties and power fluctuations, using directly in electrical appliances is not recommended

Renewable energy sources cannot meet the global energy demands since they are intermittent and dispersed. To regulate and distribute electricity effectively, efficient energy storage is necessary. However, their employment involves appropriate methods to transform energy from one form to another. Energy storage solutions must provide constant, continuous, fixed power and current as required.

1.3 Type of Renewable Energy Storage Solutions

The issues above have been major driving forces behind studying renewable energy resources. With rising energy demand, developing sustainable, secure, and adequate energy storage and conversion technologies has become essential for the world's scientific and technology community. According to the Energy Storage Market Report [13], energy storage technologies are crucial for allowing the grid's integration of renewable energy sources. The research points out issues for enhancing grid-scale utilisation and reliability that must be resolved, including the requirement for cost-effective and efficient storage solutions. Several energy storage options have been used, some of which are as follows:

1.3.1 Mechanical Energy Storage

Grid-scale mechanical energy storage systems store energy using gravitational or kinetic forces. Electric energy is used to power flywheel energy storage systems (FESSs) which stores that energy as kinetic energy. A spinning mass, known as a rotor, stores kinetic energy as it rotates in an almost frictionless environment. Typically, an electrical source from the grid or any other source of electrical energy is used as the input energy for the FESS. When temporary backup power is required because utility power fluctuates or is lost, the inertia keeps the rotor to continue spinning and the resulting kinetic energy is turned into electricity. An integrated motor generator accelerates as it stores energy and decelerates as it discharges it. Some other examples of mechanical energy storage systems are: pumped hydro-storage (PHS), compressed air energy storage (CAES), liquid air energy storage (LAES) etc. [14, 15]

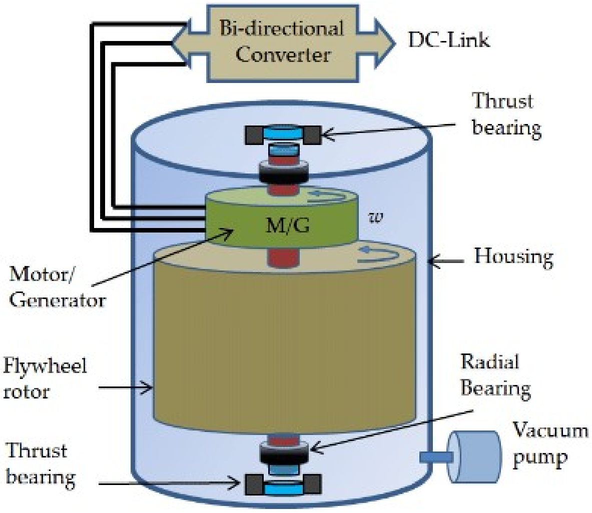

Figure 1.3 Structure of a Flywheel with components [14]

1.3.2 Thermal Energy Storage

Thermal energy storage (TES) is a type of energy storage that allows excess thermal energy to be stored and used later on requirement. It may be used to balance the energy demands of the day and night, store heat from the summer for winter heating, or store cold from the winter for summer air cooling. Sensible heat, latent heat, and thermochemical heat storage are the categories of TES. [16] Sensible TES is the most practical method to reduce energy consumption and CO_2 emissions. Several materials with different thermal characteristics may be utilised for TES, such as water, rock, and silica/sand. TES in the form of sensible heat is based on the specific heat of a storage medium, often retained in storage tanks with high thermal insulation. [17, 18]

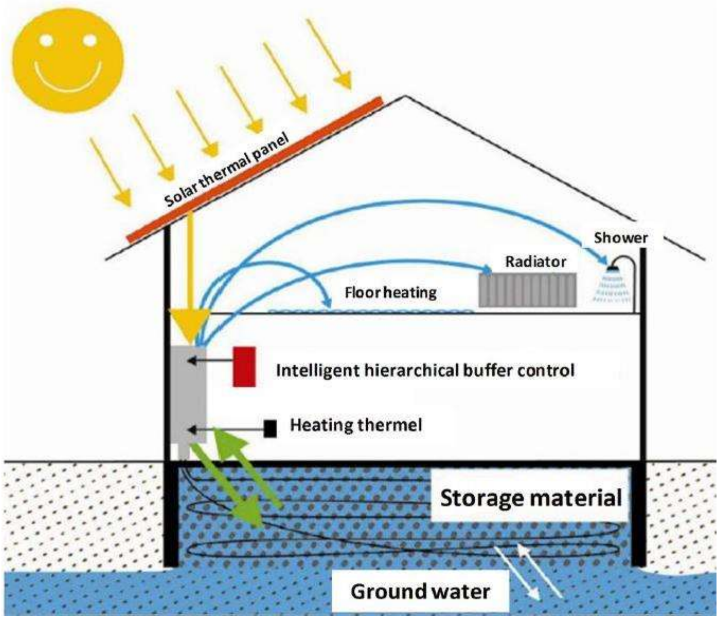

Figure 1.4 Schematic of the sensible heat storage system [18]

1.3.3 Superconducting Magnetic Energy Storage (SMES)

A direct current passing through a superconducting coil creates a magnetic field that stores energy in the SMES technology. The system's three main components are the coil, a power conditioning system (PCS), and a cooling system.

The idea is based on the observation that a superconductor will continue to conduct current even after the applied voltage has been withdrawn. Current will continue to flow (even after a voltage source is disconnected) when the coil is cooled below its superconducting critical temperature, generally in the range of 4.5 - 80K (-269 to -193°C). The current will continue to flow because the coil has negligible resistance at these lower temperatures. The magnetic field created by the current in the superconducting coil serves as a storage medium for the energy. The coil can be discharged to release it. [19, 20]

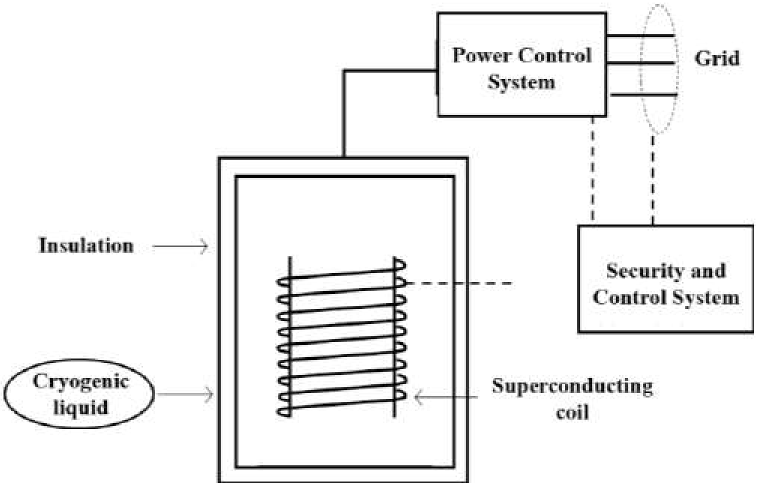

Figure 1.5 Block diagram of a SMES system [19]

1.3.4 Electrochemical Energy Storage Devices

With the worldwide energy scenario changing rapidly daily due to the increase in energy consumption, it is essential to take recourse to electrochemical energy storage (EES) devices, which play a crucial role in meeting energy demands. The development of portable electronic, electrical vehicles (EVs), and other cutting-edge technology now relies heavily on the efficient reversible electrochemical process of EES devices. According to the literature survey, ineffective energy storage methods result in a 30% loss of power. Therefore, to reduce the loss, appropriate storage techniques should be used. EES appear to be the most appropriate choice regarding energy storage efficacy. EES technologies such as batteries and electrochemical capacitors (EC) are thus playing a significant role in efficiently storing and supplying energy worldwide to address the energy challenges. To create long-term sustainable energy storage systems, competitive electrode materials with more excellent performance level are needed to meet present and future market requirements. Based on the type of EES devices, electrode materials are chosen, as these are significantly diverse in their charge storage mechanisms. [21]

1.3.4.1 Types of Electrochemical Energy Storage Devices

Scientists are forced to drift and concentrate on alternate energy sources and storage mechanisms due to the ubiquitous inherent limitations of conventional and non-conventional energy sources and the catching hold of energy storage technologies. In this vein, the global economy has started allocating funds to research and advancement of EES technologies. The electricity or energy produced by renewable sources can be stored as chemical energy, which can be more effectively converted into electrical energy. Due to their recent achievements in providing portable electronics with an efficient power supply, EES devices have gained much attention. Future technologies for meeting the requirements for bulk energy storage and quick power delivery includes redox flow batteries, metal-air batteries, and hybrid supercapacitors with pseudocapacitive electrodes.

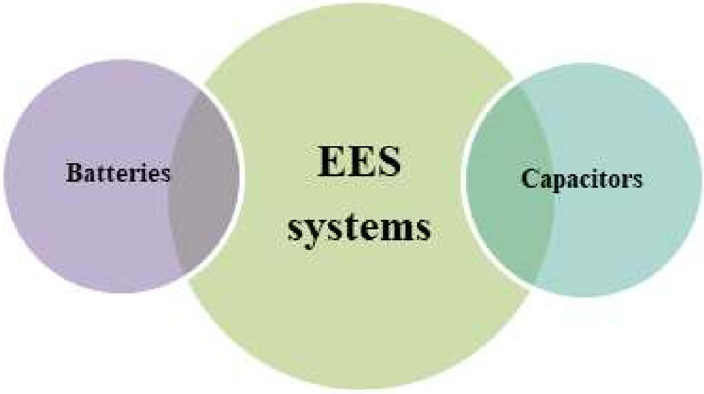

Fig. 1.6 Classification of rechargeable Electrochemical Energy storage systems

Among them, two primary rechargeable energy storage technologies, the capacitor and the battery, have energized the worldwide commercial electronics sector. (Fig. 1.6).

These devices construction and working principles are discussed in the following sections.

1.3.4.2 Battery

The battery is a commonly used power source for industrial and domestic electronics applications. It is a storage device that produces electrical energy from chemical energy through a redox reaction. It consists of one or more electrochemical cells with two electrodes in each cell that are electrically connected by an electrolyte of cations and anions. The cell's polarity can be determined based on the ion's transport. Depending upon the charging capability, batteries are classified into two types: primary batteries (disposable or non-rechargeable batteries) and secondary batteries (rechargeable batteries).

Conventional batteries are non-rechargeable and must be replaced after their stored energy is used. This battery is more affordable, with a lower discharge rate and higher energy density. It is mainly employed for short-term storage purposes. Rechargeable batteries are the evolved form of primary batteries and can be utilized throughout the battery's cycle life. The chemical energy in rechargeable batteries is converted into electrical energy during discharging, and the electrical energy is then used to restore the original chemical composition during charging. Some examples of disposable batteries are zinc-carbon batteries and alkaline batteries. The rechargeable battery category includes lead-acid, lithium-ion, nickel-cadmium, nickel metal hydride, and nickel-zinc batteries. Between these two types, disposable batteries offer higher specific energy compared to the other. Some of them are discussed below.

1.3.4.2.1 Lead-Acid Battery

Lead-acid (LA) batteries are the most commonly utilised electrical energy storage technology globally compared to other electrochemical sources. [22] The first rechargeable battery for commercial use was invented in 1859 by French physician Gaston Planté. LA batteries are suitable for medium and large energy storage applications because they offer a good combination of power parameters and a low price. This is due to their low cost and readily available lead, high voltage of the cell (2 V), high electrochemical effectivity, and cycle life from several hundred to thousands of cycles. Several series-connected lead alloy cells typically make the grid structure of a LA battery. Other metals are added to improve electrical properties and gain mechanical strength. Antimony, calcium, tin, and selenium are the most often used additives.

Lead oxide (PbO) pasted onto a grid is used as the active component in LA batteries. These are electrochemically transformed to produce reddish-brown lead dioxide PbO_2 on the positive electrode and grey spongy lead Pb on the negative electrode. Separators electrically separate the positive and negative electrodes, and an aqueous solution of H_2SO_4 with a density of 1.22-1.28 g/cm^3 is employed as the electrolyte. [23]

During discharge overall chemical reaction is:

$$\mathrm{PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O} \qquad \mathrm{E^0 = +2.048\,V} \qquad (1.1)$$

The LA battery is used to crank automobile internal combustion engines and support devices requiring electrical energy when the engine is not running. The battery has a cyclic life of about five years (1000 charge-discharge cycles). Positive plate expansion, water loss brought on by gassing or a high temperature, acid stratification, positive grid corrosion, and improper charging resulting in active mass sulphation can all have an adverse effect on LA battery. [24]

Despite the rising demand for lithium-ion batteries, LA batteries remain ahead of their peers because of their cheaper cost than other battery types.

Figure 1.7 Scheme of prismatic and spiral wound construction of Lead Acid battery [25]

1.3.4.2.2 Lithium-Ion Battery

Over the past 30 years, lithium-ion batteries have made the advancement in portable devices possible. The first battery was commercialised by Sony (1991) only after the discovery of lithiated transition metal oxides and lithium intercalation into graphite, although lithium was reportedly inserted electrochemically into transition metal compounds in the 1970s. [26]

The Li-ion battery (shown in Figure 1.8) is regarded as the best among electrochemical cells due to its high energy density (between 120-170 Wh kg^{-1}), high cell voltage (3.6 V), appropriate weight, and negligible memory effect, among other characteristics.

Despite these advantages, it has two significant drawbacks: less power density and low charge/discharge rates. The anode material is usually graphite while the cathode material is $LiCoO_2$. Lithium ions are transported from the cathode to the anode during charging and back to the cathode during discharging $LiPF_6$ is the electrolyte; ethylene carbonate and dimethyl carbonate are among the organic solvents used in the mixture. Lithium-ion batteries are made in prismatic, cylindrical, and coin formats (see Fig. 1.9).

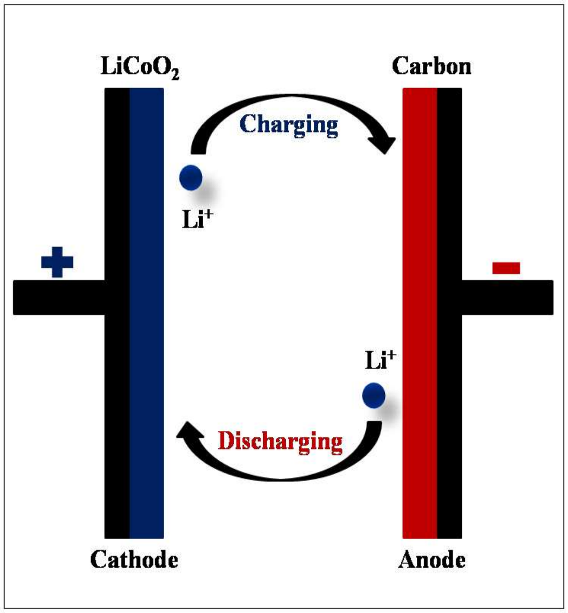

Figure 1.8 Schematic diagram of Li-ion battery through the connected load. [27]

During the energy-storage (charging) stage, the following processes occur:

$$\textbf{Cathode: } \mathrm{LiCoO_2} \leftrightarrow \mathrm{Li_{1-x}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-} \tag{1.2}$$

$$\textbf{Anode: } \mathrm{C_6} + \mathrm{Li^+} + \mathrm{e^-} \leftrightarrow \mathrm{LiC_6} \tag{1.3}$$

Due to the low voltage variations that occur during insertion and de-insertion for many materials, intercalation processes can provide high reversibility. A number of higher voltage cathodes have been suggested, among them a series of lithium-intercalated materials based on the spinel $Li_yM_xMn_{2-x}O_4$, where M = Cr, Fe, Co, Ni, and Cu. [28]

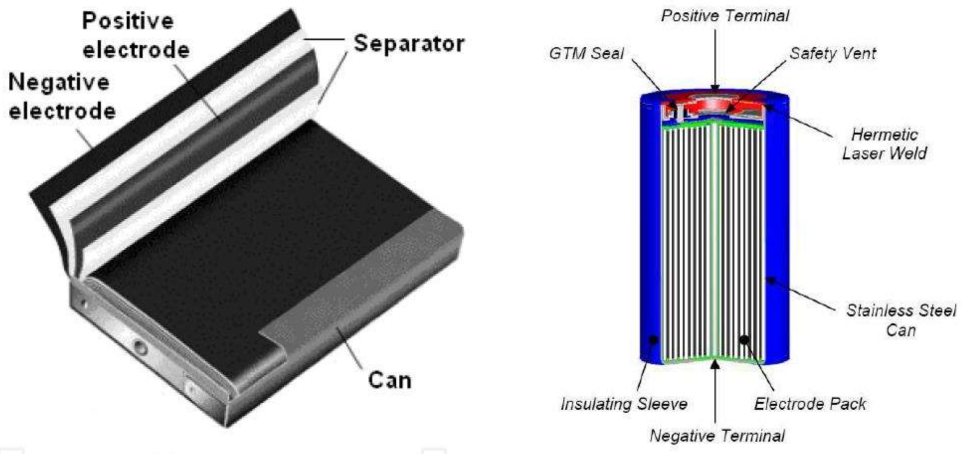

Figure 1.9 Construction of prismatic and cylindrical Li-ion cell construction [25]

Li-ion batteries still have a number of drawbacks despite their technological potential, particularly in terms of safety. High voltages can harm Li-ion batteries because they frequently overheat. This can occasionally result in thermal runaway and combustion. [29] Li-ion batteries may age, which causes them to lose capacity and frequently malfunction after a number of years. Their cost, which is around 40% higher, but the fact that they are not the best choice for applications that require rapid charge storage, such as regenerative braking, is another barrier to their wider use. [30]

1.3.4.2.3 Redox Flow Battery

A redox flow battery (RFB) is a type of electrochemical cell where active species are dissolved in liquid electrolytes, with the reaction occurring in the solid-liquid interface between the active solution and an inert electrode. In contrast, the reaction occurs in the solid electrodes in other batteries. Particularly since the required advancements that made this technology viable in the energy market, RFBs have flourished recently. New redox-active materials have been created as inexpensive and high-power-density for next-generation RFBs. Performance characteristics of RFBs, such as overpotential and cell power density, are greatly influenced by electrochemical kinetics. Electrochemical energy storage using RFBs has several benefits over other energy storage methods, including stand-alone modular design, no geographical requirement, high efficiency, swift response, etc. Several redox-flow batteries have been created by applying various active redox systems, including polysulfide/bromide, vanadium, Fe/Cr, etc. A schematic of the redox flow battery's mechanism is shown in Fig. 1.10. [31-33]

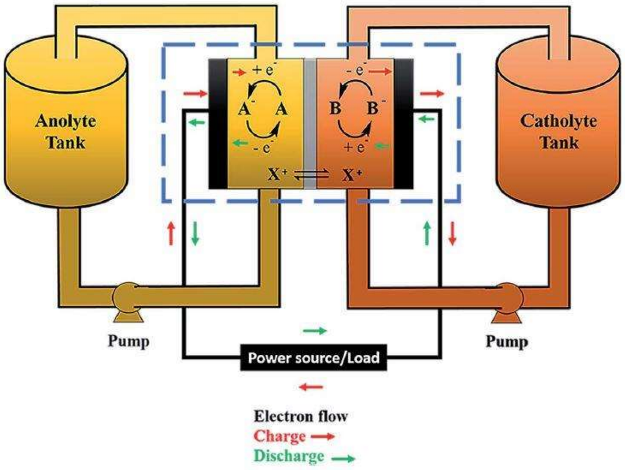

Figure 1.10 Schematic mechanism of a Redox Flow Battery [31]

1.3.4.2.4 Metal-Air Battery

Metal-air batteries have greater theoretical energy density than lithium-ion batteries as it combines the features of both conventional batteries and fuel cells. They are frequently promoted as the solution for next-generation electrochemical energy storage, including grid and electric vehicle energy storage. A metal anode and an air-breathing cathode are assembled in a metal-air battery with the appropriate electrolyte. Depending on the type of anode used, the metal anode can be an alkali metal (such as Li, Na, and K), an alkaline earth metal (such as Mg), or a first-row transition metal (such as Fe and Zn) with good electrochemical equivalence. The air-breathing cathode frequently has an open porous architecture that allows continuous oxygen supply from the surrounding air. A schematic diagram of the Li-air battery is shown in Fig. 1.11. [34-36]

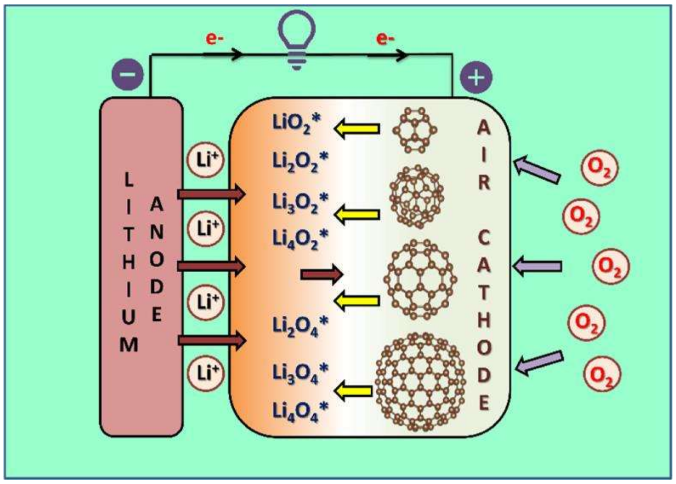

Figure 1.11 Schematic diagram of Li-air battery [35]

The electrochemical reaction of metal (Zn, Al, Fe) and oxygen in metal-air batteries are described below.

In **aqueous electrolyte**

Anode: $\mathrm{M} \rightleftharpoons \mathrm{M}^{n+} + ne^-$ (1.4)

Cathode: $\mathrm{O_2} + 2\mathrm{H_2O} + 4e^- \rightleftharpoons 4\mathrm{OH}^-$ (1.5)

In **non-aqueous electrolyte**

The working principle of Li-air battery in the non-aqueous electrolyte is given below.

Anode: $2\mathrm{Li} \rightleftharpoons 2\mathrm{Li}^+ + 2e^-$ (1.6)

Cathode: $\mathrm{O_2} + e^- \rightleftharpoons \mathrm{O_2^-}$ (1.7)

$\mathrm{O_2^-} + \mathrm{Li}^+ \rightleftharpoons \mathrm{LiO_2}$ (1.8)

$\mathrm{LiO_2} + \mathrm{Li}^+ + e^- \rightleftharpoons \mathrm{Li_2O_2}$ (1.9)

Overall reaction: $\mathrm{O_2} + 2\mathrm{Li} \rightleftharpoons \mathrm{Li_2O_2}$ (1.10)

1.3.4.2.5 Metal-Sulphur Battery

Alkali metal-sulfur batteries, which include lithium-sulfur (Li-S) and sodium-sulfur (Na-S) batteries, have a very high energy density, extended cycle and calendar life, cheap cost, and high level of safety, making them ideal for large-scale energy storage applications. Elemental sulphur impregnated in a porous matrix makes up the cathode side of metal-sulfur batteries with a metallic anode side. They attract much interest and are regarded as next-generation batteries for the following reasons.

- Due to their higher capacity than intercalation compounds, the use of active metal anodes provides an increase in specific energy
- A cathode made of elemental sulphur has a high theoretical specific capacity (1.675 Ah/g)
- Battery parts are inexpensive and non-toxic
- The high reactivity of metallic anodes (e.g., Li, Na, Mg, and Al).

In this regard, the construction and charge-discharge mechanism of the Li−S battery consists of a lithium metal (anode), an organic electrolyte and a sulfur composite (cathode). When sulfur is in charged state, the cell's function begins with discharge. Lithium metal is oxidised at the negative electrode during discharging, resulting in lithium ions and electrons. An electrical current is created when lithium ions go from the negative to the positive electrode through the electrolyte. At the same time, electrons move from the negative to the positive electrode via the external electrical circuit. Sulfur is reduced to produce lithium sulfide by accepting the electrons and lithium ions at the positive electrode. Li-S cells are presented schematically in Fig. 1.12, along with their charge and discharge processes. The reactions occurring during charge and discharge are given below

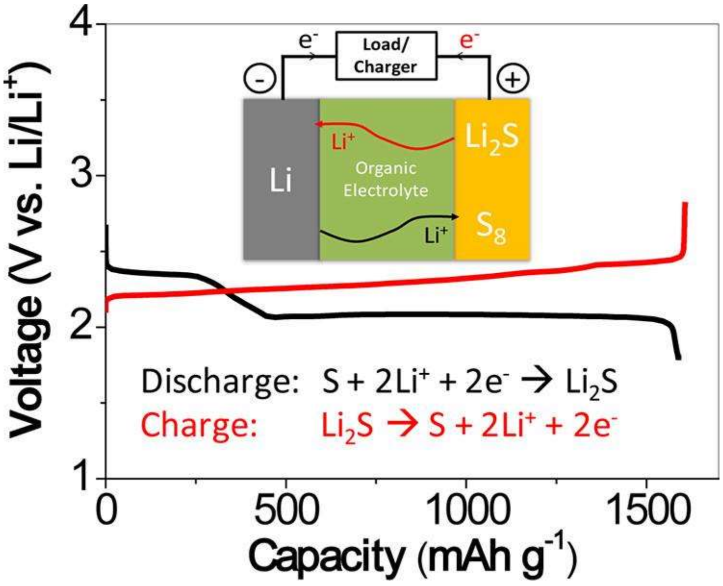

Figure 1.12 Li-S cell schematic showing its charge and discharge processes [37]

Negative electrode: anodic reaction (oxidation, loss of electrons)

$$2\mathrm{Li} \rightarrow 2\mathrm{Li}^{+} + 2e^{-} \quad (1.11)$$

Positive electrode: cathodic reaction (reduction, gaining electrons)

$$\mathrm{S} + 2\mathrm{Li}^{+} + 2e^{-} \rightarrow \mathrm{Li}_2\mathrm{S} \quad (1.12)$$

Overall cell reaction

$$2\mathrm{Li} + \mathrm{S} \rightarrow \mathrm{Li}_2\mathrm{S} \quad (1.13)$$

The theoretical cell capacity of the Li-S cell is 1.167 Ahg^{-1} since the theoretical capacities of lithium and sulphur are 3.861 and 1.672 Ahg^{-1}, respectively. The average cell voltage during the discharge reaction is 2.15 V. Therefore, a Li-S cell's theoretical gravimetric energy density is 2.51 Whg^{-1}. [37-39]

1.3.4.3 Capacitors

Capacitor, known as a condenser or an electrostatic capacitor, is an energy storage device with two electrically conducting plates or electrodes separated by a dielectric layer. The dielectric layer can be a vacuum or an electrical insulator material such as ceramics, glass, paper, plastic, and aluminium oxide.

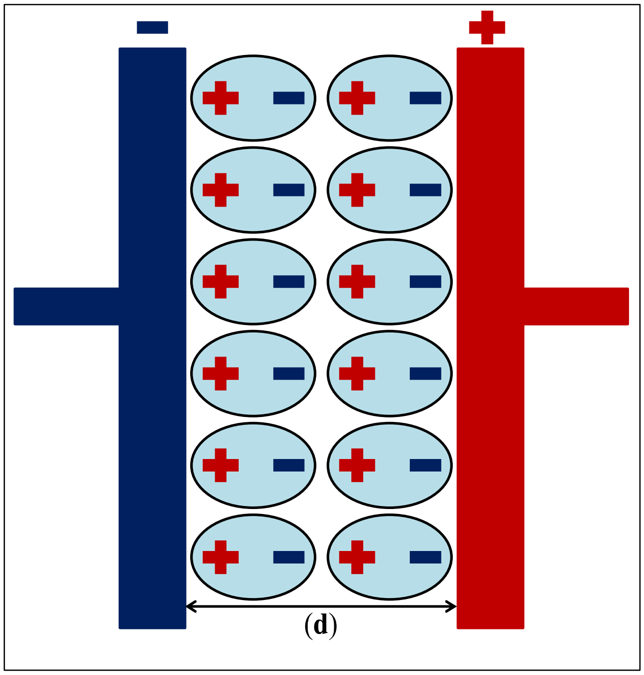

Figure 1.13 Schematic illustration of a conventional capacitor

When a voltage is applied across the plates through an external power source, which creates a potential difference between the two plates, thereby building up an electric field, and the capacitor stores electrical energy in this field by accumulating electric charges on the two surfaces of the plates insulated from each other. The conventional capacitor's schematic working principle is shown in Fig. 1.13.

Additionally, when an external power source is removed, the charges on the appropriate plates still exist, indicating the charging state of the capacitor. [40] To transfer its stored energy to a connected resistive load, the capacitor discharges positive/negative charges.

Electrochemical capacitors and dielectric capacitors are the two primary categories of capacitors. A dielectric substance serves as the medium of a dielectric capacitor, which stores charge by polarising a dipole around the electrode and dielectric interface (Fig.

1.14a). An electrolytic capacitor's medium is an electrolyte, often a solid or liquid ionic conductor. To store charge, it accumulates anions at the interface surrounding the positive electrode and electrolytes and cations at the interface around the negative electrode, as shown in Fig. 1.14b. [41] The capacitance value of a capacitor serves as a measure of its capacity for charge storage.

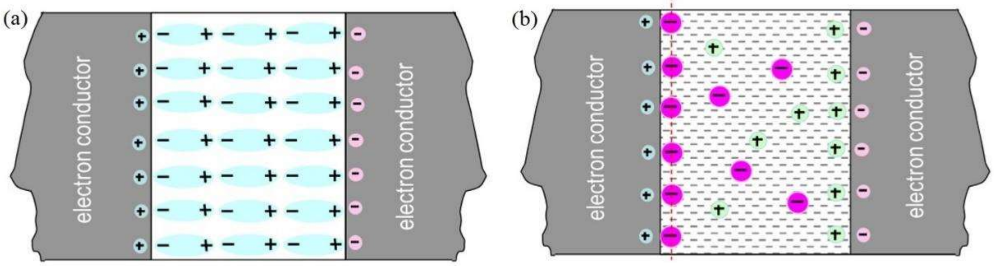

Figure 1.14 Charge storage schematics in **(a)** dielectric and **(b)** electrolytic capacitor are shown in the diagram [42]

Equation (1.14) demonstrates that the capacitance of a capacitor is inversely proportional to the distance (*d*) between the two plates and directly proportional to the area (*A*) between the electrode and the dielectric.

$$C = \mathcal{E}_0 \mathcal{E}_r \frac{A}{d} \tag{1.14}$$

here, $\mathcal{E}_r$ and $\mathcal{E}_0$ are the relative and vacuum permittivity, respectively. Electrolytic capacitors have a higher capacitance than dielectric capacitors because they have more movable free electrons. An electrolytic capacitor's capacitance is often measured in mF, whereas a dielectric capacitor's capacitance is measured in μF.

Due to their low energy density, these traditional capacitors can only be used in limited applications. Because of this, searching for a new material resulted in pseudo-capacitors (PCs) or supercapacitors (SCs) being considered a new kind of capacitors. Porous materials with a high-surface area, such as carbon particle materials, generally consist of energy storage (ES) electrodes, and the separator is either solid or liquid, forming electrode/electrolyte interfaces, in contrast to traditional capacitors. These interfaces, also known as electric double layers, have a larger surface area than

conventional capacitors and may hold more charges as a result. It is well known that PCs have a superior ability to store energy than traditional capacitors due to their enhanced structure.

1.3.4.4 Parameters of Performances for Grid-Scale Energy Storage

Grid-scale energy storage is the term used to describe the use of large-scale energy storage devices to store extra energy produced by power systems for later use. The following are some of the performance parameters for grid-scale energy storage systems that are used to assess their performance:

- Uninterruptible power supply (UPS) power quality
- Grid supported
- Bulk power
- Response time
- Cost of grid-scale energy storage systems

1.3.4.5 Supercapacitors for Grid-Scale Energy Storage Application

The current scenario calls for a device with unique capabilities, such as high power, energy density, and extended cycle life. [43] Batteries and capacitors can't meet the high energy demand and fast delivery needs of modern high-power devices. In the last several decades, supercapacitors have been designed to address the main shortcomings of traditional energy storage devices (batteries and capacitors). [44]

With their exceptional energy and power densities, SCs are suitable for promoting a paradigm shift towards green energy for a future with immense promise in the global energy market. SCs is regarded as a bridge between a battery and a capacitor, attracting much interest in energy storage devices. Batteries can store a more significant amount of energy than capacitors, which are known to charge and discharge at faster rates. SCs, also known as electrochemical capacitors or ultracapacitors, are greatly desired for commercial electronics due to their extraordinarily high power densities, extended cycle lives, wider operating temperature range (-40 °C to 70 °C) and straightforward construction and operation. [45, 46] SCs offer several significant benefits, including high power density (more than 10 kW kg^{-1}), excellent cycle life (more than 10, 00000 cycles), high rate capability, minimal service needed when operating for an extended period, and low cost. [47, 48]

SCs are made up of two electrodes isolated by a separator. The separator (soaked with electrolyte) prevents the electrical conductivity between the two electrodes. For optimal performance, the separator's thin thickness must be ion-permeable for quick ionic charge transfer and high electric resistance. SCs can store charges either chemically (interface-confined) or electrostatically. [49] The potential of an SC is a function of the charge held and indicates a simultaneous continuous shift in free energy with material transformation.

Based on an energy storage mechanism and the transit of ions from the electrolyte to the electrode surface, pseudocapacitors (PCs) and hybrid supercapacitors (HSCs) are the two main categories of supercapacitors (SCs). [50]

1.3.4.5.1 Pseudocapacitors

Pseudocapacitors, called as electrochemical capacitors is another type of supercapacitor, differ from electrostatic capacitors or EDLCs (electric double-layer capacitors). De-solvated ions that have been adsorbed on the electrode surface function as electron donors and contribute their charge as faradic current, which are the sponsors of pseudocapacitance accompanied by EDLC over the surface. The electrosorption (intercalation of ions at the electrode-electrolyte interface) processes or redox reactions may be the sources of the faradic charge transfers. [51-53] In the case of a redox process, the electrolytic electron donor ions are adsorbed over the electrode surface. In contrast, in the intercalation/deintercalation mechanism, they are channelled via the multilayer electrode surface. [54]

Transition metal oxides, metal carbides, metal nitrides, metal sulfides, as well as conducting polymers are typically considered pseudocapacitive materials due to their high ionic conductivity to induce pseudocapacitance.

The most of the pseudocapacitive electrode materials are made up of metal oxides (such as RuO_2, V_2O_5, NiO, Co_3O_4, and MnO_2), metal sulfides (such as NiS, CoS, MoS, ZnS, and CuS), and conducting polymers (such as polypyrroles, Pani and polythiophenes) provide large electrochemical capacitance due to their high ionic conductivity. The battery-type non-capacitive storage mechanisms, which obey bulk intercalation type redox faradic charge transfer, are often mistaken for the pseudocapacitive storage mechanism. Redox reactions can be diffusion-controlled and slow when electrolytic ions (Li^+ in Li-ion batteries) are inserted; however, the redox reaction in pseudocapacitance is swift because electrons quickly cross the double layer into the electrode surface without changing its inherent crystal structure or phase. [49] The voltage response of the two types of charge storage also serves as a valuable marker for the distinction between pseudocapacitive and battery-type charge storage; for electrodes to be capacitive, the storage should vary proportionally with applied voltage, whereas the maximum amount of charge stored in the battery electrode occurs at a specific applied potential. [55] Batteries' bulk redox processes are slow, but the multiple electron transfer gives them a higher storage capacity. On the other hand, pseudocapacitors act as a bridge between batteries and EDLC materials, combining an improved energy density from faradic electron transfer with a high compensatory power density from surface-confined reactions and a superior level of stability due to the minimal structural modifications.

1.3.4.5.2 Classification of Pseudocapacitance

The surface coverage of the electrodeposited species was used to determine capacitance according to the kinetic theory of pseudocapacitive storage, which postulated a linear relationship of the heat of adsorption on it. Conway hypothesised several faraday mechanisms through which capacitive electrochemical properties might be achieved. They are as follows and shown in Fig. 1.15

- Underpotential Deposition - deposition under insufficient potential occurs when metal ions form an adsorption monolayer on the surface of another metal with a strong interaction that is significantly greater than its oxidation-reduction potential (Fig. 1.15a). An excellent example of underpotential deposition is the deposition of Pb on the surface of Au electrodes. [56]
- Redox Pseudocapacitance - the electrochemical adsorption of ions to the surface or near the surface of the electrode material results in redox pseudocapacitance, accompanied by faraday charge transfer (Fig. 1.15b). Faradaic reactions mechanism occurs in hydrous RuO_2 in H_2SO_4 is a typical example of redox pseudocapacitance. [57]
- Intercalation Pseudocapacitance - there is no crystalline phase transition and Faraday charge transfer intercalation pseudocapacitance, which is the intercalation of ions into the tunnels or interlayers of redox-active materials

(Fig. 1.15c). Nb_2O_5 is a typical intercalation pseudocapacitance material where pseudocapacitive type Li-ion intercalation occurs. [42, 58]

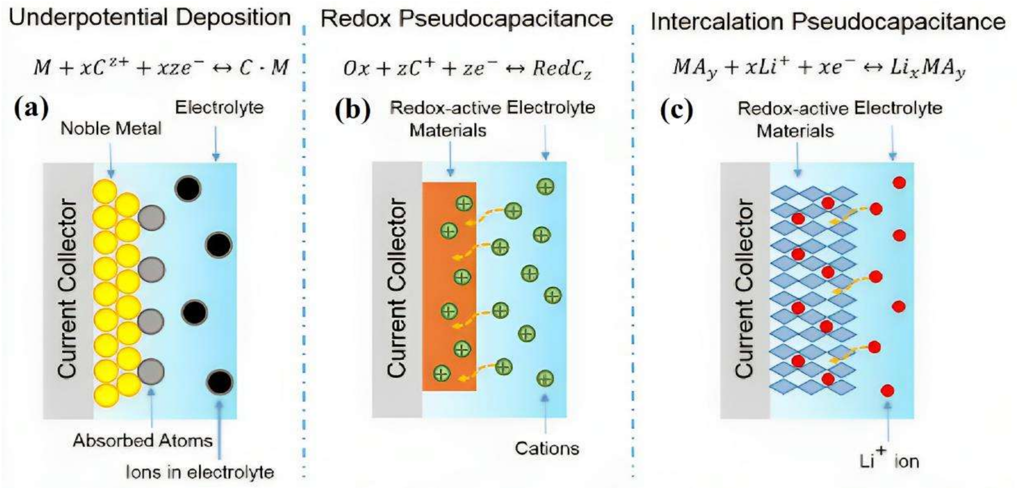

Figure 1.15 Schematic diagram about charge-storage mechanisms of various pseudocapacitive materials: **(a)** underpotential deposition, **(b)** redox pseudocapacitor and **(c)** ion intercalation pseudocapacitor.

1.3.4.5.3 Hybrid Supercapacitor

The capacitance of the electrode and the cell's voltage are the two parameters that determine the energy density of SCs. In contrast to pseudocapacitors, which had a larger specific capacitance and limited cyclic stability, EDLCs had a higher power density, low energy density, and superior cyclic stability.

Atomic charge partition length and intrinsic shell area are energy storage sources in EDL capacitors. Fast cyclic redox reactions between electroactive components positioned above the active electrode material and the electrolyte solution store energy in pseudocapacitors. The hybrid supercapacitor (HSC), comprising a blend of these two storage techniques (EDLC and a pseudocapacitor), performs better by overcoming the independent units' disadvantages [59] (Fig. 1.16). Hybrid supercapacitors show improved electrochemical behaviour when using two separate electrodes made from different materials than the individual ones. Hybrid capacitors exist in three main types

- Composite, Asymmetry and Battery type [50, 60] and may be distinguished by how their electrodes are set up.

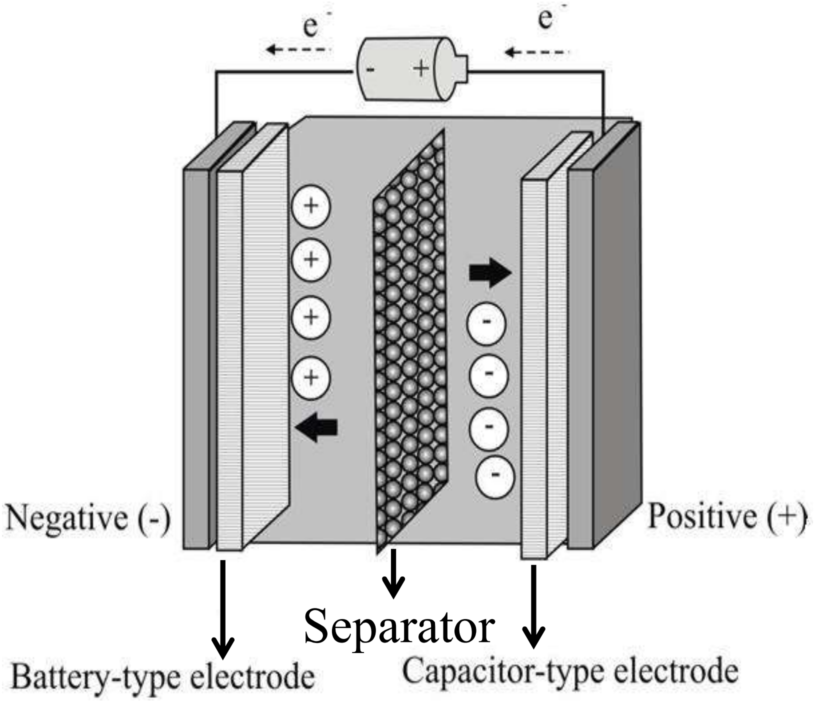

Figure 1.16 Hybrid Supercapacitor

- **Composite HSC -** Incorporating metal oxides, chalcogenides, nitrides, carbides, phosphates, or conducting polymers into carbon material results in composite SCs. The carbon material increases the pseudocapacitor material's activation sites and surface area, which leads to a higher specific capacitance and longer cycle life. Composite electrode materials could improve operating potential windows, specific capacitance, and corrosion stability.
- **Asymmetric HSC -** Asymmetric coupling refers to the use of metal oxides, chalcogenides, nitrides, carbides, phosphates, or conducting polymers as the positive electrode and carbon material as the negative electrode in materials with non-faradic and faradic processes.

- **Battery type -** The supercapacitor and battery electrodes are united in one cell, similar to an asymmetric cell. However, this cell has the characteristics of both in one. [61]

1.3.4.6 Electrochemical Characteristics of Different Charge Storage Devices

In contrast to high energy density redox-driven batteries, which can only generate extreme amounts of power, pseudocapacitors utilize both capacitive and redox processes to provide large quantities of power density with a higher energy density. [62, 63] It is essential to correctly identify the charge storage mechanism of the electrode materials in light of each one's unique potency, which needs to be understood. Batteries exhibit broad and sharp redox peaks of the associated metal centres compared to capacitors, while capacitive mechanisms exhibit a potential independent capacitance with rectangular symmetric cyclic voltammetry curves. According to broadly spread peaks that follow mirror images during a potential reversal, pseudocapacitive materials are classified (Fig. 1.17 (a-i)). The voltage vs. time plot under galvanostatic conditions can also demonstrate the transition from capacitive to battery-type storage mechanisms, with capacitive response reflecting a linear response in contrast to the plateau response of battery electrodes. [64, 65]

The possibility of surface-mediated or diffusion-controlled processes can be obtained by implementing kinetic analysis to determine rate-limiting steps of the various mechanism put forth by Lindstrom et al. using the dependency of scan rate on voltammetric current to gain insight into the transport assessment. The b value, from the power law, anticipates the kinetic constraints described in the equation 1.15. [66, 67]

$$i = av^b \qquad (1.15)$$

where i is the measured current (A), values of a & b are adjustable, and v is the scan rate (V/s).

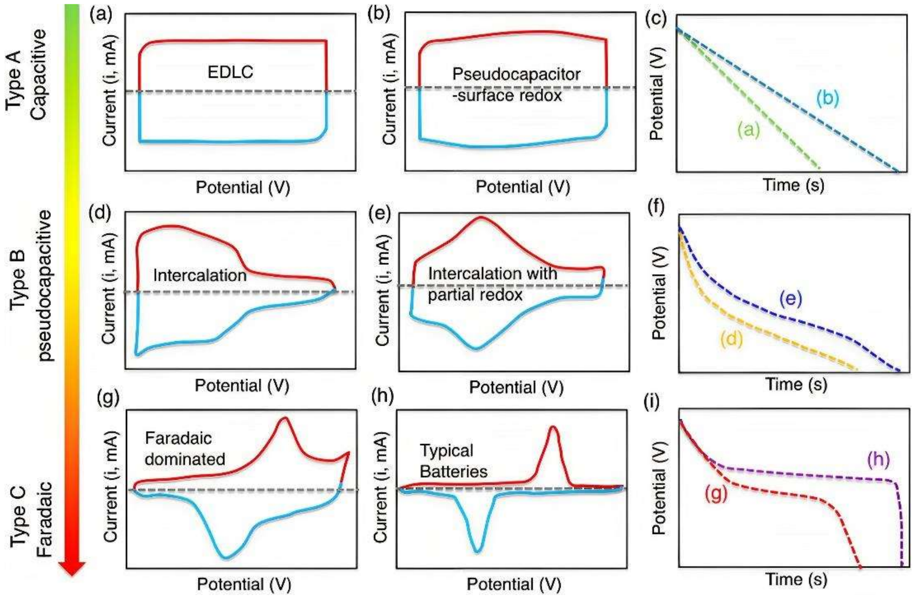

Figure 1.17 Typical cyclic voltammograms (CV) and galvanostatic discharging curves for different types of electrochemical energy-storage materials - Type-A (EDLCs), Type-B (pseudocapacitors), and Type-C (batteries) respectively; **(a)** CV profile for EDLCs, **(b)** Surface redox processes, **(d)** Intercalation-type process, **(e)** Intercalation-type with partially reversible redox peaks, respectively, displayed by pseudocapacitive electrode materials, **(g - h)** CV of characteristic battery-like materials while **(c, f, i)** Represent the corresponding galvanostatic discharging profile. [65]

The relationship between log (i) and log (v) is used to get the b value, where b is the slope of the linear fit. The b value lies between 0.5-1, $b = 1$ stands for the surface control capacitive reaction or electrosorption, while $b = 0.5$ stands for the semi-infinite diffusion control reaction for battery (intercalative) type material. [68-70] Dunn et al. [71] made additional modifications to the rate limitation kinetics to deconvolute mixed processes occurring using the equation

$$i(V) = K_1\upsilon + K_2\upsilon^{1/2} \qquad (1.16)$$

where υ is the scan rate, i is the current from CV curves at potential V. In eq. 1.16, $K_1\upsilon$ and $K_2\upsilon^{1/2}$ are the current contributions from the surface capacitive and diffusion-controlled intercalation processes, respectively. Thus, after the determination of K_1 and K_2, from the slope and intercept of the y-axis from linear fit, we can quantify their contribution to the current density at fixed specific potentials. [72, 73]

Dunn subsequently averaged current over a period of time for each step to reproduce a cyclic voltammogram with minimal ohmic responses and afterwards separated individual contributions using K_1 and K_2.

$$i_{\mathrm{ovrall}} = i_{\mathrm{c}} + i_{\mathrm{d}} + i_{\mathrm{R}} \qquad (1.17)$$

where i_{c} is the contribution of surface controlled, i_{d} is the contribution of diffusion-controlled, and i_{R} represents the contribution of residual current. [74]

Apart from all the analyses mentioned above emphasising the current responses of various mechanisms, Trassati et al. proposed voltammetric charge to distinguish between the contributions of the inner and outer surfaces to the total charge storage. According to Trassati, the electrode's inner and outer surface capacitances add to the total specific capacitance. It can be expressed as

$$C_{Total} = C_{in} + C_{out}(\mathrm{F/g}) \qquad (1.18)$$

where the outer surface charge stored can be calculated from the intercept (υ = tends to infinity) of C_{out} vs. $\upsilon^{-1/2}$ curve and maximum charge stored can be calculated from C_{total} vs. $\upsilon^{1/2}$ curve. Trasaati assumed that the inner surface depended on the scan rate provided the lesser accessibility of the active redox sites, and the outer surface was scan rate invariant. The Trasaati model was heavily criticised for failing to account for ohmic losses, yet it was shown to be viable in specific conditions, where negligent ohmic contributions were present. [75], [76]

Usually, materials with a carbon-based material are utilized as the negative electrode, while materials with a pseudocapacitor base are employed as the positive electrode. Supercapattery (supercapacitor + battery) [77] has recently been proposed as a new terminology to describe the variety of devices that benefit from both capacitive and faradaic charge storage processes. While supercapacitors have a high-power capability and batteries have a massive capacity for storage, supercapattery comprises a wide variety of combinations but still aims to reach this goal. Finally, several functional parameters of the above-discussed energy storage devices are furnished in Table 1.1.

Table 1.1 Comparisons between batteries, capacitor, and supercapacitor

Parameters	Capacitors	Batteries	Supercapacitors
Energy density (Wh/kg)	0.01-0.3	30-265	0.5-20
Power density (W/kg)	> 5000	100-3000	5000-10000
Charge/Discharge time	1ps-1ms	1-10 hrs	1ms-1s
Operating range (V)	6-800	1.2-4.2	1.0-4.5
Cycle life (Cycles)	More than 1 million	150-2000	Up to 1 million
Operating temperature range (°C)	-20 to +100	-20 to +65	-40 to +85

1.3.4.7 Factors Affecting the Performance of SCs

The efficiency of SCs largely depends on the performance of the electrode materials and their compatibility with suitable electrolyte conjugates employed for various electrode materials giving the required higher specific energy. To significantly improve the performance of SCs, new high-performance supercapacitor technologies require the rational crafting of electrode materials and the appropriate use of electrolytes. [55, 78, 79]

High accessible electrochemical active sites, porosity, high theoretical capacitance, short diffusion routes, and strong electrical conductivity are strains placed on electrode materials to obtain high performance and effectively used SC electrodes. Therefore, the development of innovative electrode materials with sustainable and affordable morphologies and compositions that can support high performance has been at the forefront of energy research. [80, 81]

The electrolyte selection can considerably influence total storage, stability, power, and energy outputs, in addition to the importance of the electrode materials. The performance of SCs may be adversely affected by the electrolyte's parameters, such as its ionic conductivity, thermal strength, charge carrier mobility, ionic radii, and dielectric constant. [82] Several large-scale studies have concentrated on synthesizing various electrolytes in terms of their required characteristics for the performance improvement of SCs. Organic electrolytes and ionic liquids can effectively offer a large potential window for SCs' enhanced energy density. However, compared to their aqueous electrolyte counterparts, their low ionic conductivity might lead to high equivalent series resistances. [83] Ionic liquids provide safety; nevertheless, they, along with organic electrolytes, have lower ionic conductivities than traditional aqueous electrolytes. The energy capacity is limited by the electrolysis of highly ion-conductive aqueous electrolytes at lower potential windows. [84] Careful consideration should be provided for material selection and the design of the energy storage system constructed to determine the output of the energy harvesting system. The time constant and total output of SCs can also be significantly influenced by the electrode thickness, separator, and packaging, demanding adequate attention to material properties vs. device performance. [85] The SCs device's manufacture requires attention to several components, as shown in Fig. 1.18, to achieve optimum performance.

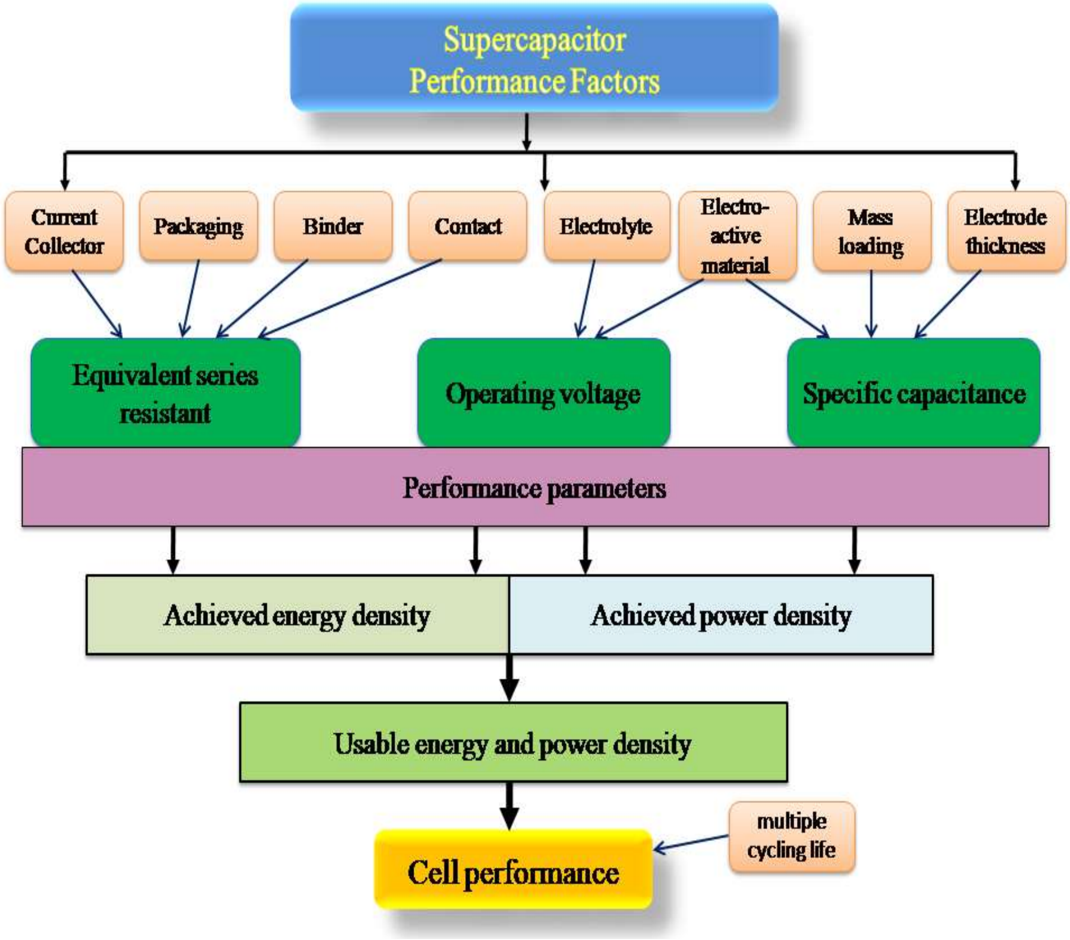

Figure 1.18 Components responsible for tuning the performance of the SCs

1.3.4.8 Electrode Materials for Supercapacitors Application

The manufacturing cost of materials, service life, environmental impact, and recyclability drives profound research and development in different energy conversion and storage devices. Therefore, SCs must provide higher energy density and lower costs for commercial applications. For this reason, electrode materials are crucial in enhancing the functionality of an electrochemical capacitor. The characteristics of an optimal electrode material for excellent-performance supercapacitors are as follows: [50, 86]

- It should possess a high specific surface area (1000-2000 m^2/g) (which helps specific capacitance)
- It should have optimized porosity and surface wettability with minimized internal electrolyte resistance (which affects the rate capability and specific capacitance)
- High electrical conductivity with a maximum operating potential range of cycling is within the solution's decomposition limit (which is crucial to power density and rate capability)
- It should possess desirable electroactive sites (which enables pseudo-capacitance)
- The actual electrode material and contacts must have minimal ohmic resistance (which affects the rate capability and specific capacitance)

1.3.4.9 Pseudocapacitor Electrode Materials

Due to their redox behavior, conducting polymers, metal sulfides, and transition-metal oxides are generally used as pseudocapacitor electrodes. During the charging and discharging cycle, the redox reaction occurs at the electrode and electrolyte interface. The supercapacitor's capacitance and energy densities are more significant than those of EDLCS because it uses charge carriers generated from redox reactions. However, the main disadvantage is the short life spans.

1.3.4.9.1 Conducting Polymers

Conducting polymers are one of the most promising pseudocapacitor electrode materials for flexible supercapacitors. They are frequently investigated because of their low cost and facile synthesis. Conductive polymers can be used in diverse applications due to the possible doping forms of conducting polymers. Conductive polymer capacitors may be divided into three main categories. The first type comprises an entirely identical p-type doped conductive polymer. This capacitor releases just half of the charge, and the potential difference between the two poles is slight. [87]

The second capacitor comprises various conducting polymers, which can have p-type doping of different conducting polymers. The potential range of doping is variable according to the various conductive polymer electrode materials, allowing the capacitor to have a greater voltage differential when it is completely charged. [88, 89]

The last type comprises an n-type and a doped p-type doped electrode. In the fully charged state, the cathode of the capacitor is in an entirely n-doped state. At the same time, the positive electrode is in a fully p-doped condition, increasing the voltage difference between the two electrodes. The critical advantage of utilizing complex polymer electrodes is that, unlike conventional metal oxides, which provide high capacitance, the entire polymer structure is exposed to the doping of ions. Polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), and polypyrrole (PPy) are the conducting polymers employed for the charge storage mechanism. For instance, PANI [90] demonstrated a high capacitance of 609 F/g.

1.3.4.9.2 Perovskite Oxides

The perovskite with general formula ABO_3, where “A” is usually an alkali earth metal or a lanthanide and “B” is a transition metal (such as Fe, Mn, Ni, Co etc.) are well-known, promising materials for pseudocapacitors. Due to its ability to accommodate various sizes and valence cations in A and B-sites, perovskite oxides can be considered an inorganic chameleon. Such compositional flexibility causes structural distortion and occasionally an excess or a shortage of oxygen. The tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where r_A, r_B, and r_O correspond to the radius of the cation

(A/B) and oxygen anion and are 1 for the ideal cubic case, can be used to predict the ease of production and stability of these distorted perovskite structures. [91]

$Nd_{1-x}Sr_xCoO_{3-\delta}$ was the first material that Kudo et al. described, and it exhibits reversible anion intercalation exchange in the range of $0 \leq \delta \leq x/2$, leading to superior pseudocapacitive charge storage in an alkaline electrolyte. [92]

The use of perovskite oxides in pseudocapacitors has several benefits. Below are some of them:

- Tuneable properties: Perovskite oxides have tuneable properties that can be adjusted by substituting elements strategically. This makes it possible to enhance their performance in pseudocapacitors.
- High capacitance: Perovskite oxides are the best choice in high-performance pseudocapacitors because of their excellent pseudocapacitance value.
- Multiple valence states: Some perovskite oxides, such as $LaNiO_3$, have many valence states. This enables the storage of charge in various ways, leading to improved pseudocapacitance.
- Stability: Perovskite oxides are ideal for long-term application in pseudocapacitors due to their exceptional structural stability.
- Catalytic activity: The catalytic activity of perovskite oxides can improve the performance of pseudocapacitors.
- Oxygen ion mobility: High oxygen ion mobility in perovskite oxides can enhance their electrochemical performance. [93-97]

The concept of doping on an A-site with a lower valence state is utilized by Alexander et al. while synthesizing high-charge storage perovskite. To balance the charge, oxygen vacancies are generated when a lower valence state is doped or the B-site (Fe, Mn, or Co) is oxidised in $La_{1-x}Sr_xBO_3$. In this regard, Cao et al. synthesised $LaNiO_3$ nanofibers using the electro spun technique and investigated the impact of Sr substitution (A-site) on their structure and electrochemical performance. [98] Due to its redox active sites, the B-site is crucial for efficient charge storage. A large voltage asymmetric supercapacitor is constructed using the significant redox potential difference between two distinct B-site perovskites. Fe, Co, and Mn - based perovskite oxides completed the whole perovskite asymmetric supercapacitor, with Fe as the negative potential electrode and Co as the positive electrode. [99] Consequently, several studies are ongoing to assess the impact of B-site doping on producing electrodes with a large potential window. A review and summary of some of the perovskite oxides utilized in past investigations are shown in Table 1.2.

Table 1.2 Literature review on several perovskite oxide-based supercapacitors and their specific values

Electrode material	**Electrolyte**	**Specific capacitance**	**Ref.**
$SrRuO_3$	6 M KOH	270 F/g at 20 mV/s	[92]
$LaNiO_3$	1 M Na_2SO_4	160 F/g at 10 mV/s	[100]
$LaMnO_{2.91}$	1 M KOH	610 F/g at 1 mV/s	[101]
$LaCoO_3$	6 M KOH	706.9 F/g at 1 A/g	[102]
$BiFeO_3$	6 M KOH	1060 F/g at 1 A/g	[103]
$La_{0.7}Sr_{0.3}FeO_{3-\delta}$	1 M Na_2SO_4	523.2 F/g at 0.8 A/g	[104]
$SrCo_{0.9}Mo_{0.1}O_{3-\delta}$	6 M KOH	1223.3 F/g at 1 A/g	[105]
$Sr_{0.8}Ba_{0.2}MnO_3$	0.5 M Na_2SO_4	446.8 F/g at 0.5 A/g	[106]

1.3.4.9.3 Transition Metal Oxides

Due to their exceptional structural flexibility and high specific capacitance, several transition metal oxides in different oxidation states are appealing materials for supercapacitors. The electric double-layer storage and the reversible redox process are the foundation for energy storage in transition metal oxides. Therefore, the main component of the charge storage mechanism is pseudocapacitance. Compared to traditional carbon materials, metal oxides can offer a greater energy density for EC and more electrochemical stability than polymer materials. Metal oxides undergo electrochemical faradaic reactions between electrode materials and ions within specific potential windows and can store energy similarly to carbon-based materials. In general, metal oxide exhibits poorer electrochemical performance and has lower electrical conductivity than carbon-based materials. To overcome this, additions of carbon scaffolds are generally employed. [107]

Ruthenium oxide (RuO_2), for instance, is regarded as the best electrode material for pseudocapacitors because of its broad potential window, high specific capacitance (450 F/g at 125 mV/s), thermal stability, and extended cycle life, among other advantages. [108] However, these benefits are diminished by the high expense and toxicity. This may be avoided by using inexpensive metal oxides. Compared to RuO_2, a less expensive metal oxide, and its ions can make a reversible transfer among the multiple valences has been the subject of much interest. MnO_2 has been actively researched as a substitute for RuO_2 due to its low cost, abundance, and high "theoretical" capacity, since Lee and Goodenough (1999) described its pseudocapacitive behavior. Several transition metal oxides were employed for the supercapacitor, including vanadium oxide, cobalt oxide, zinc oxide, tin oxide, and cobalt oxide. Due to their increased reversible capacity, excellent structural stability, and high electronic conductivity, binary transition metal oxides have received much attention recently as researchers look for new electrode materials for supercapacitors. A review and summary of some of the metal oxides utilized in past investigations may be found in Table 1.3.

Table 1.3 Literature review on several metal oxide-based supercapacitors and their specific values

Electrode material	Electrolyte	Specific capacitance	Ref.
NiO	1 M KOH	2018 F/g at 2.27 A/g	[109]
V_2O_5	0.5 M K_2SO_4	375 F/g at 0.5 A/g	[110]
MnO_2	1 M Na_2SO_4	391 F/g at 5 mV/s	[111]
Mn_3O_4	6 M KOH	583 F/g at 1 A/g	[112]
Co_3O_4	1 M KOH	548 F/g at 8 A/g	[113]
CuO	6 M KOH	536 F/g at 2 A/g	[114]
Fe_2O_3	6 M KOH	520 F/g at 5 mV/s	[115]
$NiCo_2O_4$	6 M KOH	2876 F/g at 1 A/g	[116]
CeO_2	1 M HCl	927 F/g at 2 A/g	[117]
RuO_2	0.5 M H_2SO_4	650 F/g at 20 mV/s	[118]
MoO_3	1 M Na_2SO_4	176 F/g at 1 mA/g	[119]
SnO_2	0.5 M Na_2SO_4	66 F/g at 10 mV/s	[120]

1.3.4.9.4 Transition Metal Sulfides

Metal oxides and carbon materials have previously dominated the field of research for SCs as effective pseudocapacitive and EDLC electrode materials. In contrast to their oxides counterparts, transition metal sulfides (TMS) have recently captured the spotlight and emerged as a new paradigm for supercapacitors due to their superior electrical conductivity, strong thermal and mechanical stability, electrochemically rich redox reactions, and sulfur facilitating improved ion transport. [121-123]

Table 1.4 Literature reviews of TMS based supercapacitors and its specific capacitance

Electrode material	**Electrolyte**	**Specific Capacitance**	**Reference**
NiS_2	3 M KOH	695 F/g at 1.25 A/g	[125]
Ni_3S_4	2 M KOH	1797.5 F/g at 0.5 A/g	[126]
MoS_2	3 M KOH	357 F/g at 10 mV/s	[127]
β-CoS	2 M KOH	1535 F/g at 2 A/g	[128]
CoS_2	2 M KOH	236.5 F/g at 1 A/g	[129]
Co_9S_8	2 M KOH	1887 F/g at 1 A/g	[130]
Co_3S_4	6 M KOH	2427 F/g at 2 mV/s	[131]
$NiCo_2S_4$	6 M KOH	1,036 F/g at 1 A/g	[132]
CuS	6 M KOH	948 F/g at 1 A/g	[133]
SnS	3 M KOH	284 F/g at 5 A/g	[134]
SnS_2	2 M KOH	431.82 F/g at 1 A/g	[135]
VS_2	0.5 M H_2SO_4	235 F/g at 100 mV/s	[136]
WS_2	1 M H_2SO_4	383.6 F/g at 0.5 A/g	[137]
FeS_2	3.5 M KOH	260 F/g at 1 A/g	[138]

The two most common forms of TMS are three-dimensional covalently bonded non-layered assemblies (FeS_2, CoS_2, and NiS_2) and layered assemblies made of three atom layers that are covalently bound (S-M-S; M = W, Co, Sn, and V). Mostly TMS are readily accessible, non-toxic (minerals), and may be used as cost-effective technologies using large-scale synthesis. [121, 124] To achieve better electrochemical performance, sulfide materials can be rationally designed in terms of composition, structure, and size to serve as electrode materials. This can result in shorter diffusion paths and increased conductivity. TMS has made a considerable impact as promising electrodes with great potential, easily synthesized, modified, and tailored toward energy storage devices, are being thoroughly explored through different studies and are continuing. However, other problems must be addressed, such as sluggish kinetics, low electrochemical stability, and volumetric changes. [37]

Among several metal sulfides, cobalt and nickel sulfide have been extensively studied due to their multiple phases, cheap cost, abundance, superior capacitance, less toxicity, and large surface area with vast applications in lithium-ion batteries and supercapacitors.

1.3.5 Nanomaterials and their Scope in the Context of Energy Storage

Novel nanostructured MSs are typically porous. They can confer a larger surface area compared to bulk metal oxide and sulfide materials, making them more advantageous for the infiltration of electrodes, complete contact between the active materials and electrolyte, the mobility of charges in the electrolytes, and the use of the active materials at high rates of charging and discharging. [139] Further high specific surface area in nanomaterials leads to more significant ion adsorption and charge-transfer processes, which increases specific capacitance. The movement of electrolyte ions is facilitated by shorter diffusion lengths and ion transport channels, significantly enhancing the usage of active materials. Due to the surface redox reactions that occur faster than in bulk materials, materials with nanometer-sized morphological characteristics and a large electrochemically sensitive interface can redefine the trend of energy storage and enable noticeably improved power and cycle life. [140]

Ordinary substances that cannot be utilised as electrodes become appropriate to be used as anodes and cathodes by nano-structuring. Alloying metals are one such example in which the metals undergo substantial volume and structural changes in the nanostructuring process. Due to nanostructuring, the diffusion distance became shorter, making it possible to charge faster or draw high currents quickly, thus increasing power. [141, 142]

Because of their high theoretical capacity and high energy density, metal sulfide nanoparticles can store much energy in a small volume. The exceptional stability and extended cycle life of metal sulfide nanoparticles make them perfect for energy storage applications. The performance of metal sulfide nanoparticles in energy storage devices may be enhanced by functionalizing them with catalysts. Due to their numerous sources, transition metal sulfides are a cheap option for energy storage applications. [124, 143-145]

1.3.6 Suitability of Transition Metal Sulfides

Transition MSs have several advantages as electrode materials for energy storage devices. They have high theoretical capacity, good cycling stability, and low cost, making them promising anode materials for lithium-ion batteries. [146] They also have high specific capacitance, excellent rate capability, and long cycle life, making them a promising class of materials for advanced supercapacitors. [147] Additionally, transition MS have easily-controlled structures and modifiable compositions, making them highly versatile for various applications. They also have good electrical conductivity, high redox activity, and unique crystal structures, which contribute to their outstanding properties. [37, 148] Overall, transition MS have shown great potential as electrode materials for energy storage devices due to their advantageous features and low cost.

1.3.7 Challenges and Methods of Synthesis in Transition Metal Sulfides

Even though MS have numerous benefits, there are also several issues. First, there is a chance that the final discharge products will interact adversely with the electrolyte. Second, significant volume expansion is caused by the other metal participating in the electrochemical reaction. Third, the first cycle has a significant irreversible capacity due to the solid electrolyte interphase (SEI) layer. Fourthly, the poor conductivity and ion-diffusion coefficient retard the rate performance. The most often used strategies to address these problems are nanostructure design, electrolyte optimization, carbon modification, and voltage range selection. [149]

It is generally known that natural MS were widely spread on the earth, including pyrite, mackinawite, chalcocite, chalcopyrite, molybdenite, etc. However, due to their high purity, strong reactivity, and good dispersion, researchers are likely to employ synthetic MS. Several techniques are currently used to synthesize metal sulfides, including hydrothermal and solvothermal, template, precipitation, reflux, Solid state, ball milling, thermal composition, electrochemical, etc. Nanosized particles may effectively reduce the impacts of volume expansion and give a short ion-diffusion length for morphological design. [149, 150]

The choice of method depends on the specific application and the desired product characteristics. Compared to conventional methods for MS synthesis, solution-controlled synthesis is more efficient and economical. Because multiphase products are a problem for traditional MS synthesis techniques, we target to synthesise single-phase MS nanoparticles using a solution-controlled approach for high-performance PCs electrodes. [151]

1.4 Scope of this Work

Researchers have recently been interested in nanosized single-phase metal sulfides because of their forthcoming pseudo-capacitive performance. Therefore, in this thesis, we use a solution-based method to produce nanosized single-phase transition metal sulfide materials for high-performance pseudocapacitive electrodes. The electrochemical performance depends on voltage, crystallinity, synthesis methods, and morphological characteristics. Hence, the present work mainly focuses on the following objectives.

- To synthesize various metal sulfide (NiS, CoS, and $Ni_{0.5}Co_{0.5}S$) by solution-based method
- To characterize synthesized nanostructures (NiS, CoS, and $Ni_{0.5}Co_{0.5}S$) with various characterization techniques such as XRD, SEM, HRTEM, UV-Vis, FTIR, TGA, BET etc.
- To study the electrochemical performance of the synthesized nanostructures by cyclic voltammogram (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy

1.5 References

1. Nykvist, B. and M. Nilsson, *Rapidly falling costs of battery packs for electric vehicles.* Nature Climate Change, 2015. **5**(4): p. 329-332.
2. Liu, J., et al., *Advanced energy storage devices: basic principles, analytical methods, and rational materials design.* Advanced science, 2018. **5**(1): p. 1700322.
3. Sieminski, A., *International energy outlook 2013.* US Energy Information Administration (EIA) Report Number: DOE/EIA-0484, 2013.
4. Pásztor, A., *Advanced biofuel production: Engineering metabolic pathways for butanol and propane biosynthesis.* Turku: University of Turku, 2015.
5. Kebede, A.A., et al., *A comprehensive review of stationary energy storage devices for large scale renewable energy sources grid integration.* Renewable and Sustainable Energy Reviews, 2022. **159**: p. 112213.
6. Mitali, J., S. Dhinakaran, and A. Mohamad, *Energy storage systems: A review.* Energy Storage and Saving, 2022.
7. Chakraborty, M.R., et al., *A Comparative Review on Energy Storage Systems and Their Application in Deregulated Systems.* Batteries, 2022. **8**(9): p. 124.
8. Al-Sharafi, A., et al., *Techno-economic analysis and optimization of solar and wind energy systems for power generation and hydrogen production in Saudi Arabia.* Renewable and Sustainable Energy Reviews, 2017. **69**: p. 33-49.
9. Wei, P., et al., *Progress in Energy Storage Technologies and Methods for Renewable Energy Systems Application.* Applied Sciences, 2023. **13**(9): p. 5626.

10. Ramadoss, A., et al., *Fully flexible, lightweight, high performance all-solid-state supercapacitor based on 3-Dimensional-graphene/graphite-paper.* Journal of Power Sources, 2017. **337**: p. 159-165.
11. Nations, U., *Renewable Energy–Powering a Safer Future.*
12. Agency, I.E., *Renewables 2022 - Analysis and forecast to 2027*. 2022, International Energy Agency: www.iea.com. p. 159.
13. Mann, M., S. Babinec, and V. Putsche, *Energy storage grand challenge: Energy storage market report*. 2020, National Renewable Energy Lab.(NREL), Golden, CO (United States).
14. Amiryar, M.E. and K.R. Pullen, *A review of flywheel energy storage system technologies and their applications.* Applied Sciences, 2017. **7**(3): p. 286.
15. Brun, K., T.C. Allison, and R. Dennis, *Thermal, mechanical, and hybrid chemical energy storage systems*. 2020: Academic Press.
16. Storage, T.E., *Technology Brief.* IEA-ETSAP and IRENA© Technology Brief E17-January, 2013.
17. Achkari, O. and A. El Fadar, *Renewable Energy Storage Technologies-A.* Proceedings of Engineering and Technology–PET, 2018. **35**: p. 69-79.
18. Hailemariam, H. and F. Wuttke, *Hydrothermal modelling and analysis of sensible heat energy storages for small-scale dwellings considering natural convection.* Energy Procedia, 2016. **97**: p. 462-469.
19. Pullano, S., et al., *Biomass plant and sensors network for process monitoring and energy storage in a superconducting magnetic device.* Safety of Technogenic Environment, 2014. **6**: p. 28-35.
20. Breeze, P., *Power system energy storage technologies*. 2018: Academic Press.

21. Chen, S., L. Qiu, and H.-M. Cheng, *Carbon-Based Fibers for Advanced Electrochemical Energy Storage Devices.* Chemical Reviews, 2020. **120**(5): p. 2811-2878.

22. Evans, A., V. Strezov, and T.J. Evans, *Assessment of utility energy storage options for increased renewable energy penetration.* Renewable and Sustainable Energy Reviews, 2012. **16**(6): p. 4141-4147.

23. Pavlov, D., *Lead-acid batteries: science and technology*. 2011: Elsevier.

24. Calábek, M., et al., *A fundamental study of the effects of compression on the performance of lead accumulator plates.* Journal of power sources, 2001. **95**(1-2): p. 97-107.

25. Krivik, P. and P. Baca, *Electrochemical energy storage.* Energy Storage-Technologies and Applications, 2013: p. 79-100.

26. Goodenough, J.B. and K.-S. Park, *The Li-ion rechargeable battery: a perspective.* Journal of the American Chemical Society, 2013. **135**(4): p. 1167-1176.

27. Tarascon, J.-M. and M. Armand, *Issues and challenges facing rechargeable lithium batteries.* nature, 2001. **414**(6861): p. 359-367.

28. Zheng, H., et al., *Cathode performance as a function of inactive material and void fractions.* Journal of The Electrochemical Society, 2010. **157**(10): p. A1060.

29. Jeong, H.-S., S.C. Hong, and S.-Y. Lee, *Effect of microporous structure on thermal shrinkage and electrochemical performance of Al2O3/poly (vinylidene fluoride-hexafluoropropylene) composite separators for lithium-ion batteries.* Journal of Membrane Science, 2010. **364**(1-2): p. 177-182.

30. Hou, C.-L., et al. *Application of adaptive algorithm of solar cell battery charger*. in *2004 IEEE International Conference on Electric Utility Deregulation, Restructuring and Power Technologies. Proceedings*. 2004. IEEE.

31. Arévalo-Cid, P., et al., *Redox flow batteries: a new frontier on energy storage.* Sustainable Energy & Fuels, 2021. **5**(21): p. 5366-5419.

32. Milshtein, J.D., et al., *High current density, long duration cycling of soluble organic active species for non-aqueous redox flow batteries.* Energy & Environmental Science, 2016. **9**(11): p. 3531-3543.

33. Zhang, Z., et al., *Chloride ions as an electrolyte additive for high performance vanadium redox flow batteries.* Applied Energy, 2021. **289**: p. 116690.

34. Li, Y. and J. Lu, *Metal–air batteries: will they be the future electrochemical energy storage device of choice?* ACS Energy Letters, 2017. **2**(6): p. 1370-1377.

35. Bharadwaj, N., et al., *Size-Dependent Effects in Fullerene-Based Catalysts for Nonaqueous Li–Air Battery Applications.* ACS Applied Energy Materials, 2022. **5**(3): p. 3380-3391.

36. Yi, J., et al., *Challenges, mitigation strategies and perspectives in development of zinc-electrode materials and fabrication for rechargeable zinc–air batteries.* Energy & Environmental Science, 2018. **11**(11): p. 3075-3095.

37. Barik, R. and P.P. Ingole, *Challenges and prospects of metal sulfide materials for supercapacitors.* Current Opinion in Electrochemistry, 2020. **21**: p. 327-334.

38. Ryu, H., et al., *Self-discharge of lithium–sulfur cells using stainless-steel current-collectors.* Journal of Power Sources, 2005. **140**(2): p. 365-369.

39. Su, Y.-S. and A. Manthiram, *A new approach to improve cycle performance of rechargeable lithium–sulfur batteries by inserting a free-standing MWCNT interlayer.* Chemical communications, 2012. **48**(70): p. 8817-8819.

40. Kim, B.K., et al., *Electrochemical supercapacitors for energy storage and conversion.* Handbook of clean energy systems, 2015: p. 1-25.

41. Chen, G.Z., *Understanding supercapacitors based on nano-hybrid materials with interfacial conjugation.* Progress in Natural Science: Materials International, 2013. **23**(3): p. 245-255.

42. Sun, J., B. Luo, and H. Li, *A Review on the conventional capacitors, supercapacitors, and emerging hybrid ion capacitors: Past, present, and future.* Advanced Energy and Sustainability Research, 2022. **3**(6): p. 2100191.

43. Christensen, J., et al., *A critical review of Li/air batteries.* Journal of the Electrochemical Society, 2011. **159**(2): p. R1.

44. Tang, Y., et al., *Experimental investigation of dynamic performance and transient responses of a kW-class PEM fuel cell stack under various load changes.* Applied Energy, 2010. **87**(4): p. 1410-1417.

45. Jia, R., et al., *Flexible on-chip micro-supercapacitors: Efficient power units for wearable electronics.* Energy Storage Materials, 2020. **27**: p. 169-186.

46. Satpathy, S., S. Das, and B.K. Bhattacharyya, *How and where to use super-capacitors effectively, an integration of review of past and new characterization works on super-capacitors.* Journal of Energy Storage, 2020. **27**: p. 101044.

47. Zhang, Y., et al., *Progress of electrochemical capacitor electrode materials: A review.* International journal of hydrogen energy, 2009. **34**(11): p. 4889-4899.

48. Lu, X., et al., *Flexible solid-state supercapacitors: design, fabrication and applications.* Energy & Environmental Science, 2014. **7**(7): p. 2160-2181.

49. Simon, P., Y. Gogotsi, and B. Dunn, *Where do batteries end and supercapacitors begin?* Science, 2014. **343**(6176): p. 1210-1211.

50. Iro, Z.S., C. Subramani, and S. Dash, *A brief review on electrode materials for supercapacitor.* Int. J. Electrochem. Sci, 2016. **11**(12): p. 10628-10643.

51. Das, A., et al., *Performance and future directions of transition metal sulfide-based electrode materials towards supercapacitor/supercapattery.* Wiley Interdisciplinary Reviews: Energy and Environment, 2022. **11**(1): p. e414.

52. Conway, B.E., V. Birss, and J. Wojtowicz, *The role and utilization of pseudocapacitance for energy storage by supercapacitors.* Journal of power sources, 1997. **66**(1-2): p. 1-14.

53. Liu, Y., S. Jiang, and Z. Shao, *Intercalation pseudocapacitance in electrochemical energy storage: recent advances in fundamental understanding and materials development.* Materials Today Advances, 2020. **7**: p. 100072.

54. Augustyn, V., P. Simon, and B. Dunn, *Pseudocapacitive oxide materials for high-rate electrochemical energy storage.* Energy & Environmental Science, 2014. **7**(5): p. 1597-1614.

55. Panda, P.K., et al., *Progress in supercapacitors: roles of two dimensional nanotubular materials.* Nanoscale Advances, 2020. **2**(1): p. 70-108.

56. Sudha, V. and M. Sangaranarayanan, *Underpotential deposition of metals: structural and thermodynamic considerations.* The Journal of Physical Chemistry B, 2002. **106**(10): p. 2699-2707.

57. Bi, R.-R., et al., *Highly dispersed RuO2 nanoparticles on carbon nanotubes: facile synthesis and enhanced supercapacitance performance.* The Journal of Physical Chemistry C, 2010. **114**(6): p. 2448-2451.

58. Kong, L., et al., *High-power and high-energy asymmetric supercapacitors based on Li+-intercalation into a T-Nb 2 O 5/graphene pseudocapacitive electrode.* Journal of Materials Chemistry A, 2014. **2**(42): p. 17962-17970.

59. Naoi, K. and Y. Nagano, *Li-Ion-Based Hybrid Supercapacitors in Organic Medium.* Supercapacitors: Materials, Systems, and Applications, 2013: p. 239-256.

60. Cherusseri, J., D. Pandey, and J. Thomas, *Symmetric, asymmetric, and battery-type supercapacitors using two-dimensional nanomaterials and composites.* Batteries & Supercaps, 2020. **3**(9): p. 860-875.

61. Halper, M. and J. Ellenbogen, *Ultra-capacitors: A Brief Overview.* MITRE Nanosystems Group, 2006.

62. Brousse, T., D. Bélanger, and J.W. Long, *To be or not to be pseudocapacitive?* Journal of The Electrochemical Society, 2015. **162**(5): p. A5185.

63. Lokhande, P.E., U.S. Chavan, and A. Pandey, *Materials and fabrication methods for electrochemical supercapacitors: overview.* Electrochemical Energy Reviews, 2020. **3**: p. 155-186.

64. Conway, B.E., *Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage.* Journal of the Electrochemical Society, 1991. **138**(6): p. 1539.

65. Gogotsi, Y. and R.M. Penner, *Energy storage in nanomaterials–capacitive, pseudocapacitive, or battery-like?* 2018, ACS Publications. p. 2081-2083.

66. Lindström, H., et al., *Li+ ion insertion in TiO2 (anatase). 2. Voltammetry on nanoporous films.* The Journal of Physical Chemistry B, 1997. **101**(39): p. 7717-7722.

67. Su, D., et al., *High-capacity aqueous potassium-ion batteries for large-scale energy storage.* Advanced Materials, 2017. **29**(1): p. 1604007.

68. Fleischmann, S., et al., *Pseudocapacitance: from fundamental understanding to high power energy storage materials.* Chemical Reviews, 2020. **120**(14): p. 6738-6782.

69. Daum, P., et al., *Diffusional charge transport through ultrathin films of radiofrequency plasma polymerized vinylferrocene at low temperature.* Journal of the American Chemical Society, 1980. **102**(14): p. 4649-4653.

70. Ardizzone, S., G. Fregonara, and S. Trasatti, *"Inner" and "outer" active surface of RuO2 electrodes.* Electrochimica Acta, 1990. **35**(1): p. 263-267.

71. Wang, J., et al., *Pseudocapacitive contributions to electrochemical energy storage in TiO2 (anatase) nanoparticles.* The Journal of Physical Chemistry C, 2007. **111**(40): p. 14925-14931.

72. Kim, H.-S., et al., *Oxygen vacancies enhance pseudocapacitive charge storage properties of MoO3− x.* Nature materials, 2017. **16**(4): p. 454-460.

73. Brezesinski, T., et al., *On the correlation between mechanical flexibility, nanoscale structure, and charge storage in periodic mesoporous CeO2 thin films.* ACS nano, 2010. **4**(2): p. 967-977.

74. Dupont, M.F. and S.W. Donne, *A step potential electrochemical spectroscopy analysis of electrochemical capacitor electrode performance.* Electrochimica acta, 2015. **167**: p. 268-277.

75. Baronetto, D., N. Krstajić, and S. Trasatti, *Reply to "note on a method to interrelate inner and outer electrode areas" by H. Vogt.* Electrochimica acta, 1994. **39**(16): p. 2359-2362.

76. Vogt, H., *Note on a method to interrelate inner and outer electrode areas.* Electrochimica acta, 1994. **39**(13): p. 1981-1983.

77. Yu, L. and G.Z. Chen, *Redox electrode materials for supercapatteries.* Journal of Power Sources, 2016. **326**: p. 604-612.

78. Fan, Z., et al., *Asymmetric supercapacitors based on graphene/MnO2 and activated carbon nanofiber electrodes with high power and energy density.* Advanced Functional Materials, 2011. **21**(12): p. 2366-2375.

79. Ho, K.-C. and L.-Y. Lin, *A review of electrode materials based on core–shell nanostructures for electrochemical supercapacitors.* Journal of materials chemistry A, 2019. **7**(8): p. 3516-3530.

80. Shi, J., et al., *Review of transition metal nitrides and transition metal nitrides/carbon nanocomposites for supercapacitor electrodes.* Materials Chemistry and Physics, 2020. **245**: p. 122533.

81. Yang, Y., *A mini-review: emerging all-solid-state energy storage electrode materials for flexible devices.* Nanoscale, 2020. **12**(6): p. 3560-3573.

82. Pal, B., et al., *Electrolyte selection for supercapacitive devices: a critical review.* Nanoscale Advances, 2019. **1**(10): p. 3807-3835.

83. Pal, B., et al., *In situ encapsulation of tin oxide and cobalt oxide composite in porous carbon for high-performance energy storage applications.* Journal of Electroanalytical Chemistry, 2018. **817**: p. 217-225.

84. Tan, S., et al., *Recent progress in research on high-voltage electrolytes for lithium-ion batteries.* ChemPhysChem, 2014. **15**(10): p. 1956-1969.

85. Kroupa, M., G.J. Offer, and J. Kosek, *Modelling of supercapacitors: Factors influencing performance.* Journal of The Electrochemical Society, 2016. **163**(10): p. A2475.

86. Forouzandeh, P., V. Kumaravel, and S.C. Pillai, *Electrode materials for supercapacitors: a review of recent advances.* Catalysts, 2020. **10**(9): p. 969.

87. Hanemann, T. and D.V. Szabó, *Polymer-nanoparticle composites: from synthesis to modern applications.* Materials, 2010. **3**(6): p. 3468-3517.

88. Zeng, T., et al., *A novel Fe 3 O 4–graphene–Au multifunctional nanocomposite: green synthesis and catalytic application.* Journal of Materials Chemistry, 2012. **22**(35): p. 18658-18663.

89. Ermiş, E., D. Yiğit, and M. Güllü, *Synthesis of poly (N-alkyl-3, 4-dihydrothieno [3, 4-b][1, 4] oxazine) derivatives and investigation of their supercapacitive performances for charge storage applications.* Electrochimica Acta, 2013. **90**: p. 623-633.

90. Zhou, H., et al., *The effect of the polyaniline morphology on the performance of polyaniline supercapacitors.* Journal of Solid State Electrochemistry, 2005. **9**: p. 574-580.

91. Vasala, S. and M. Karppinen, *A2B' B "O6 perovskites: a review.* Progress in solid state chemistry, 2015. **43**(1-2): p. 1-36.

92. Wohlfahrt-Mehrens, M., et al., *New materials for supercapacitors.* Journal of power sources, 2002. **105**(2): p. 182-188.

93. Che, W., et al., *Perovskite LaNiO3-δ oxide as an anion-intercalated pseudocapacitor electrode.* Journal of Alloys and Compounds, 2018. **731**: p. 381-388.

94. Forslund, R.P., et al., *Comparison of perovskite and perovskite derivatives for use in anion-based pseudocapacitor applications.* Journal of Materials Chemistry A, 2019. **7**(37): p. 21222-21231.

95. Alexander, C.T., *Perovskites oxides for metal-air batteries and pseudocapacitor applications*. 2019.

96. Nan, H.-s., X.-y. Hu, and H.-w. Tian, *Recent advances in perovskite oxides for anion-intercalation supercapacitor: a review.* Materials Science in Semiconductor Processing, 2019. **94**: p. 35-50.

97. Ahangari, M., et al., *Investigation of structural and electrochemical properties of SrFexCo1-xO3-δ perovskite oxides as a supercapacitor electrode material.* Journal of Energy Storage, 2023. **63**: p. 107034.

98. Cao, Y., et al., *Sr-doped lanthanum nickelate nanofibers for high energy density supercapacitors.* Electrochimica Acta, 2015. **174**: p. 41-50.

99. Kuznetsov, D.A., et al., *Tuning redox transitions via inductive effect in metal oxides and complexes, and implications in oxygen electrocatalysis.* Joule, 2018. **2**(2): p. 225-244.

100. Hwang, D.K., et al., *Phase evolution of perovskite LaNiO 3 nanofibers for supercapacitor application and p-type gas sensing properties of LaOCl–NiO composite nanofibers.* Journal of Materials Chemistry, 2011. **21**(6): p. 1959-1965.

101. Mefford, J.T., et al., *Anion charge storage through oxygen intercalation in LaMnO3 perovskite pseudocapacitor electrodes.* Nature materials, 2014. **13**(7): p. 726-732.

102. Guo, G., et al., *Facile synthesis of LaCoO3 with a high oxygen vacancy concentration by the plasma etching technique for high-performance oxygen ion intercalation pseudocapacitors.* ACS Applied Energy Materials, 2019. **3**(1): p. 300-308.

103. Ma, C.-J., et al., *Bismuth ferrite: an abnormal perovskite with electrochemical extraction of ions from A site.* Journal of Materials Chemistry A, 2019. **7**(19): p. 12176-12190.

104. Wang, W., et al., *Synthesis, morphology and electrochemical performances of perovskite-type oxide LaxSr1-xFeO3 nanofibers prepared by electrospinning.* Journal of Physics and Chemistry of Solids, 2019. **124**: p. 144-150.

105. Tomar, A.K., G. Singh, and R.K. Sharma, *Fabrication of a Mo-doped strontium cobaltite perovskite hybrid supercapacitor cell with high energy density and excellent cycling life.* ChemSusChem, 2018. **11**(23): p. 4123-4130.

106. George, G., et al., *Effect of doping on the performance of high-crystalline SrMnO3 perovskite nanofibers as a supercapacitor electrode.* Ceramics International, 2018. **44**(17): p. 21982-21992.

107. Ho, M., et al., *A review of metal oxide composite electrode materials for electrochemical capacitors.* Nano, 2014. **9**(06): p. 1430002.

108. Gujar, T., et al., *Spray deposited amorphous RuO2 for an effective use in electrochemical supercapacitor.* Electrochemistry communications, 2007. **9**(3): p. 504-510.

109. Lu, Z., et al., *Stable ultrahigh specific capacitance of NiO nanorod arrays.* Nano Research, 2011. **4**(7): p. 658-665.

110. Li, M., et al., *Synthesis and electrochemical performance of V2O5 nanosheets for supercapacitor.* AIP Advances, 2022. **12**(5): p. 055203.

111. Kumar, Y., et al., *Low temperature synthesis of MnO2 nanostructures for supercapacitor application.* Materials Science for Energy Technologies, 2020. **3**: p. 566-574.

112. Luo, Y., et al., *High performance of Mn3O4 cubes for supercapacitor applications.* Materials Letters, 2016. **178**: p. 171-174.

113. Meher, S.K. and G.R. Rao, *Ultralayered Co3O4 for High-Performance Supercapacitor Applications.* The Journal of Physical Chemistry C, 2011. **115**(31): p. 15646-15654.

114. Senthilkumar, V., et al., *Comparative supercapacitance performance of CuO nanostructures for energy storage device applications.* RSC Advances, 2015. **5**(26): p. 20545-20553.

115. Wan, L.-M., et al., *Stabilizing charge storage of Fe2O3-based electrode via phosphate ion functionalization for long cycling life.* Rare Metals, 2023. **42**(1): p. 39-46.

116. Hao, C., et al., *Preparation of Hierarchical Spinel NiCo2O4 Nanowires for High-Performance Supercapacitors.* Industrial & Engineering Chemistry Research, 2018. **57**(7): p. 2517-2525.

117. Maheswari, N. and G. Muralidharan, *Hexagonal CeO2 nanostructures: an efficient electrode material for supercapacitors.* Dalton Transactions, 2016. **45**(36): p. 14352-14362.

118. Patake, V., C. Lokhande, and O.S. Joo, *Electrodeposited ruthenium oxide thin films for supercapacitor: Effect of surface treatments.* Applied Surface Science, 2009. **255**(7): p. 4192-4196.

119. Prakash, N.G., et al., *High performance one dimensional α-MoO3 nanorods for supercapacitor applications.* Ceramics International, 2018. **44**(8): p. 9967-9975.

120. Pusawale, S., P. Deshmukh, and C. Lokhande, *Chemical synthesis of nanocrystalline SnO2 thin films for supercapacitor application.* Applied Surface Science, 2011. **257**(22): p. 9498-9502.

121. Kulkarni, P., et al., *Nanostructured binary and ternary metal sulfides: synthesis methods and their application in energy conversion and storage devices.* Journal of Materials Chemistry A, 2017. **5**(42): p. 22040-22094.

122. Chandrasekaran, S., et al., *Recent advances in metal sulfides: from controlled fabrication to electrocatalytic, photocatalytic and photoelectrochemical water splitting and beyond.* Chemical Society Reviews, 2019. **48**(15): p. 4178-4280.

123. Theerthagiri, J., et al., *Recent advances in metal chalcogenides (MX; X= S, Se) nanostructures for electrochemical supercapacitor applications: a brief review.* Nanomaterials, 2018. **8**(4): p. 256.

124. Rui, X., H. Tan, and Q. Yan, *Nanostructured metal sulfides for energy storage.* Nanoscale, 2014. **6**(17): p. 9889-9924.

125. Pang, H., et al., *Microwave-assisted synthesis of NiS2 nanostructures for supercapacitors and cocatalytic enhancing photocatalytic H2 production.* Scientific reports, 2014. **4**(1): p. 3577.

126. Wang, H., et al., *Rose-like Ni3S4 as battery-type electrode for hybrid supercapacitor with excellent charge storage performance.* Chemical Engineering Journal, 2018. **350**: p. 523-533.

127. Isacfranklin, M., et al., *Rare Earth-Doped MoS2 for Supercapacitor Application.* Energy & Fuels, 2022. **36**(12): p. 6476-6482.

128. Qu, B., et al., *β-Cobalt sulfide nanoparticles decorated graphene composite electrodes for high capacity and power supercapacitors.* Nanoscale, 2012. **4**(24): p. 7810-7816.

129. Xing, J.-C., et al., *Fabrication and shape evolution of CoS2 octahedrons for application in supercapacitors.* Electrochimica Acta, 2014. **136**: p. 550-556.

130. Sun, S., et al., *Metal–Organic Framework Derived Honeycomb Co9S8@ C Composites for High-Performance Supercapacitors.* Advanced Energy Materials, 2018. **8**(25): p. 1801080.

131. Grace, A.N., et al., *Facile synthesis and electrochemical properties of Co3S4-nitrogen-doped graphene nanocomposites for supercapacitor applications.* Electroanalysis, 2014. **26**(1): p. 199-208.

132. Shen, L., et al., *Formation of nickel cobalt sulfide ball-in-ball hollow spheres with enhanced electrochemical pseudocapacitive properties.* Nature communications, 2015. **6**(1): p. 6694.

133. Heydari, H., et al., *Nanoporous CuS nano-hollow spheres as advanced material for high-performance supercapacitors.* Applied Surface Science, 2017. **394**: p. 425-430.

134. Dar, M.A., D. Govindarajan, and G.N. Dar, *Facile synthesis of SnS nanostructures with different morphologies for supercapacitor and dye-sensitized solar cell applications.* Journal of Materials Science: Materials in Electronics, 2021. **32**: p. 20394-20409.

135. Parveen, N., et al., *Facile synthesis of SnS2 nanostructures with different morphologies for high-performance supercapacitor applications.* ACS omega, 2018. **3**(2): p. 1581-1588.

136. Archana, B., N. Kottam, and C.S. KB, *Synthesis, characterization and supercapacitor electrode performances of VS2 nanosheets.* Materials Today: Proceedings, 2021. **46**: p. 545-549.

137. Chen, W., et al., *Hierarchical architecture of coupling graphene and 2D WS2 for high-performance supercapacitor.* Electrochimica Acta, 2019. **298**: p. 313-320.

138. Venkateshalu, S., et al., *Solvothermal synthesis and electrochemical properties of phase pure pyrite FeS2 for supercapacitor applications.* Electrochimica Acta, 2018. **290**: p. 378-389.

139. Wang, F., et al., *Latest advances in supercapacitors: from new electrode materials to novel device designs.* Chemical Society Reviews, 2017. **46**(22): p. 6816-6854.

140. Dunn, B., H. Kamath, and J.-M. Tarascon, *Electrical energy storage for the grid: a battery of choices.* Science, 2011. **334**(6058): p. 928-935.

141. Wu, H., et al., *Stable cycling of double-walled silicon nanotube battery anodes through solid–electrolyte interphase control.* Nature nanotechnology, 2012. **7**(5): p. 310-315.

142. Gogotsi, Y., *What nano can do for energy storage*. 2014, ACS Publications. p. 5369-5371.

143. Xiong, L., et al., *Prospective applications of transition metal-based nanomaterials.* Journal of Materials Research, 2022. **37**(13): p. 2109-2123.

144. Kajana, T., et al., *Potential transition and post-transition metal sulfides as efficient electrodes for energy storage applications.* RSC advances, 2022. **12**(28): p. 18041-18062.

145. Pham, D.T., et al., *Colloidal metal sulfide nanoparticles for high performance electrochemical energy storage systems.* Current Opinion in Green and Sustainable Chemistry, 2022. **34**: p. 100596.

146. Ma, M., et al., *Progress and prospects of transition metal sulfides for sodium storage.* Advanced Fiber Materials, 2020. **2**: p. 314-337.

147. Theerthagiri, J., et al., *Recent progress and emerging challenges of transition metal sulfides based composite electrodes for electrochemical supercapacitive energy storage.* Ceramics international, 2020. **46**(10): p. 14317-14345.

148. Gao, Y. and L. Zhao, *Review on recent advances in nanostructured transition-metal-sulfide-based electrode materials for cathode materials of asymmetric supercapacitors.* Chemical Engineering Journal, 2022. **430**: p. 132745.

149. Hu, Z., et al., *Advances and challenges in metal sulfides/selenides for next-generation rechargeable sodium-ion batteries.* Advanced materials, 2017. **29**(48): p. 1700606.

150. Wu, Z., Z. Xiong, and B. Lai, *Metal sulfide-based catalysts in advanced oxidation processes for water decontamination.* Environmental Functional Materials, 2023.

151. Balischewski, C., et al., *Metal Sulfide Nanoparticle Synthesis with Ionic Liquids–State of the Art and Future Perspectives.* ChemistryOpen, 2021. **10**(2): p. 272-295.