Chapter 1

Supercapacitors

Contents

1.1. Introduction

The exploitation and over dependency on non-renewable energy sources has led to serious damage to the environment along with fossil fuel depletion. Much of the recent research has been on renewable energy sources and their conversion and storage systems [1]. Because of their remarkable performance, batteries have been widely employed and thoroughly investigated among the energy storage devices. However, batteries have the following limitations: 1) Lesser power density: This restricts the use of batteries in applications that call for high power charge, discharge, and recharge. 2) Generation of heat: The Faradaic redox reaction may result in generation of Joule's heat and eventual thermal runaway. 3) Limited cycle life: The lack of completely reversible redox process causes it to have a short cycle life. 4) Environmental pollution: The toxic material used in the batteries, as Nickel-Cadmium, Lead acid, lithium carbonate etc. leads to severe environmental pollution. 5) Non-flexibility: The non-flexibility of batteries restricts their applications in wearable electronics and similar fields [2-4]. Due to the above limitations, Supercapacitor or Ultracapacitors emerged as the focus of attention in the past few years.

Supercapacitor, an electrochemical energy storage device, that stores and releases energy through the reversible adsorption and desorption of ions at the electrode/electrolyte interface [5]. The supercapacitor serves as the bridge between electrolytic capacitors and rechargeable batteries because of its superior energy density, greater power density, cycling stability, and longer cycle life, among other advantages [6]. The Supercapacitor have 4 major parts namely: Electrode, Current collector, Separator and Electrolyte (Fig.1.1).

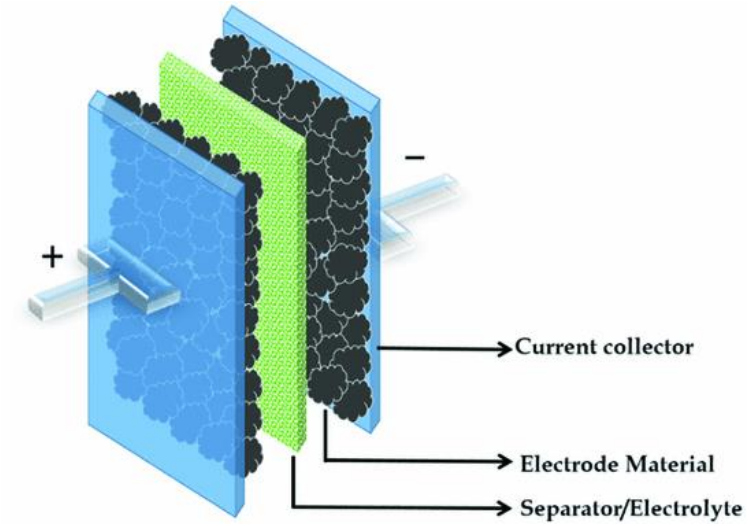

Fig.1.1 Basic structure of a Supercapacitor [7]

Electrode: It is the material that stores charge either through electrostatic charge accumulation or redox reactions. **Current collectors**: They are metals on which electrodes are attached to enhance electrical conductivity. E.g. Stainless steel, Nickel foam. **Separator**: They allow electrolyte ions to travel across the membrane while electrically isolating the electrodes from one another to prevent short circuit. E.g. Gore (polytetrafluoroethylene) or Celgard (polypropylene). **Electrolyte**: It is a solution that moves ions across electrodes to create redox or double layer capacitance. E.g. KOH, H_2SO_4, PVA/KOH.

History

Becker was granted the first supercapacitor patent in 1957 after a team of General Electric engineers working with porous carbon electrodes observed an unusually high capacitance [8]. Later in 1966, Standard Oil Ohio (SOHIO) researchers accidentally rediscovered the Electric Double Layer Capacitor (EDLC) phenomenon [9]. Eventually, Nippon Electric Company (NEC) came up with the term "supercapacitor" in 1978, and it was utilised to supply backup power for preserving computer memory. In 1982, Panasonic introduced the first commercially available supercapacitor, known as the "Gold Cap," which had a high equivalent series resistance (ESR). The Pinnacle Research Institute (PRI) developed the first electric double-layer capacitor (EDLC) supercapacitor with a very low ESR for use in military applications in 1982. After 10 years, Maxwell Laboratories released a variety of EDLC supercapacitors having a very low ESR under the brand name "BoostCap," with a rated capacity of 1kF [10]. Until 1990, the application of supercapacitors was very limited. Significant research is now being conducted in SC technology for ameliorating electrode materials' electrical performance [11].

Types of supercapacitors

Depending on the charge storing method, supercapacitors fall into three kinds: (1) Electrochemical Double Layer Capacitors (EDLC) utilizes the electrostatic charge that builds on the surface of electrode, and is proportional to the electrode surface area. (2) Pseudocapacitance arises due to quick and reversible electrode surface faradaic redox reactions. (3) Asymmetric supercapacitors that combine EDLC and pseudocapacitive characteristics or EDLC and battery electrode.

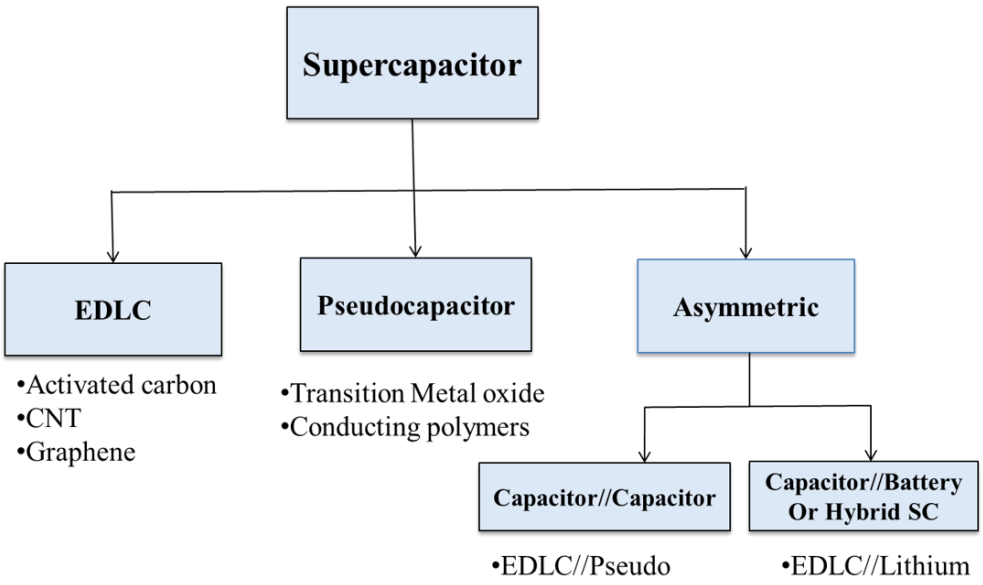

Fig.1.2. Supercapacitor types [1]

Electrochemical Double Layer Capacitor (EDLC)

EDL Capacitor store energy by accumulation of charge at the electrode-electrolyte region of interface. Charge is held by the alignment of electrolyte ions producing a capacitance layer on both electrode surfaces when an electric charge is supplied to an EDLC, thus the term Electric Double Layer Capacitor. Owing to their large surface area, thermal stability, superior conductivity, and non-corrosive nature, carbon and carbon-derived materials like graphene, activated carbon (AC), CNT, and others exhibit EDLC features [12]. Hermann von Helmholtz first suggested a model for EDLCs in 1853. On the basis of this model, at the electrode-electrolyte contact, opposing charges are aligned with an atomic distance separation [13]. Gouy and Chapman developed the diffusive layer model as a modification of the Helmholtz model [14, 15]. They considered the diffuse layer, a thermally-driven continuous dispersion of both cations and anions in the electrolyte solution. The Gouy–Chapman model, however, incorrectly overestimates EDL capacitance. The capacitance rises in the two separated arrangement of charges as their separation distance decreases, due to which point charge ions at the surface of electrode would erroneously show a very high capacitance value. Stern [16] subsequently combined the Helmholtz and Gouy-Chapman models to distinguish between two ion distribution zones: the diffuse layer and the inner zone known as the compact layer or Stern layer (Fig.1.3c). The compact layer gets its name from the electrode's strong adsorbed ions within it which are very often hydrated. Additionally, the compact layer comprises of counter ions that are not particularly adsorbed ions (which are often anions regardless of the electrode's charge state). The inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP) serve to

differentiate between the two kinds of adsorbed ions. The Gouy-Chapman model helps to describe the diffusive layer area. The counter-ions' kinetic energy has an effect on the thickness of the diffuse double layer. The combined sum of both Stern layer capacitance (C_H) and diffusive region capacitance (C_{diff}) gives the capacitance of EDLC (C_{dl}). Therefore, C_{dl} can be mathematically represented as:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The electrical field across the electrode, the types of electrolyte ions, the solvent utilized for dissolving the electrolyte as well as chemical affinity between the adsorbed ions and the electrode surface are all factors that influence EDL behaviour at a planar electrode surface. Porosity has a significant impact on EDLC performance because porous structured electrode possess high specific area.

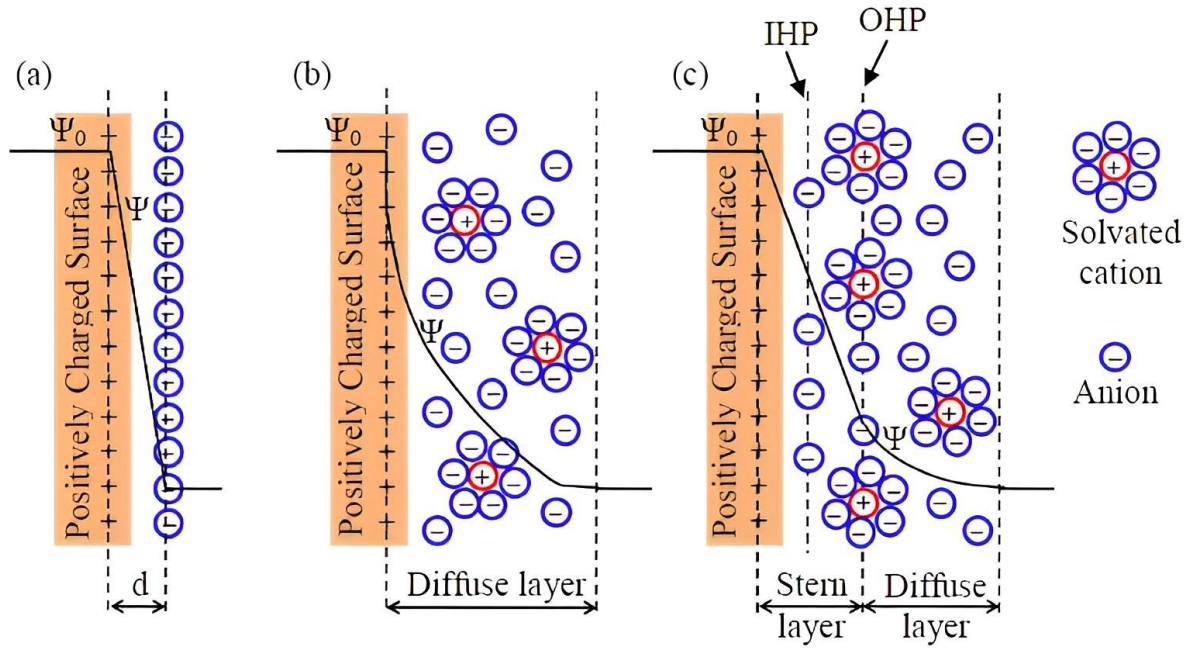

Fig.1.3. EDL models, (a) Helmholtz model (b) Gouy-Chapman model (c) Stern model [1]

Pseudocapacitors

Energy storage in pseudocapacitors occurs through the surface or near-surface redox activities related to the faradaic process, which may achieve high energy density at high charge-discharge rates [17]. The pseudocapacitance intrinsically depends upon particle size and morphology. In 1971, RuO_2 was reported as the first pseudocapacitive material [18]. Formally, the term "pseudocapacitance" refers to electrode materials where charge storage is accomplished through charge-transfer Faradaic process across a double layer despite having capacitive

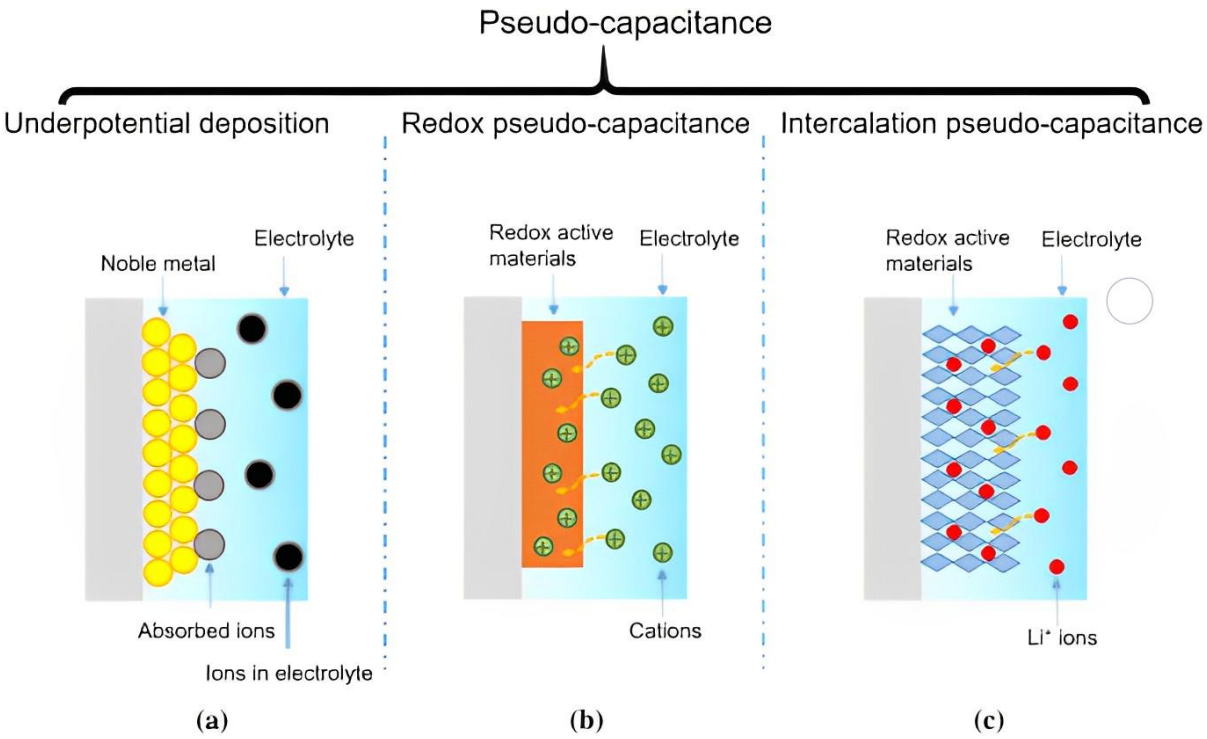

Fig.1.4. Classification of pseudocapacitive electrodes: (a) Underpotential deposition, (b) Redox pseudocapacitor, and (c) Ion intercalation pseudocapacitor [1]

electrochemical characteristics [19]. The quick as well as reversible surface redox thermodynamic mechanism that gave rise to this process are Faradaic in nature, where the capacitance alters linearly with the amount of charge (Q) and change in potential (U). The active centres contributing to the pseudocapacitance are situated in close proximity to the metal oxides' surfaces, at a distance of $L \ll (2Dt)^{1/2}$,in which D refers to the diffusion coefficient for charge-compensating ions (cm^2/s), t is the diffusion time scale (s) [20]. Pseudocapacitors act as link between batteries, which depend mostly on transfer of Faradaic electron to metal centres, and EDLCs storing charge only in the double-layer on a conductor of large surface area. Pseudocapacitors show 10-100 folds of capacitance as compared to EDLC but they exhibit only a fraction of the power density owing to the sluggish Faradaic mechanism and poor cycle life and mechanical stability affected by the material's volume change during charge-discharge process [21].

Conway reported a number of faradaic mechanisms that are involved in pseudocapacitive characteristics. (a) Underpotential deposition: It occurs when a monolayer of metal ion deposits over another metal which have a higher redox potential. Example: monolayer of lead deposition over gold electrode surface [22]. (b) Redox pseudocapacitance: It arises while ion adsorption at the surface or near-surface of the material is taking place with a faradaic charge transfer

(redox process) occurring at the same time. Example: RuO_2 [23] or MnO_2 [24] as well as other similar metal oxides along with some conducting polymers [25, 26]. (c) Intercalation pseudocapacitance: This is due to the ions intercalating into the tunnels or redox-active material's layers while undergoing a faradaic charge transfer and without going through a phase shift in crystallography. Example: Nb_2O_5 [27, 28]. These processes may be triggered by a variety of physical conditions, and they are also material-dependent. The similarity in electrochemical behaviour is caused due to the potential-charge quantity relationship that occurring because of adsorption or desorption mechanism at the electrode/electrolyte boundary or within the inner surface of a material [29].

Asymmetric Supercapacitors (ASC)

The charge storage method of two electrodes differs in asymmetric supercapacitors and, depending on the material used, may be Faradaic or non-Faradaic. The total cell voltage is raised by utilising the benefit of potential difference between the two electrodes. There are mainly 2 types of ASC: (a) capacitor type/capacitor type electrodes SC (Eg: EDLC//redox type). (b) capacitor type/battery type electrodes SC which is also termed as Hybrid supercapacitors [30, 31].

Performance evaluation parameters

Specific Capacitance (C_s)

The electrode's specific capacitance is measured from the current vs. voltage plot using the equation:

$$C_s = \int \frac{I\, dv}{2*w*s*V} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, I stands for current (A), s is the scan rate (V/s), V refers to the potential window (V) and w corresponds to the active material's mass (g) or surface area of electrode (cm^2) or volume of the electrode (cm^3). Cs is referred to as gravimetric capacitance (F/g) if w is the mass of the active material. and w is area, then areal capacitance (F/cm^2) and if volume then volumetric capacitance (F/cm^3).

The Galvanostatic Charge/discharge curve also gives the specific capacitance as seen in the eq:

$$C_s\,(F/g) = \frac{I\,\Delta t}{m\,V} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where, I/m is the current density (A/g), Δt is the discharge time (s) and V is the potential window (V).

Energy density (E)

The equation for calculating the energy density of an electrode, which is obtained by dividing total amount of energy stored by electrode's weight, is as follows:

$$E\ \left(\frac{Wh}{kg}\right) = \frac{1}{2}\ C_s V^2 * \frac{1}{3.6} \text{..... (3)}$$

Power density (P)

Power density is defined as the rate at which the SC may be discharged and is computed using the equation:

$$P\ \left(\frac{W}{kg}\right) = \frac{E}{\Delta t} * 3600 \text{..... (4)}$$

Coulombic efficiency (η)

The coulombic efficiency of a device is measured as the ratio of the amount of charge extracted from the electrode during discharge to the amount of charge stored in the electrode during charging at the same current density.

$$\eta\ (\%) = \frac{t_d}{t_c} * 100$$

where, t_d, t_c refers to the discharge time (s) and $t_c$is the charging time (s) respectively.

Cycle life

Cycle life defines the number of charging and discharging cycles an electrode can withstand over the course of its lifetime without any considerable degradation from its initial capacitance.

Equivalent Series Resistance (ESR)

The output voltage of a capacitor that receives sinusoidal ac should be 90º out of phase, regardless of frequency. Supercapacitors, however, have an output voltage that is out of phase by less than 90º, indicating the influence of an equivalent series ohmic resistance which will affect the power density. The ESR is influenced by the electrolyte's ionic resistance, the electrode material's intrinsic resistance, the electrolyte's ion mass transfer resistance and the contact resistance developed between the active material and current collector [32].

Characterization techniques for energy storage mechanisms

The Supercapacitor parameters are determined by performing the following characterization techniques.

Cyclic Voltammetry (CV)

Cyclic voltammetry, an electrochemical method, that detects the current generated at the electrode when the applied potential is higher than what would be expected according to the

Nernst equation. Here, on the introduction of a time dependent triangular voltage waveform to the working electrode, the resultant current generated is recorded. The scan rate (V/s) is the rate at which the potentials are scanned. This technique is used to study the electrochemical redox process, energy storage process and charge kinetics. The energy storage mechanism's information is given by the CV's shape. The ideal CV of an EDLC is rectangular in shape but practically it may deviate from its ideal rectangular shape due to different resistances in the electrode and electrolyte etc. For pseudocapacitors, the CV is non-rectangular and shows sharp peaks because of the Faradaic redox process taking place at the electrode surface. The upper half cycle of the CV denotes oxidation, and the lower half cycle represents reduction processes with peak currents as anodic peak current (i_{pa}) and cathodic peak current (i_{pc}). As the scan rate increases specific capacitance decreases [33]. At higher scan rates, ions accumulate exclusively on the electrode surface while at low scan rates, it will have more time to penetrate the electrode

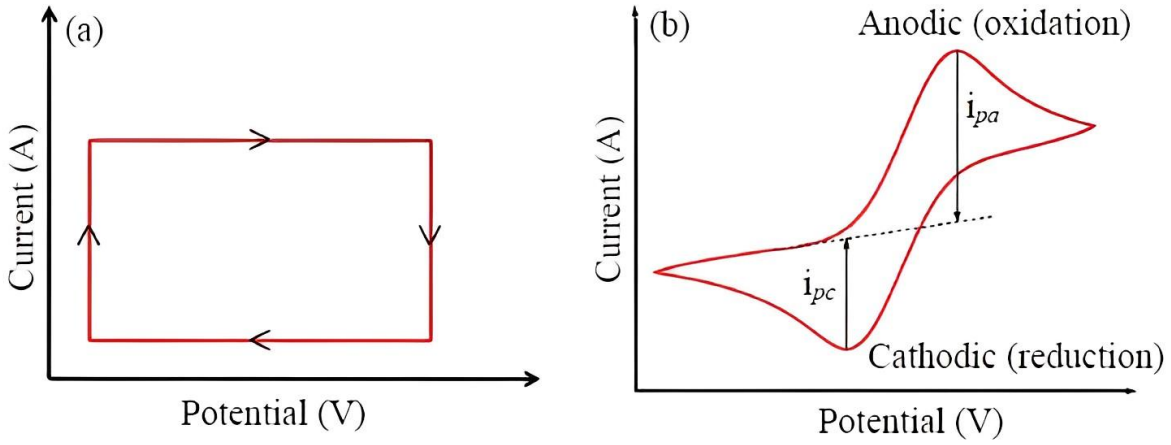

Fig.1.5. Representation of CV of (a) Ideal EDL capacitor, and (b) Pseudocapacitor [1]

material's pores. Furthermore, on the electrode surface, the faradaic reactions that occurs are unable to keep up with the rapid change in electrode potential, resulting in incomplete reactions and limited current output, which reduces capacitance at high scan rates.

Galvanostatic Charge/Discharge (GCD)

The Galvanostatic Charge/Discharge method involves applying a constant current to an electrode and monitoring the resulting voltage over time. The polarity of the current is reversed when a predetermined voltage is achieved. This technique is also referred to as chronopotentiometry. This is the most accurate method for determining specific capacitance (Eq.2). The abrupt decrease in potential in the first section of the discharge curve is caused by

the electrode's ESR (Fig.1.6.b). This technique is also helpful to study the cyclic stability of the SCs.

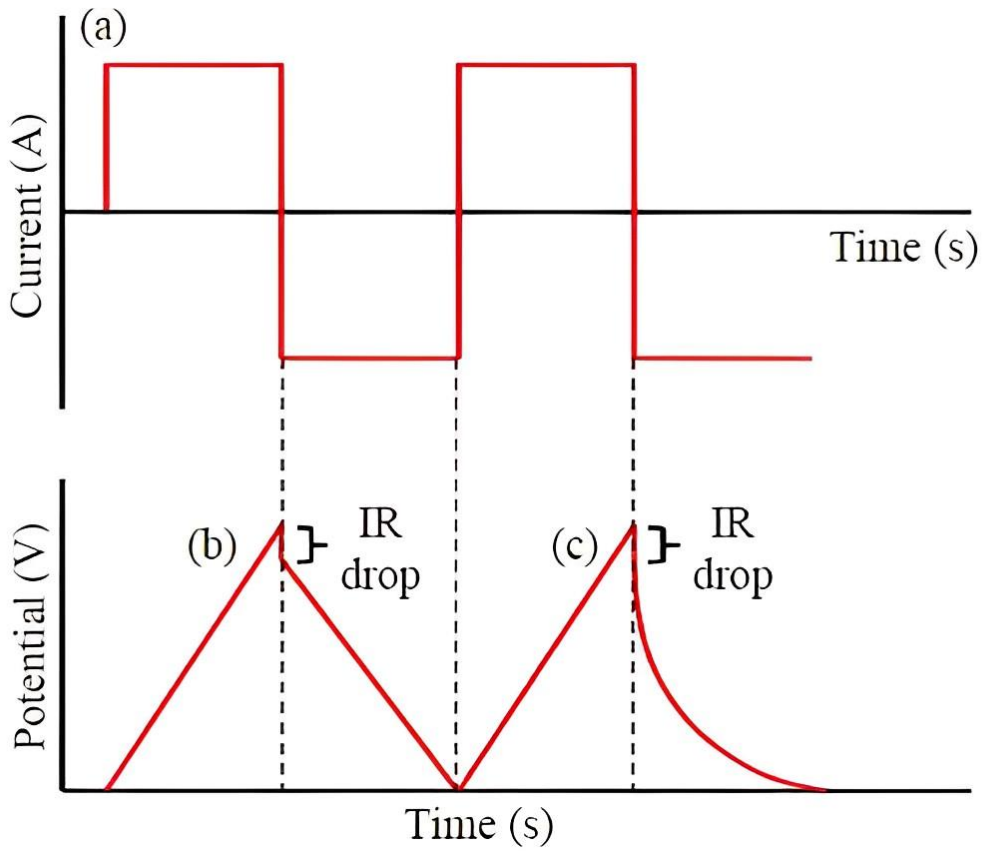

Fig.1.6. (a) Constant current reversal cyclic chronopotentiometry; Representation of GCD curve for (b) EDL capacitor, and (c) Pseudocapacitor [1]

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy is utilised to monitor the internal resistances associated with electrode and electrolyte of the SC. In EIS measurement, a low amplitude (5-10 mV) sine wave is applied over a broad frequency range (e.g., 0.01-100kHz) and the corresponding impedance data are collected. EIS can be used to calculate capacitance as $C = \frac{1}{2\pi f|Z|}$, where |Z| is the impedance's imaginary section and f denotes frequency. This calculation utilizes a linear section of the Bode plot (log |Z| vs log(f) curve). In the Nyquist curve, the following 3 regions are observed: semicircle's initial x-intercept gives the equivalent series resistance (R_s); semi-circle's diameter in the high frequency zone is the charge transfer resistance (R_{ct}), and 45º straight line present in the low frequency region is because of diffusion resistance or Warburg resistance (W). The contact resistance between the active material and

current collector, electrolyte's ionic resistance, intrinsic resistance of the active material combinedly give rise to R_s. R_{ct} is the resistance when the electrons crossing the electrode-

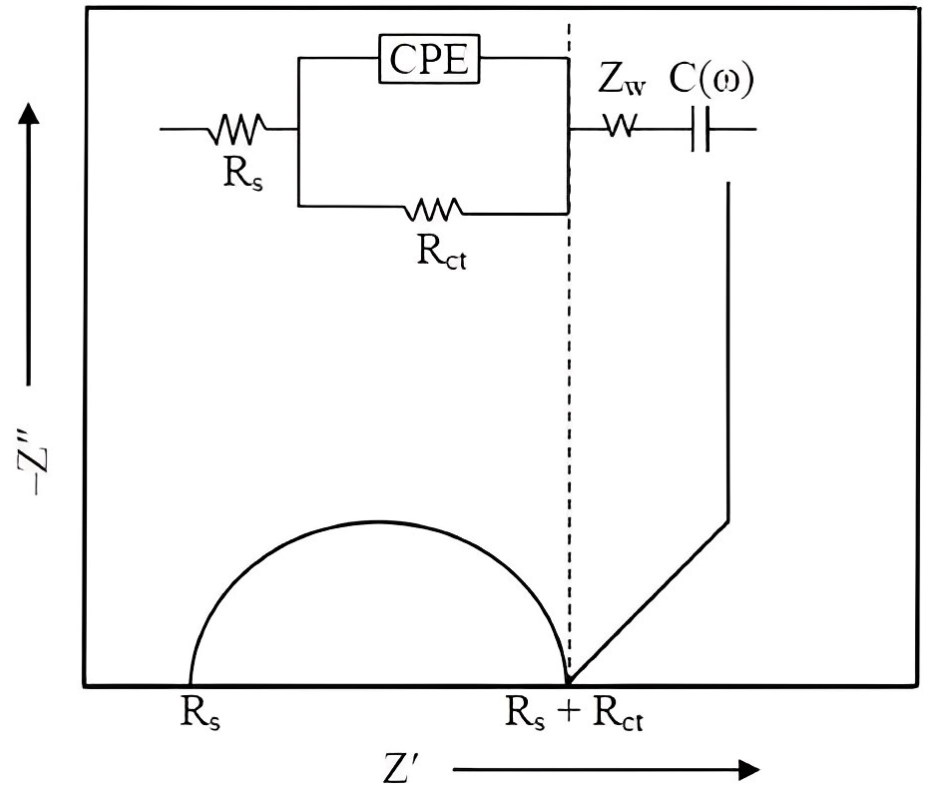

Fig.1.7. Impedance behaviour of a supercapacitor. Inset represents the corresponding equivalent circuit for the Nyquist plot [1]

electrolyte boundary. W results from the ion diffusion from the electrolyte into the electrode.

1.2. Motivation and Significance of Research

The looming need to upgrade many developed nations' power grids, as well as the predicted growth in global energy demand in the near future, have sparked an increased interest in electrochemical energy storage devices. Although there are several prospects for such devices, these systems also face a number of difficulties, most of which stem from the need of identifying materials with improved energy storing and delivering ability. The SC performance is heavily influenced by a number of factors, including the electrochemical performance of the electrode materials, the choice of electrolyte, and voltage window of the electrode [2]. As a result, a substantial amount of research effort has been devoted for the innovation of superior nanomaterials for SC electrodes with suitable structural designs to enable efficient electron transport and ionic diffusion [34].

The poor energy density, small potential window, internal resistance, and other characteristics of electrode materials are major roadblocks in the development of supercapacitors. Hence, it is crucial to develop novel electrode materials that have improved electrochemical characteristics. To obtain novel nanocomposites for high performance supercapacitor applications, the synergetic effect of both EDLC (high power density) and pseudocapacitive (high energy density) materials are taken into consideration of our research.

1.3. Objective of Research

The aim of the proposed research work is to synthesize novel graphene based 2D/2D heterostructures for high performance supercapacitor applications which will be achieved by the following objectives,

- To develop a novel green synthesis method for reduced graphene oxide using phytochemicals.
- Synthesis and characterization of graphene based 2D/2D heterostructures for supercapacitors.
- Synthesis and characterization of graphene based 2D/2D heterostructures@metal oxide/polymer nanocomposite.
- Fabrication of prototype supercapacitor using the above developed nanocomposite and their performance analysis.

1.4. Methodologies applied

The objectives of the research work are executed in the following phases:

Phase 1: Defining the research objectives and literature survey on graphene based heterostructures/metal oxides and supercapacitors with their limitations.

During this phase a thorough review on the previous work done on supercapacitor material synthesis and fabrication methods are carried out. The area on which further development on the process is required is listed out and the probable solution for betterment of the performance is planned out.

Phase 2: Synthesis and characterization of graphene based 2D/2D heterostructures for Supercapacitors.

During this phase different graphene based 2D/2D heterostructures like graphene/h-BN, graphene/g-C_3N_4 will be synthesised in order to improve the electrochemical characteristics of the electrode material.

Phase 3: Synthesis and characterization of graphene based 2D/2D heterostructures@ metal sulfide/polymer nanocomposite based electrode material for supercapacitor applications.

During this phase the nanocomposites of different metal sulphides (CdS, $NiCo_2S_4$) and conducting polymers like polyaniline, polypyrrole, PEDOT:PSS with different graphene based 2D/2D heterostructures will be synthesized and characterised.

Phase 4: Fabrication of prototype using developed nanocomposite and evaluation of supercapacitor.

During this phase a prototype of supercapacitor will be developed using the developed material for efficient energy storage applications. The developed prototype will be evaluated by several characterisation techniques like CV, GCD, EIS, etc.

1.5. Organization of the Thesis

In this thesis, novel graphene based 2D/2D nanomaterials were synthesized for high performance supercapacitor applications. The synthesized materials were used to develop supercapacitor prototypes to analyse the practical application of the materials. The dissertation is organized as follows:

Chapter 1 mention the introduction which includes motivation, objective and scope of the research and finally thesis organization.

Chapter 2 provides a detailed review on literature on the work done on supercapacitor material synthesis and fabrication methods using 2D nanomaterials and their composites.

Chapter 3 discusses a green perspective for reduced graphene oxide synthesis. This chapter is further sub divide into two. Firstly, a novel synthesis method of highly oxidized graphene (HOG) by using HNO_3 and $KMnO_4$ as oxidizing agents was developed. This approach was found to be superior compared to the existing Hummers method [35] and Marcano's method [36].

Finally, a green method for graphene oxide reduction using phytochemicals extracted from Pomelo Grandis and Tamarindus indica was developed. This method was found to be green and cheap for mass production of reduced graphene oxide. It also avoided utilizing harmful as well as toxic reducing agents and the byproducts were mainly organic compounds and water.

Chapter 4 covers the synthesis of a novel band-gap tuned highly stable hexagonal-boron nitride/reduced graphene oxide superlattice wrapped cadmium sulfide/Polypyrrole nanocomposite as an efficient supercapacitor electrode material. The nanocomposite's characteristics are discussed at length. Also, an asymmetric supercapacitor (ASC) fabricated employing h-BN/rGO/CdS@PPy//AC presented a specific capacitance of 102F/g (1A/g) and

maximum energy density of 32Wh/kg at a power density of 750W/kg. Furthermore, the device showed a capacitance retention of 88.50% (5000 cycles) assuring it as a potential material for use in supercapacitors.

Chapter 5 presents the synthesis of a novel carbon self-repairing g-C_3N_4/reduced graphene oxide heterostructure and its hybridisation with $NiCo_2S_4$. There are two divisions in this chapter.

Here, a novel hierarchical porous N, S doped reduced graphene oxide- $NiCo_2S_4$ hybrid nanocomposite was synthesized by in-situ growth of $NiCo_2S_4$ over porous rGO framework by a facile hydrothermal route. The prepared GNCS3 electrode presented outstanding specific capacitance (1640F/g at current density of 1A/g). The synergetic impact of $NiCo_2S_4$ and rGO, wherein rGO served as an excellent conductor and ideal framework is responsible for the enhancement in electrochemical activity. Further, an all-solid-state GNCS3//AC ASC fabricated showed exceptional capacitance retention of 92.5% after 5000 cycles and highest energy density of 27Wh/kg at a power density of 600W/kg. $NiCo_2S_4$/rGO is a great electrode material for use in supercapacitors since it is easy to synthesize and exhibits high capacitance.

Finally, a porous carbon self-repairing g-C_3N_4 (pCCN) nanosheets were synthesised by a solvothermal process followed by thermal treatment in air and acid treatment. As a hybrid material for supercapacitor electrodes, $NiCo_2S_4$ nanocomposite are grown on a porous carbon self-repairing g-C_3N_4/rGO heterostructure using a simple hydrothermal technique. The as-synthesised pCRNCS electrode exhibited exceptional specific capacitance (1938F/g at current density of 2A/g). Synergistic effects of large surface area rGO and highly reactive region and defects in pCCN, which allowed for the nucleation and restricted growth of $NiCo_2S_4$ in the framework, are responsible for the superior electrochemical activity. A maximum energy density of 66Wh/kg was achieved at a power density of 751W/kg, and the produced pCRNCS//AC ASC exhibited exceptional capacitance retention of 93.6% after 6000 cycles. The porous carbon self-repairing g-C_3N_4/rGO@$NiCo_2S_4$ electrode material's superior capacitive behaviour makes it an attractive electrode material for use in supercapacitors.

Chapter 6 summarizes the contribution of this thesis work and discusses the scope of further research work.

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