**Review of Supercapacitor Applications based on electrochemical materials and devices**

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**Abstract:**

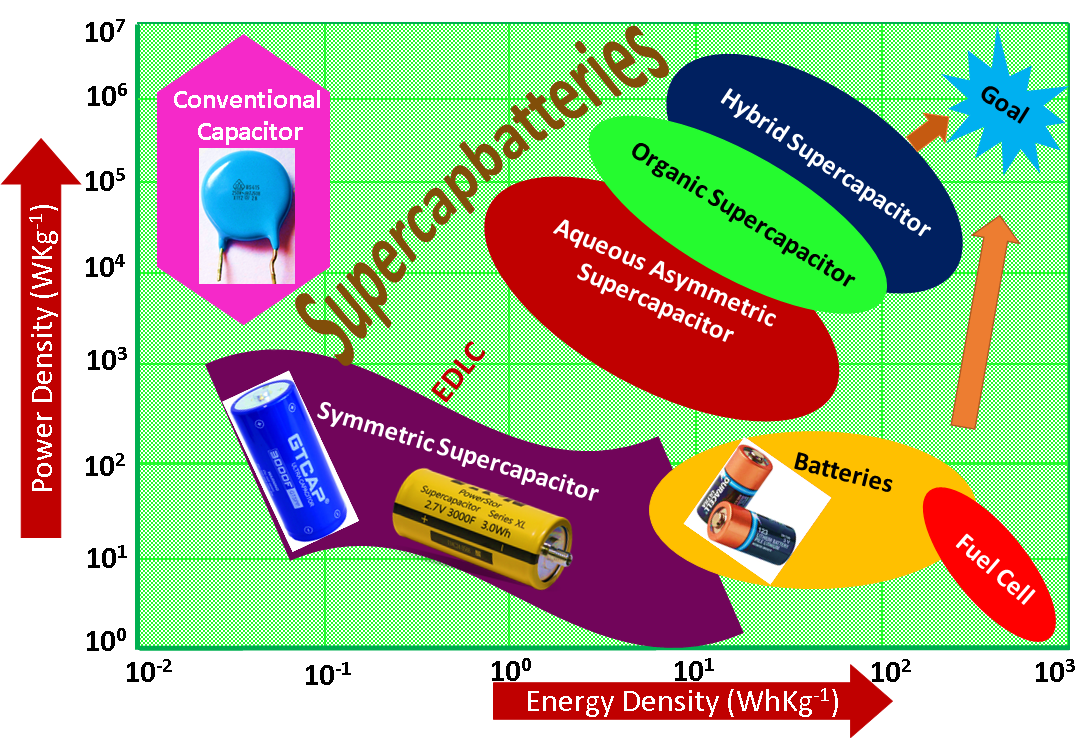
Super-capacitors (SCs) are important because of their unique characteristics, such as long cycle life, high strength, and environmental friendliness. They share similar fundamental equations with traditional capacitors and use electrode materials with thinner dielectrics and higher specific surface areas to achieve high capacitance. 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. The main focus has been on materials such as carbon-based nanomaterials, metal oxides, conducting polymers and their nanocomposites along with some novel materials such as metal-organic frameworks, MXenes, metal nitrides, covalent organic frameworks, and black phosphorus. The performance of the composites was evaluated using metrics such as capacitance, energy, cycle performance power, and rate capability, which also provides information on the electrolyte materials.

**Keywords:** TMOs, EDLC, Pseudocapacitor, Power density (Pd), Energy density (Ed), CV, GCD.

**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 leads to Ecological disturbance factors such as Global warming, climatic change, raising sea levels, and poor rainfall. In addition, Global warming also leads to increased intensity of heat waves [1]. We know that every human action is reliant on the nature environment. A stable and healthy climate is the precious resource of the world. In this ambiance, there is a thirst for energy storage devices. The speedy requirement is material for electrochemical storage with high-geared performance[2]. 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 supercapacitors having the great capability to give 100 to 1000 times higher rate power in the same volume, the supercapacitors are not able to store the same charge density as batteries do (i.e.,) 3-30 times lower[3].

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



**Figure 1.** A Ragone plot of the power-energy density range for different electrochemical energy storage devices[4].

As seen in Figure 2, the supercapacitor's cyclic voltammetry (CV) curve (Figure 2a) stays rectangular throughout the charge and discharge operation, while the current is nearly constant. Additionally, the GCD curve (Figure 2c) of this device is typically inclined with a constant slope. A battery maintains a constant voltage except when it is close to 100% charged/discharged; the GCD curve displays a reasonably flat charge-discharge platform. A battery exhibits Faradaic reactions during the charge and discharge process, and its CV curve displays a redox peak.

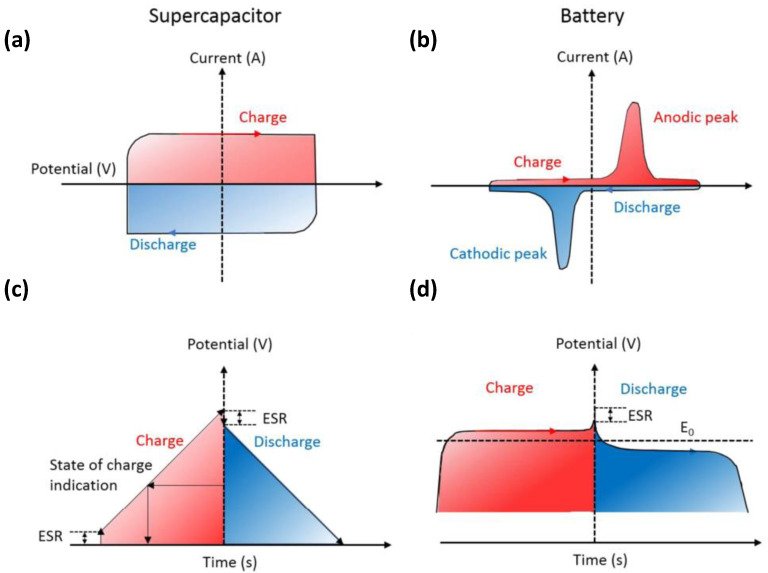


Fig. 2(**a**,**b**) cyclic voltammetry (CV) curves and (**c**,**d**) galvanostatic charge-discharge (GCD) curves of supercapacitors and batteries. Reproduced with permission [5].

Researchers have attention to supercapacitors because of their high-range power capabilities and the life cycle is the main reason for choosing the supercapacitor as an energy storage device. 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, have become an electrochemical reaction that can be stored in the form of electrical energy. 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]. Supercapacitors are broadly classified into three major types namely Electric Double Layer Capacitors (EDLC), Pseudocapacitors, and Hybrid capacitors [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 role of dielectric in the capacitor is to cut down the electric field strength inside the capacitor. It results in a smaller voltage between the plates for the same charge. 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) [11].

Pseudocapacitor also called a redox capacitor. In this material, energy can be stored in the form of electrochemically fast and reverse faradaic reactions. Pseudocapacitors are consists of transition metal oxides and conducting polymers. Transition metal oxides such as RuO2 [12], TiO2 [13], V2O5 [14], MnO2 [15], Co3O4 [16], MoO2 [17], NiO [18], Fe3O4 [19], 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 [20].Conducting polymers such as PPy, PANI, and PVDF, to improve the electrochemical performance[21].

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[22]. 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 [23]. The asymmetric type supercapacitor consists of two dissimilar electrodes one is an activated carbon (porous) electrode and another is a battery-type electrode [24].

In recent years Two dimensional (2 D) sheets-like structure dichalcogenides supercapacitor materials such as WS2, MoS2, and VS2 are 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 MoS2 supercapacitor materials show only moderate performance as electrode materials due to the relatively poor electronic conductivity and stability. In addition, MoS2@ZIF-67 composites have been used as one of the most effective ways to increase their conductivity and electrochemical properties. Finally, we have developed in this work to synthesize MoS2@ZIF-67 composites through the hydrothermal method[25].

**Electrochemical Performance for EDLC Type Supercapacitor Materials:**

**Carbon materials:**

Carbon materials are the electrode materials with the best possibilities for industrialization. They have extensive natural reserves, a low price, easy processing, are non-poisonous, have a big specific surface area, great conductivity, strong chemical stability, and a wide working temperature range[26]. Carbon materials utilize an electrochemical double layer produced at the electrode-electrolyte interface as a storage mechanism. As a result, the capacitance is mostly determined by the surface area accessible to electrolyte ions. Specific surface area, pore shape and structure, pore size distribution, surface functionality, and electrical conductivity are all important aspects that affect electrochemical performance[27]. In the case of carbon materials, having a high specific surface area leads to a high capacity for charge accumulation at the electrode-electrolyte interface. When it comes to enhancing specific capacitance for carbon materials. Carbon materials such as activated carbon (AC), carbon aerogels, carbon nanotubes (CNTs), carbon nanofibres, and others are used. With a theoretical capacitance of 100⁓300 F g-1, conventional alternating current has high cycling stability in a variety of electrolytes. However, due to double-layer capacitance processes, the specific capacitance cannot be greatly enhanced. 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[28].

**Activated carbon (AC):**

Among various types of Electrochemical Double Layer Capacitors (EDLCs), porous activated carbon (AC) has been widely recognized as one of the most prominent and commonly used electrode materials. This is primarily due to the exceptional properties that make it well-suited for energy storage in supercapacitors. Activated carbon exhibits excellent electrochemical stability, allowing it to undergo numerous charge-discharge cycles without significant degradation. This characteristic is crucial for long-lasting and reliable supercapacitor performance[29]. Activated carbon possesses an extensive internal surface area, often measured in thousands of square meters per gram. This high surface area provides ample space for electrolyte ions to adsorb, resulting in a higher capacitance and energy storage capacity. The porous structure of activated carbon further enhances its capacity to store charge. The presence of numerous small and interconnected pores increases the available active sites for the electrochemical double-layer formation, leading to higher capacitance values. Efficient charge transport is crucial for rapid charge and discharge in supercapacitors[30]. 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 means that the cell can be charged and discharged thousands of times without deterioration in performance[31].

**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[32]. 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. This high electrical conductivity enables rapid charge and discharge rates in supercapacitors, leading to quick energy storage and release. 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[33]. Graphene exhibits outstanding mechanical strength, which is essential for maintaining the structural integrity of supercapacitor electrodes during charge and discharge cycles. Its durability ensures a longer lifespan and better cycling performance for supercapacitors. Graphene can be combined with other materials, such as metal oxides or conductive polymers, to form graphene-based composites. These composites can further improve the specific capacitance and overall energy storage capabilities of supercapacitors. Graphene is composed solely of carbon atoms, making it environmentally friendly compared to certain materials used in traditional energy storage devices, such as lithium-ion batteries, which can contain heavy metals and other hazardous materials[34]. Due to these remarkable properties, graphene and graphene-based materials have gained significant attention in the development of next-generation supercapacitors with improved energy density, power density, and cycling stability. 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].

**Pseudocapacitor:**

Pseudocapacitors are also called faradaic [supercapacitors](https://www.sciencedirect.com/topics/materials-science/supercapacitors).When compared to EDLCs, pseudocapacitors are electronic devices with electrodes made of redox-active materials. These devices store electrical charge (and consequently energy) through a different process. 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.

In a pseudocapacitor, the electrode material undergoes both reduction and oxidation when a voltage is applied. It entails the movement of charge across the double layer, which causes faradic current to flow through the electrode material of the supercapacitor. In comparison to EDLCs, the faradic technique used in pseudocapacitors accelerates the electrochemical processes that lead to higher specific capacitance and energy densities[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].

**Transition Metal Oxides (TMO):**

Metal oxide is one type of pseudocapacitive material that displays quick and reversible redox reactions outside of the electrode materials. Because of this material's low resistance and high specific capacitance, it is simple and efficient to build supercapacitors. They offer a higher specific capacitance than carbon-based materials and better cycle stability than conductive polymers because metal oxides made of transition metal families store charges through quick and reversible redox processes[39]. To enhance the electrochemical capabilities of supercapacitors, transition metal oxides are therefore particularly appealing electrode materials. For better energy densities in aqueous asymmetric supercapacitor devices, metal oxides can be employed as cathode and anode materials. In the past few years, metal oxides, mainly including single metal oxides such as Fe2O3, V2O5, RuO2, MnO2, MoO3, and WO3, bimetallic oxides such as conversion-type MN2O4, where M or N = Ni, Co, Zn, Mn, Fe, Cu, etc. and intercalation-type such as LiCoO2, LiMn2O4, etc.and metal oxide heterostructures, have been widely investigated as electrode materials for aqueous asymmetric supercapacitor devices[40]. The following introduces various electrode materials based on Fe, V, Ru, Mn, and Co, as well as single metal oxides.RuO2 is regarded as the most promising metal oxide among them all due to its high specific capacitance (720 F g-1), high price, and high electrical conductivity[41].

**Fe-based Iron Oxide Supercapacitor Materials:**

Iron-based substances, such as Fe2O3, Fe3O4, FeOOH, FeOx, CoFe2O4, and MnFe2O4, have recently drawn a lot of interest as extremely promising electrode materials for SCs because of their high theoretical specific capacitances, abundance in nature, low cost, and non-toxicity[42]. The majority of these Fe-based SC electrodes, however, have low conductivity and/or electrochemical instability, which severely limits their use as high-performance SC electrodes. To address these problems, significant attempts have been made to increase their cycle stability and conductivity, and wonderful methods have been accomplished[43].

**Vanadium Based materials:**

Vanadium-based oxides, such as VO2, V2O3, and V2O5, 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[44].

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[45].

**Ru based**

Ruthenium-based materials, such as ruthenium metal (Ru), ruthenium dioxide (RuO2), hydrated ruthenium dioxide (RuO2·xH2O), and various ruthenium compounds, have been identified as highly promising traditional electrode materials for various electrochemical applications[46].

RuO2 has demonstrated outstanding capacitive performance due to its higher rate capability, superior electrical conductivity, great cycling stability, and excellent charge-carrying properties[47]. However, its high cost has been a limiting factor in its widespread commercialization as an electrode material in supercapacitors. As inexpensive substitutes to RuO2, vanadium (V2O5), manganese (MnO2 and Mn3O4), cobalt (CoO and Co3O4), nickel (NiO and Ni2O3), copper (Cu2O and CuO), and zinc (ZnO) oxides are employed as active electrode materials. The electrochemical properties of transition metal oxides could be improved further by using binary (CoMn2O4 and NiCo2O4) and ternary (CoNiFeO4) metal oxides, which introduce additional redox states and improve electrical conductivity[48].

**Conducting Polymer:**

Conducting polymers have been extensively studied and used for supercapacitor applications due to their unique properties, such as high electrical conductivity, processability, mechanical flexibility, electrochemical stability, and large surface area[49]. Some of the commonly known electrical CPs include polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), Poly(3,4-ethylenedioxythiophene) (PEDOT), polyacetylene (PA), and Poly(3,4-propylenedioxythiophene) (PProDOT)[50]. These CPs have attracted considerable attention due to their high pseudocapacitance, conductivity, and ease of manufacturing and processing. Polyaniline is one of the most extensively studied and widely used conducting polymers for supercapacitors. It exhibits good redox reversibility and has the potential for high specific capacitance[51]. 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[52].

**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. Furthermore, the hybrid capacitors were a previously unattainable combination of performance properties. They are also combining the best features of pseudo-capacitors and EDLCs into a unified Supercapacitor[53]. It aims to provide higher energy densities than conventional supercapacitors while maintaining their advantageous high-power density and long cycle life. These devices (EDLC) store energy through the charge separation at the electrode-electrolyte interface. In supercapacitors, ions are adsorbed onto the surface of high-surface-area electrodes, resulting in high power density and rapid charge/discharge capabilities. These components (pseudocapacitors or batteries) utilize fast, faradaic redox reactions that occur at the electrode surface to store energy. 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[54].

**Electrochemical Performance:**

**Cyclic Voltammetry:**

Indeed, Cyclic Voltammetry (CV) is a common electrochemical technique used to study the redox behavior and charge storage mechanisms of electrode materials. As described, it involves applying a potential to the working electrode concerning a reference electrode and measuring the resulting current response. By performing two linear potential sweeps in opposite directions, valuable information about the electrochemical processes and charge storage mechanisms can be obtained[55].

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

1. **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). EDLC is related to the reversible adsorption and desorption of ions at the electrode-electrolyte interface, resulting in a capacitive response. 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[56].
2. **Quasi-Rectangular CV:** The quasi-rectangular CV shape is characterized by sloping or curved lines at the edges of the rectangular region. This indicates the presence of pseudocapacitance in addition to EDLC. Pseudocapacitance arises from redox reactions occurring at or near the electrode surface. These redox reactions involve faradaic processes and are not solely based on surface adsorption/desorption. Common materials that exhibit pseudocapacitance behavior are transition metal oxides and conducting polymers[57].

By analyzing the area enclosed by the rectangular region in the CV, it is also possible to estimate the specific capacitance of the electrode material. 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 summary, the shape of the cyclic voltammogram provides valuable insights into the underlying charge storage mechanism, whether it’s dominated by electrical double-layer capacitance (EDLC) or involves pseudocapacitance. This information is crucial for understanding the electrochemical behavior of electrode materials and their potential use in various energy storage devices, such as supercapacitors.From the cyclic voltammogram, the specific capacitance (, F g−1) of the electrode material can be calculated by using this equation

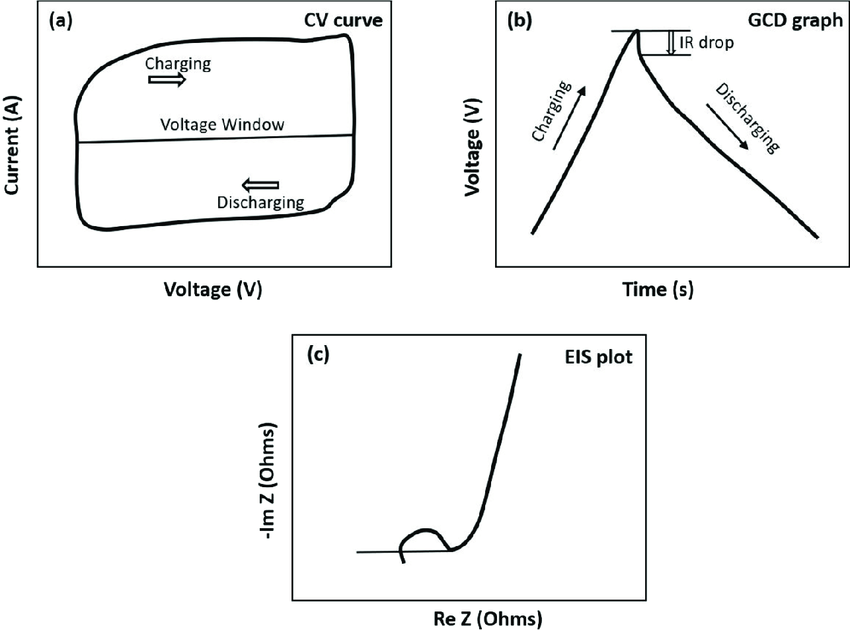
where is calculated by integrating the area under the CV. It should be noted that the preceding equation is only valid for calculating capacitance if the CV is rectangular or very close to being rectangular[58].

**Galvanostatic charge and discharge:**

Galvanostatic charge and discharge are two common techniques used to characterize the performance of supercapacitors, which are also known as electrochemical capacitors or ultracapacitors. These techniques involve applying a constant current during the charging and discharging processes (Fig. 3b), respectively, to analyze the behavior of the supercapacitor[59].

**Galvanostatic Charge:** During galvanostatic charge, a constant current is applied to the supercapacitor, and the voltage across the device is measured as a function of time. This process leads to the accumulation of charge on the electrodes and the formation of an electric double layer at the electrode-electrolyte interface. The charge stored in the supercapacitor increases linearly with time during this process.

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



#### Figure 3.Typical profiles of a) CV, and b) GCD,

**Conclusion:**

Electrochemical SCs are emerging as promising energy storage devices. This review provides a detailed description of electrode materials based on carbon materials, CPs, MOs, and their composites. Supercapacitors with high energy density, high voltage resistance, and high/low-temperature resistance will be a long-term research focus. Developing high-performance supercapacitors with improved energy density, power density, and cycle life requires optimizing electrode materials and electrolytes. The electrochemical signatures of EDLC, pseudocapacitive, and hybrid (battery) materials have been studied, including CVs and GCDs.Carbonaceous materials are promising electrodes because they have a high specific surface area, good chemical and thermal stability, and low electrical resistance; however, their low energy density, caused by surface or quasi-surface energy storage, limits their use on a large scale. Because of their variety, excellent specific capacitance, and environmental friendliness, TMOs such as RuO2, V2O5, and MnO2 performed exceptionally well as electrode materials (both cathode and anode). The most critical challenges for the widespread use of SCs appear to be the innovations in material technologies mentioned in this article, as well as overcoming application difficulties, becoming more efficient, and becoming more attractive in the market in terms of price.

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