

# REVIEW OF SUPERCAPACITOR APPLICATIONS BASED ON ELECTROCHEMICAL MATERIALS AND DEVICES

## Abstract

Super-capacitors (SCs) are important because of their unique characteristics, such as long cycle life, high strength, and environmental friendliness. They use electrode materials with lower dielectrics and higher specific surface areas to generate high capacitance and share similar fundamental equations to traditional capacitors. The creation of three different forms of SCs—electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid supercapacitors—as well as the most recent developments in material production and modification are covered in this article. The paper's conclusion covers current advancements in supercapacitor technology. Carbon-based nanomaterials, metal oxides, conducting polymers and their nanocomposites, as well as a few unique materials which include metal-organic frameworks, MXenes, metal nitrides, covalent organic frameworks, and black phosphorus, have received the majority of attention. Utilizing evaluations that reveal details about the electrolyte materials, such as capacitance, energy, cycle performance power, and rate capability, the performance of the composites was evaluated.

**Keywords:** TMOs, EDLC, Pseudocapacitor, Power density ( $P_d$ ), Energy density ( $E_d$ ), CV, GCD.

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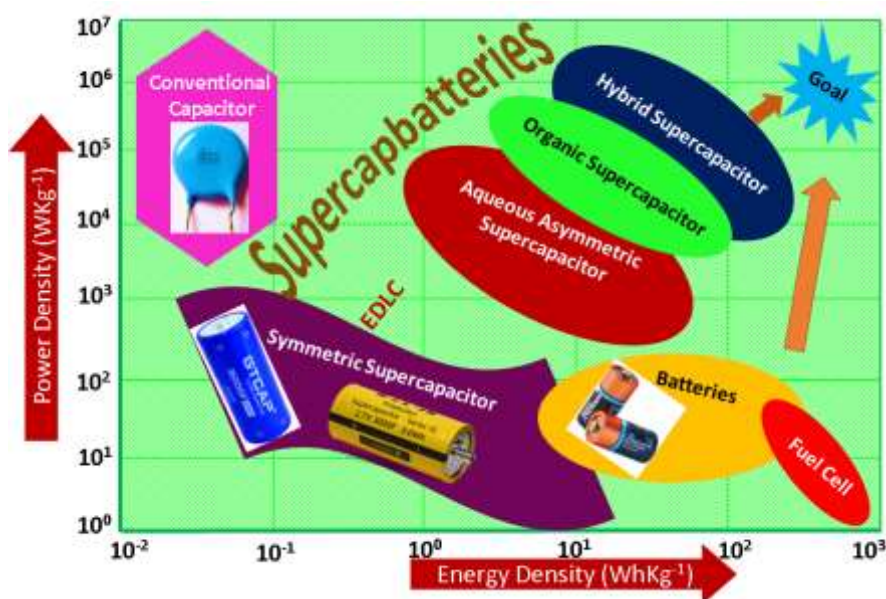
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## I. INTRODUCTION

The abundant consumption of fossil fuels and the degree of concentration of greenhouse gases in the atmosphere is always increasing. On the other hand, there is expeditious growth in industrialization leading to Ecological disturbance factors such as Global warming, climatic change, rising sea levels, and poor rainfall. In addition, Global warming also leads to increased intensity of heat waves<sup>[1]</sup>. We know that every human action is reliant on the natural environment. A stable and healthy climate is the precious resource of the world. Energy storage technologies are in high demand in this environment. The speedy requirement is material for electrochemical storage with high-gear performance<sup>[2]</sup>. Our study is focused on supercapacitors within energy storage systems. In other to utilize energy efficiently, supercapacitors are superior devices capable of directing high power rates. Despite having the potential to provide 100 to 1000 times more rate power in an identical volume, supercapacitors cannot store the same charge density as batteries (i.e., 3-30 times lower).<sup>[3]</sup>

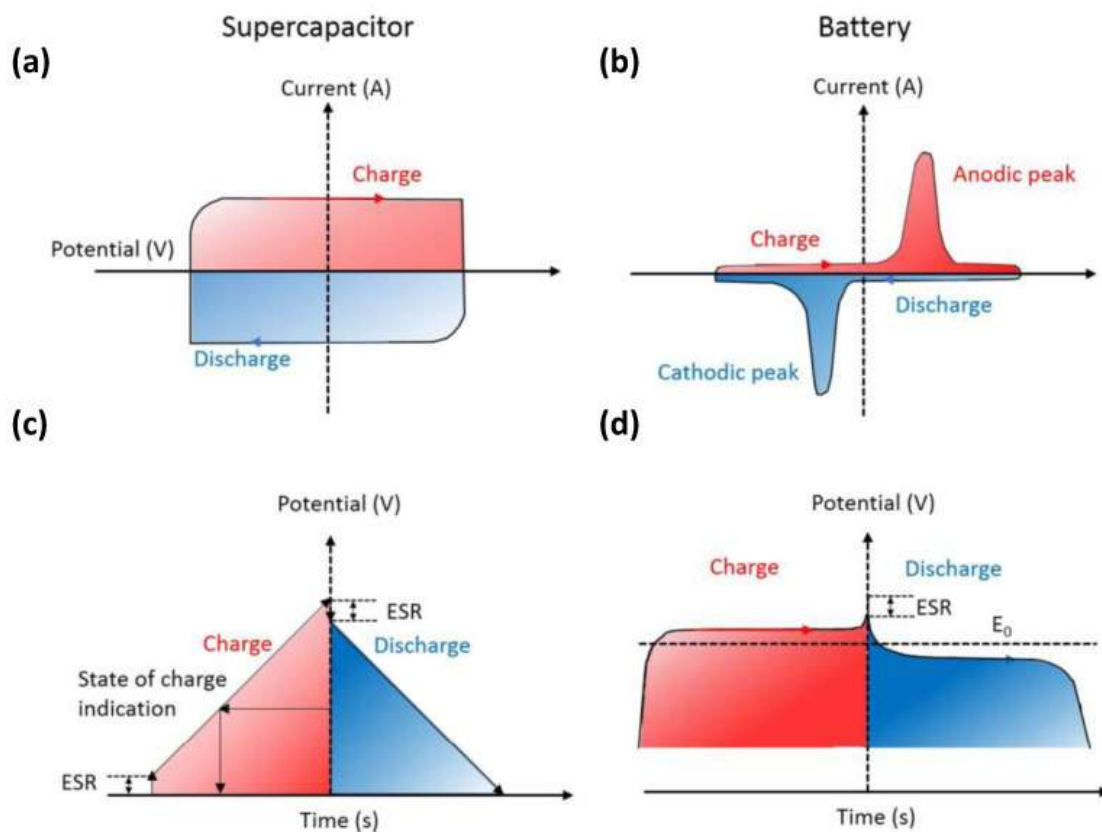
Figure 1 shows a Ragone plot comparing conventional capacitors, fuel cells, lithium-ion batteries, and hybrid supercapacitors as different energy storage devices in terms of power density ( $P_d$ ) and Energy Density ( $E_d$ ), with hybrid supercapacitors exhibiting a significant feature of  $P_d$  in comparison to batteries and fuel cells but a significantly lower  $P_d$  than conventional capacitors.



**Figure 1:** A Ragone Plot of the Power-Energy Density Range for Different Electrochemical Energy Storage Devices<sup>[4]</sup>.

The supercapacitor's cyclic voltammetry (CV) curve (Figure 2a) maintains a rectangular shape throughout the charge and discharge process, indicating that the current is likely to be nearly constant. Additionally, this device's GCD curve (Figure 2c) is typically inclined with a constant slope. A battery maintains a constant voltage other than when it is almost completely charged or depleted; the GCD curve shows a relatively flat charge-

discharge platform. A battery exhibits Faradaic reactions during the charge and discharge cycles, and its CV curve has a redox peak.



**Figure 2 (a, b):** Shows Cyclic Voltammetry (CV) Curves, and (C,D) Shows Galvanostatic Charge-Discharge (GCD) Curves of Supercapacitors and Batteries[5].

Researchers pay attention to supercapacitors because of their high-range power capabilities and the life cycle is the main reason for utilizing a supercapacitor as a device for energy storage. The rechargeable batteries can store the electrical energy that arises from the chemical reaction through the redox process at the anode and cathode electrodes [6]. Supercapacitors, also known as electrochemical capacitors, are a type of electrochemical reaction that allows electrical energy to be stored. They possess salient features, such as their high theoretical capacitance, long cyclic life, high power density, ultrafast charge/discharge cycles, and large surface area [7]. Pseudocapacitors, Electric double-layer capacitors (EDLC), and Hybrid capacitors are the three main categories of supercapacitors [8].

EDLC is the energy storage system that depends on both charging and discharging. Normally, EDLC predominantly employs carbon electrode materials. The carbon electrode material may be activated carbon, graphene, carbon fibers, carbon aerogels, amorphous carbon, and carbon nanotubes (SWCNT & MWCNT) [9]. The main purpose of employing carbon electrode material is for the accumulation of charge through reversible absorption/desorption of ions at the electrode/electrolyte hookup. The dielectric behavior of conventional (electrostatic) capacitors is equivalent to the process of both charging/discharging in EDLC [10]. The dielectric in the capacitor plays the role of reducing

the strength of the electric field inside the capacitor. As a result, for a given charge, there is a lower voltage between the plates. In addition, there is no faradaic process that occurs during the energy storage process. The main attributes of EDLC are (i) efficient electrical conductivity, (ii) excellent mechanical stability, and (iii) high cycle efficiencies. The key Pro of EDLC are (i) feasible to charge/discharge, (ii) its long life cycle because of the absorption/desorption of electrolyte ions, (iii) Nowadays, EDLC is used as a memory backup power source for electric devices, because of their lightness. The researcher has kept an eye on EDLC, only because of the large specific surface area (SSA) <sup>[11]</sup>.

A pseudocapacitor is also called a redox capacitor. Reverse faradaic reactions, which are electrochemically quick and efficient, can be used to store energy in this substance. Pseudocapacitors consist of transition metal oxides and conducting polymers. Transition metal oxides such as  $\text{RuO}_2$  <sup>[12]</sup>,  $\text{TiO}_2$  <sup>[13]</sup>,  $\text{V}_2\text{O}_5$  <sup>[14]</sup>,  $\text{MnO}_2$  <sup>[15]</sup>,  $\text{Co}_3\text{O}_4$  <sup>[16]</sup>,  $\text{MoO}_2$  <sup>[17]</sup>,  $\text{NiO}$  <sup>[18]</sup>,  $\text{Fe}_3\text{O}_4$  <sup>[19]</sup>, etc. These materials are used in superconductors due to high specific capacitance and specific energy density. The conducting polymer can be used as a superconductor because of its superior properties like good intrinsic conductivity <sup>[20]</sup>. Conducting polymers such as PPy, PANI, and PVDF, to improve the electrochemical performance <sup>[21]</sup>.

Although, supercapacitors tolerate low energy density. Therefore, a supercapacitor to enhance the specific energy and power density is to develop asymmetric (or hybrid) supercapacitors using two electrodes <sup>[22]</sup>. Supercapacitors are normally classified as symmetric supercapacitors and asymmetric supercapacitors. In the symmetric type, both electrodes (Positive and negative) are suppressed in the same type of electrode material <sup>[23]</sup>. One electrode of the asymmetric type supercapacitor is made of activated carbon, which is porous, and the other electrode is made of a battery material <sup>[24]</sup>.

In recent years two dimensional (2D) sheets-like structure dichalcogenides supercapacitor materials such as  $\text{WS}_2$ ,  $\text{MoS}_2$ , and  $\text{VS}_2$  have been widely used in energy storage applications due to their extensive surface area for double-layer charge storage to enhance the better electrochemical charging/discharging performance. Pure  $\text{MoS}_2$  supercapacitor materials show only moderate performance as electrode materials due to the relatively poor electronic conductivity and stability. In addition,  $\text{MoS}_2@\text{ZIF-67}$  composites have been used as one of the most effective techniques to boost their conductivity and electrochemical properties. Finally, we have developed in this work to synthesize  $\text{MoS}_2@\text{ZIF-67}$  composites through the hydrothermal method <sup>[25]</sup>.

## II. ELECTROCHEMICAL PERFORMANCE FOR EDLC TYPE SUPERCAPACITOR MATERIALS

**1. Carbon Materials:** The electrode materials with the greatest potential for industrialization are carbon-based compounds. They have a huge specific surface area, excellent conductivity, good chemical stability, a wide operational temperature range, enormous natural reserves, low cost, and ease of production. They are also non-poisonous [26]. Carbon compounds are stored in an electrochemical double layer that forms at the electrode-electrolyte contact. Therefore, a significant factor in determining capacitance is the surface area that is accessible to electrolyte ions. Several variables, including specific surface area, pore shape and structure, pore size distribution, surface functionality, and electrical conductivity, have a major impact on electrochemical performance [27].

Carbon materials with a high specific surface area have a greater capacity for charge buildup at the electrode-electrolyte contact. When it comes to increasing carbon material's specific capacitance. Activated carbon (AC), carbon aerogels, carbon nanotubes (CNTs), carbon nanofibres, and other carbon materials are employed. Conventional alternating current has a strong cycle stability in a range of electrolytes and a theoretical capacitance of  $100\text{--}300\text{ F g}^{-1}$ . However, the specific capacitance cannot be significantly increased due to double-layer capacitance procedures. At the moment, the combination of carbon material with pseudocapacitive material can have a synergistic effect, resulting in high electrochemical performance for the total system<sup>[28]</sup>.

- 2. Activated Carbon (AC):** One of the most popular and frequently used electrode materials among the several types of electrochemical double-layer capacitors (EDLCs) is porous activated carbon (AC), which has long been acknowledged. The excellent qualities that make it suitable for energy storage in supercapacitors are the main cause of this. Due to its exceptional electrochemical stability, activated carbon can withstand multiple charge-discharge cycles without suffering significant deterioration. This quality is essential for the durable and dependable operation of supercapacitors<sup>[29]</sup>. Activated carbon possesses an extensive internal surface area, often measured in thousands of square meters per gram. This large surface area gives electrolyte ions plenty of room to adsorb, increasing capacitance and energy storage capacity. Activated carbon's ability to store charge is further improved by its porous nature. The availability of active sites for the creation of an electrochemical double layer is increased by the presence of multiple small, interconnected pores, which raises capacitance values. Efficient charge transport is crucial for rapid charge and discharge in supercapacitors<sup>[30]</sup>. Activated carbon possesses good electrical conductivity, ensuring fast ion diffusion and electron transfer within the electrode material. Due to these advantageous properties, activated carbon-based electrodes have found wide applications in various energy storage systems, especially supercapacitors. When it comes time to discharge the stored energy, activated carbon makes it possible to do so quickly and without major energy loss, restoring optimal capacity to the supercapacitor cell. This indicates that the battery's performance won't be affected by thousands of charges and discharges<sup>[31]</sup>.
- 3. Graphene:** Graphene plays a crucial role in supercapacitor applications due to its exceptional properties, making it an ideal material for enhancing the performance of supercapacitors. Graphene possesses an extremely high surface area per unit mass due to its single-layered carbon atom arrangement<sup>[32]</sup>. This large surface area provides ample sites for storing electrical charge, enhancing the energy storage capacity of supercapacitors. Graphene is an excellent conductor of electricity, with electrons moving through its lattice with minimal resistance. Supercapacitors can quickly store and release energy owing to their high electrical conductivity, which permits fast charge and discharge rates. Graphene is an incredibly lightweight material, which is beneficial in supercapacitors as it contributes to their high-power density. The low mass of graphene allows for fast movement of charge carriers, resulting in high power output<sup>[33]</sup>. The structural integrity of the electrodes in supercapacitors must be preserved during charge and discharge cycles, and graphene's exceptional mechanical strength is crucial for this. Because of its toughness, supercapacitors will last longer and perform better when cycling. To create graphene-based composites, graphene can be mixed with other substances like metal oxides or conductive polymers. These materials can help

supercapacitors store more energy overall and with greater specific capacitance. Comparing certain components used in conventional energy storage technologies, such as lithium-ion batteries, which may contain heavy metals and other dangerous compounds, graphene is made entirely of carbon atoms, making it more environmentally friendly [34]. Graphene and graphene-based materials have attracted a lot of interest in the development of next-generation supercapacitors with higher energy density, power consumption, and cycling stability as a result of these outstanding features. As research continues, we can expect further advancements in supercapacitor technology with graphene playing a central role in making energy storage devices more efficient and sustainable [35].

- 4. Pseudocapacitor:** Pseudocapacitors are also called faradaic supercapacitors. Pseudocapacitors are electronic components that differ from EDLCs in that they have electrodes constructed of redox-active substances. Through a distinct mechanism, these gadgets use electrical charge to store energy. When an electrode is being charged, the activation of the redox pair is made easier by the introduction of external potential [36]. The redox-active surface groups redirect to their initial state upon discharge, which is the opposite of this process.

When a voltage is applied to a pseudocapacitor, charge moves across the double layer, resulting in faradic current flowing through the electrode material of the supercapacitor. The electrode material undergoes both reduction and oxidation, resulting in higher specific capacitance and energy densities than in EDLCs. [37].

When compared to non-Faradic processes, faradic processes are thought of as having comparatively sluggish reactions. Pseudocapacitors have a low power density as a result. Reversible adsorption processes, transition metal oxide reactions, and electrochemical doping reactions (reversible) are three general classifications for the redox reactions that occur in this supercapacitor [38].

- 5. Transition Metal Oxides (TMO):** One form of pseudocapacitive material that exhibits rapid and reversible redox reactions without the presence of electrode materials is metal oxide. It is quick and easy to construct supercapacitors using this material due to its low resistance and high specific capacitance. Metal oxides formed from transition metal families store charges through rapid and reversible redox reactions, which give them a higher specific capacitance than carbon-based materials and better cycle stability than conductive polymers [39]. Transition metal oxides are therefore particularly attractive electrode materials for enhancing the electrochemical capabilities of supercapacitors. Metal oxides can be used as cathode and anode materials in aqueous asymmetric supercapacitors for higher energy density. In recent years, metal oxides have undergone substantial research as electrode materials for aqueous asymmetric supercapacitor systems. These metal oxides mainly consist of single metal oxides like  $\text{Fe}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{RuO}_2$ ,  $\text{MnO}_2$ ,  $\text{MoO}_3$ , and  $\text{WO}_3$ , bimetallic oxides like  $\text{MN}_2\text{O}_4$  (conversion type), where M or N = Ni, Co, Zn, Mn, Fe, Cu, etc., and intercalation type like  $\text{LiCoO}_4$  (liquid cobalt oxide),  $\text{LiMn}_2\text{O}_4$  (liquid manganese oxide) [40]. The following provides an introduction to several single metal oxides, Fe, V, Ru, Mn, and Co-based electrode materials. Due to its large specific capacitance ( $720 \text{ F g}^{-1}$ ), high cost, and excellent electrical conductivity,  $\text{RuO}_2$  is seen to be the most promising metal oxide of all [41].

- 6. Fe-based Iron Oxide Supercapacitor Materials:** Due to their high theoretical specific capacitances, natural abundance, low cost, and non-toxicity, iron-based compounds, including  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeOOH}$ ,  $\text{FeOx}$ ,  $\text{CoFe}_2\text{O}_4$ , and  $\text{MnFe}_2\text{O}_4$ , have recently attracted a lot of attention as extremely promising electrode materials for SCs<sup>[42]</sup>. As a result of their poor conductivity and/or electrochemical instability, the majority of these Fe-based SC electrodes are not suitable for use as high-performance SC electrodes. Significant efforts to improve their cycle stability and conductivity have been made to solve these issues, and fantastic ways have been accomplished<sup>[43]</sup>.
- 7. Vanadium Based materials:** Vanadium-based oxides, such as  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ , possess several advantageous properties, including high power density, natural abundance, and high theoretical specific capacity. These features make them promising materials for various applications, particularly in energy storage systems. However, their practical use has been hindered by certain limitations, primarily related to structural stability and poor electrical conductivity<sup>[44]</sup>.

One of the key challenges with vanadium oxides is their poor electrical conductivity. To address this issue, researchers have employed carbon-based materials as anchors to improve the electrical conductivity of vanadium oxides. This approach has shown promise in enhancing the performance of these materials<sup>[45]</sup>.

- 8. Ru Based:** Ruthenium-based materials, such as ruthenium metal (Ru), ruthenium dioxide ( $\text{RuO}_2$ ), hydrated ruthenium dioxide ( $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ ), and various ruthenium compounds, have been identified as highly promising traditional electrode materials for various electrochemical applications<sup>[46]</sup>.

$\text{RuO}_2$ 's increased rate capacity, better electrical conductivity, excellent cycling stability, and outstanding charge-carrying characteristics have all contributed to its exceptional capacitive performance<sup>[47]</sup>. However, its high cost has been a limiting factor in its widespread commercialization as an electrode material in supercapacitors. As inexpensive substitutes to  $\text{RuO}_2$ , vanadium ( $\text{V}_2\text{O}_5$ ), manganese ( $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$ ), cobalt ( $\text{CoO}$  and  $\text{Co}_3\text{O}_4$ ), nickel ( $\text{NiO}$  and  $\text{Ni}_2\text{O}_3$ ), copper ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ), and zinc ( $\text{ZnO}$ ) oxides are employed as active electrode materials. The electrochemical characteristics of transition metal oxides could be enhanced further by the use of binary compounds ( $\text{CoMn}_2\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$ ) and ternary ( $\text{CoNiFeO}_4$ ) metal oxides, which introduce additional redox states and improve electrical conductivity<sup>[48]</sup>.

- 9. Conducting Polymer:** Due to their distinctive qualities, including strong electrical conductivity, processability, mechanical flexibility, electrochemical stability, and large surface area, conducting polymers have been thoroughly investigated and exploited for supercapacitor applications<sup>[49]</sup>. Polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(3,4-ethylenedioxythiophene) (PEDOT), polyacetylene (PA), and poly(3,4-propylenedioxythiophene) (PProDOT) are a few of the more well-known electrical CPs<sup>[50]</sup>. Due to their superior pseudocapacitance, electrical conductivity, and rapid manufacturing and processing, these CPs have drawn a lot of interest. One of the most thoroughly investigated and often used conducting polymers for supercapacitors is polyaniline. It exhibits good redox reversibility and has the potential for high specific capacitance<sup>[51]</sup>. Polypyrrole is another popular conducting polymer used in

supercapacitors. It offers good mechanical stability and high electrical conductivity when doped with suitable dopants. Polythiophene is another conducting polymer that has been considered for supercapacitor applications due to its electrochemical properties and stability. PEDOT is a conducting polymer with high stability and good electrochemical properties. It can be used in various supercapacitor configurations. Similar to PEDOT, PProDOT is a conducting polymer with promising properties for supercapacitor applications. These conducting polymers can be employed in various electrode configurations, such as in the form of thin films, composites with other materials, or as part of hybrid systems. The choice of conducting polymer depends on factors such as the desired specific capacitance, voltage window, and the overall performance requirements of the supercapacitor device<sup>[52]</sup>.

**10. Hybrid Supercapacitor:** A hybrid supercapacitor, also known as an asymmetric or combination supercapacitor, is an energy storage device that combines the characteristics of both supercapacitors and batteries. In addition, the hybrid capacitors combined performance attributes that were previously impossible. The greatest qualities of EDLCs and pseudo-capacitors are also being combined to create a single Supercapacitor<sup>[53]</sup>. It attempts to create supercapacitors with higher energy densities than current supercapacitors while preserving their beneficial high-power density and lengthy cycle life. This technology (EDLC) stores energy by separating charges at the electrode-electrolyte interface. In supercapacitors, ions are adsorbed onto the surface of electrodes with a large surface area, producing a high power density and quick charge/discharge rates. These parts (pseudocapacitors or batteries) store energy through quick, faradaic redox processes that take place at the electrode surface. Unlike supercapacitors, the energy storage in pseudocapacitors involves reversible redox reactions, leading to higher energy densities but usually with a slower response time compared to EDLCs<sup>[54]</sup>.

### III. ELECTROCHEMICAL PERFORMANCE

**1. Cyclic Voltammetry:** In actuality, the electrochemical method known as cyclic voltammetry (CV) is frequently employed to investigate the redox behavior and charge storage mechanisms of electrode materials. The working electrode is given a potential about a reference electrode, and the current response is then measured as specified. By performing two linear potential sweeps in opposite directions, valuable information about the electrochemical processes and charge storage mechanisms can be obtained<sup>[55]</sup>.

When analyzing the shape of the cyclic voltammogram, it can typically exhibit two commontypes of shapes: rectangular and quasi-rectangular.

- **Rectangular CV:** In this type of CV (Fig.3a), the current response shows a well-defined rectangular shape. This shape is often indicative of a charge storage mechanism dominated by electrical double-layer capacitance (EDLC). The reversible adsorption and desorption of ions at the electrode-electrolyte interface results in a capacitive response in EDLC. Electrodes that mainly store charge through EDLC usually have high specific surface areas and are commonly associated with materials like activated carbons and some other conductive porous materials<sup>[56]</sup>.



- **Quasi-Rectangular CV:** The quasi-rectangular CV shape is characterized by sloping or curved lines at the edges of the rectangular region. This shows that there is also pseudocapacitance present in addition to EDLC. Redox processes that take place on or near the electrode surface give rise to pseudocapacitance. These redox processes don't just rely on surface adsorption/desorption; they also involve faradaic processes. Transition metal oxides and conducting polymers are typical examples of materials that display pseudocapacitance behavior<sup>[57]</sup>.

The rectangular region in the CV's surrounding area can be examined to determine the electrode material's specific capacitance. Specific capacitance quantifies the ability of a material to store charge and is an important parameter in evaluating its performance for energy storage applications.

In conclusion, whether the underlying charge storage mechanism is dominated by electrical double-layer capacitance (EDLC) or contains pseudocapacitance, the shape of the cyclic voltammogram offers important insights. This knowledge is crucial for researching how electrode materials behave electrochemically and how they might be used in various energy storage systems, such as supercapacitors. This equation can be used to extract the specific capacitance ( $C_{sp}$ ,  $F\ g^{-1}$ ) of the electrode material from the cyclic voltammogram.

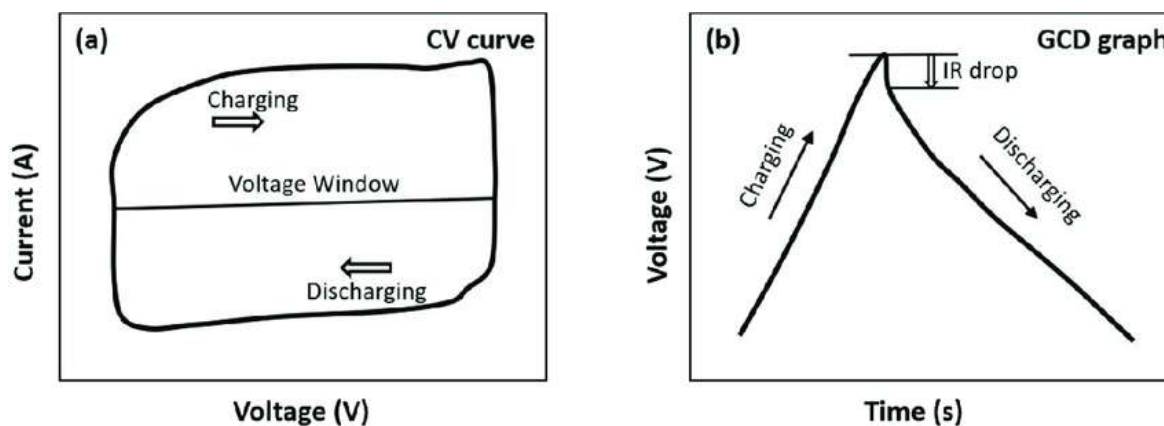
$$C_{sp} = \frac{\int_{v_1}^{v_2} Idv}{m \times v \times \Delta v}$$

Where  $\int_{v_1}^{v_2} Idv$  is computed by integrating the area above the CV. It should be emphasized that the previous equation may only be used to calculate capacitance if the CV is rectangular or nearly so<sup>[58]</sup>.

2. **Galvanostatic charge and discharge:** Galvanostatic charge and discharge are two frequently used methods to evaluate the performance of supercapacitors, also known as electrochemical capacitors or ultracapacitors. To analyze the behavior of the supercapacitor, both techniques apply a constant current during the charging and discharging operations, respectively (Fig. 3b)<sup>[59]</sup>.
3. **Galvanostatic Charge:** A constant current is provided to the supercapacitor during galvanostatic charge, and the voltage across the component is monitored as a function of time. The electrodes pick up a charge as a result of this process, and an electric double layer forms at the electrode-electrolyte interface. Throughout this process, the charge that is held in the supercapacitor grows linearly over time.

The galvanostatic charge process is typically used to determine the capacitance of the supercapacitor. The capacitance value can be calculated using the equation<sup>[60]</sup>:

$$C_{sp} = \frac{i \times t}{m \times \Delta v}$$



**Figure 3:** Typical Profiles of A) CV, And B) GCD,

#### IV. CONCLUSION

Electrochemical SCs are emerging as promising energy storage devices. This article offers a thorough explanation of carbon-based electrode materials, including CPs, MOs, and their composites. Long-term research will focus on supercapacitors with high energy density, considerable voltage resistance, and extreme/low-temperature resistance. To build high-performance supercapacitors with increased energy density, power consumption, and cycle life, electrode materials and electrolytes must be adjusted. Electrochemical IDs for EDLC, pseudocapacitive, and hybrid (battery) materials, such as CVs and GCDs, have been studied. High specific surface area, superior chemical and thermal stability, and low electrical resistance make carbonaceous materials promising electrodes; yet, their low energy density, brought on by surface or quasi-surface energy storage, prevents their employment on a broad scale. Because of their variety, excellent specific capacitance, and environmental friendliness, TMOs such as  $\text{RuO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{MnO}_2$  performed exceptionally well as electrode materials (both cathode and anode). The advancements in material technology discussed in this article, as well as overcoming application hurdles, improving efficiency, and lowering prices, appear to be the biggest obstacles to the widespread adoption of SCs.

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