A BRIEF REVIEW OF THE ELECTRODES AND ELECTROLYTES INFLUENCING THE SUPERCAPACITOR'S BEHAVIOR

Abstract

Energy storage systems have recently become absolutely necessary for day-to-day existence because of energy issues. Super capacitors are among the most significant forms of energy storage devices. Supercapacitors rely on electrodes to store and release energy. Electrodes and electrolytes are crucial components that play an essential role in the performance and efficiency of the supercapacitor. Hence, for better super capacitor performance, choosing the appropriate components is of utmost importance as well. In order to understand their functionality and potential applications, various factors like their energy density, power density, and capacitance are considered. The sorts of supercapacitors, their electrodes, and their taxonomy, as well as electrolytes and the variables affecting specific capacitance, are briefly studied in the current study. It includes an extensive discussion of the importance of transition metal oxides, their doping, and their composites. Additionally, studying these components can provide insights into their efficiency and durability, allowing for improvements in their design and performance. This paper provides an overview of certain significant electrodes, their characteristics, and the electrolyte behavior affecting a specific capacitance.

Keywords: Supercapacitors; Electrodes; Electrolyte; specific capacitance

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I. INTRODUCTION

The majority of the energy that should be necessary for every-day needs has been utilized by modern society. Additionally, contemporary life relies on automotive machines to complete all the labor effortlessly and quickly. There must be a demand for energy for these automobile operations. Certainly, fossil fuels, including coal, unrefined oil, and gas from natural sources, have been utilized. They have limited availability and are difficult to obtain, and certain petroleum products are prohibitively expensive. When they are burned, harmful gases are released into the atmosphere, inflicting air pollution and acid rain. Each passing day, the climate changes, ecological health evolves, and fossil fuel reserves deplete. Furthermore, the cost of gasoline is steadily rising. Everyone desires green and sustainable energy storage systems, as well as highly efficient gadgets that are low-cost and environmentally beneficial. Therefore, the number of portable electronics and electric vehicles is increasing continuously. There is an immense amount of fascination with creating super capacitors, which are one type of energy storage technology.

For a good energy storage system, high power density, cyclic stability, charge discharge capability, a fast charge-discharge process, low maintenance, low cost, and environmental friendliness are necessary characteristics. Super capacitors are known for their ability to deliver high power density, making them ideal for applications that require quick bursts of energy. Additionally, they exhibit excellent cyclic stability, allowing them to endure numerous charge and discharge cycles without significant degradation. They maintain their performance and storage capacity for a longer duration compared to traditional batteries. This makes them a reliable and durable energy storage solution for various applications. They are commonly used in electric cars, wind turbines, and photographic flash units to provide quick bursts of power. Additionally, supercapacitors are also utilized in flywheels within machines to store and release energy efficiently. Furthermore, they play a crucial role in medical devices, uninterruptible power sources, hybrid electric vehicles, MP3 players, enabling longer battery life and faster charging times. Supercapacitors are also employed in regenerative braking systems within the automotive industry. The key improved feature of super capacitors is their quick charge and discharge processes. And, in this regard, energy and power densities play an important role, competing for good electrochemical energy storage devices. It is simpler to construct a super capacitor with nanotechnology and nanomorphology as active materials for the electrode and a specific electrolyte. Because of their nanosize, tunable morphologies, strong conductivities, high chemical stability, and vast surface area. They can be utilized to make supercapacitors.

Most conductive materials, such as carbon nanotubes and graphene, are the most important for super capacitors, as they possess high electrical conductivity and a large surface area. These materials allow for efficient charge storage and quick discharge, making them ideal for applications requiring high power density. Additionally, their mechanical strength and flexibility enable the design of lightweight and compact supercapacitors. However, entire super capacitors cannot be created using merely graphenes because they are extremely limited, their minerals are also not abundant, and preparing graphene-based nanomaterials is extremely expensive. Maximum energy density is also necessary for the main commercial super capacitors. If the electrode layer is multilayer, it has several advantages for simultaneously storing high energy densities and Large-scale manufacturing.

II. SUPERCAPACITORS

1. **Types of Supercapacitors:** We can find three types of them. One is double-layered capacitors, pseudo capacitors. Another involves both characteristics and is called a hybrid capacitor. Figure1. shows the taxonomy of supercapacitors with examples. The pseudo capacitor stores energy in the form of electrochemical energy via the faraday charge transfer process, whereas energy is stored electrostatically in double-layer capacitors without interaction between the electrode and ions, but there is interaction between the electrolyte ions and the electrode in the pseudo capacitor. A pseudocapacitance with the same electrode surface can be a hundred times greater than a double-layer capacitance. Hybrid capacitors, on the other hand, store energy both electrostatically and electrochemically by combining these two properties. This paper investigates pseudo capacitors, their development utilizing various electrodes, and the electrolytes that influence the performance of the pseudo capacitors.

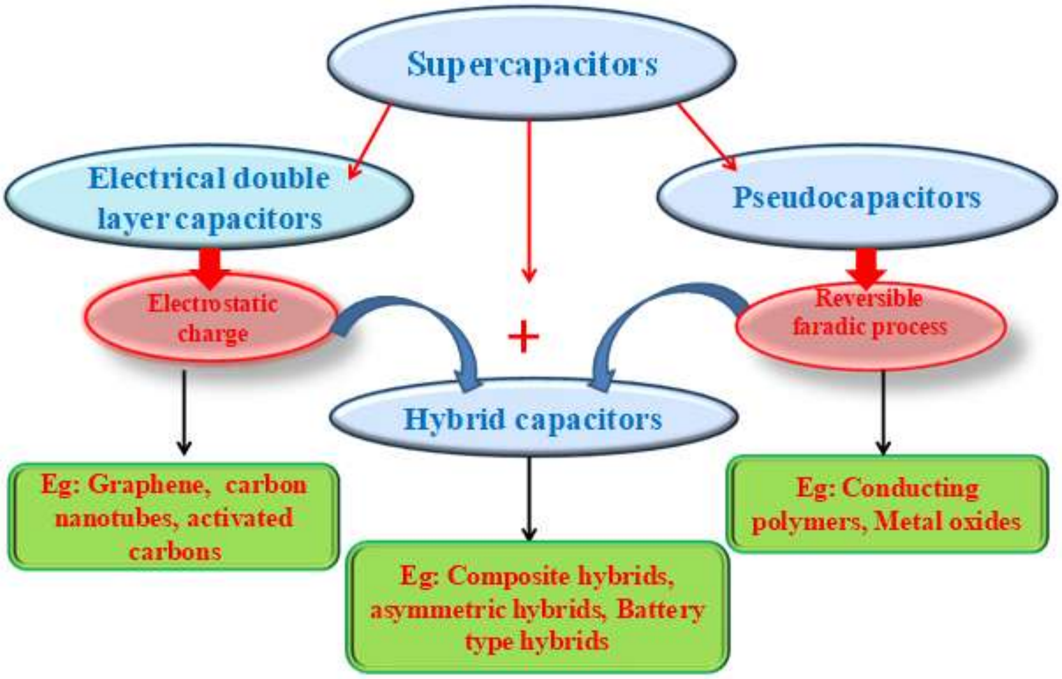

Figure 1: Classification of Supercapacitors.

Mechanism of energy storage in Pseudo capacitors through a faradic mechanism that involves transferring charges over electrode and electrolyte [1]. Once a pseudo capacitor is provided with a potential, it causes reduction and oxidation of the electrode material, resulting in charge flow across the double layer and faradic current traveling through the supercapacitor cell. When compared to EDLCs, the faradic technique used in pseudo capacitors allows them to reach superior specific capacitance and energy densities. The best examples of pseudo capacitors are metal oxides and conducting polymers. This piques interest in these materials

III. ELECTRODES FOR SUPERCAPACITORS

The electrode is the key component in the improvement of super capacitors, so selecting an electrode is critical. It should be able to store large amounts of energy, and bio inspired materials can be employed as electrodes in most super capacitors.

1. **Nano Tubular Materials:** Nanotubes can be used as electrode materials in super capacitors as they have mesoporosity and a large surface area [2]. They have the capability of storing energy and charge at the electrode/electrolyte contact. Single-walled nanotubes and multi-walled nanotubes constitute effective electrode materials for super capacitors. When compared to single-walled nanotubes, multi-walled nanotubes show some higher capacitance, and these types of electrodes exhibit rectangular box-shaped voltammetric properties, are electrostatic in nature, and have double-layer capacitance. Pseudo-capacitance behavior develops when nanotubes are combined with or fabricated into a composite with any metal oxide particles or any conducting materials. Electrostatic attraction and faradic reactions occur in such materials, enhancing the capacitance of the electrode.

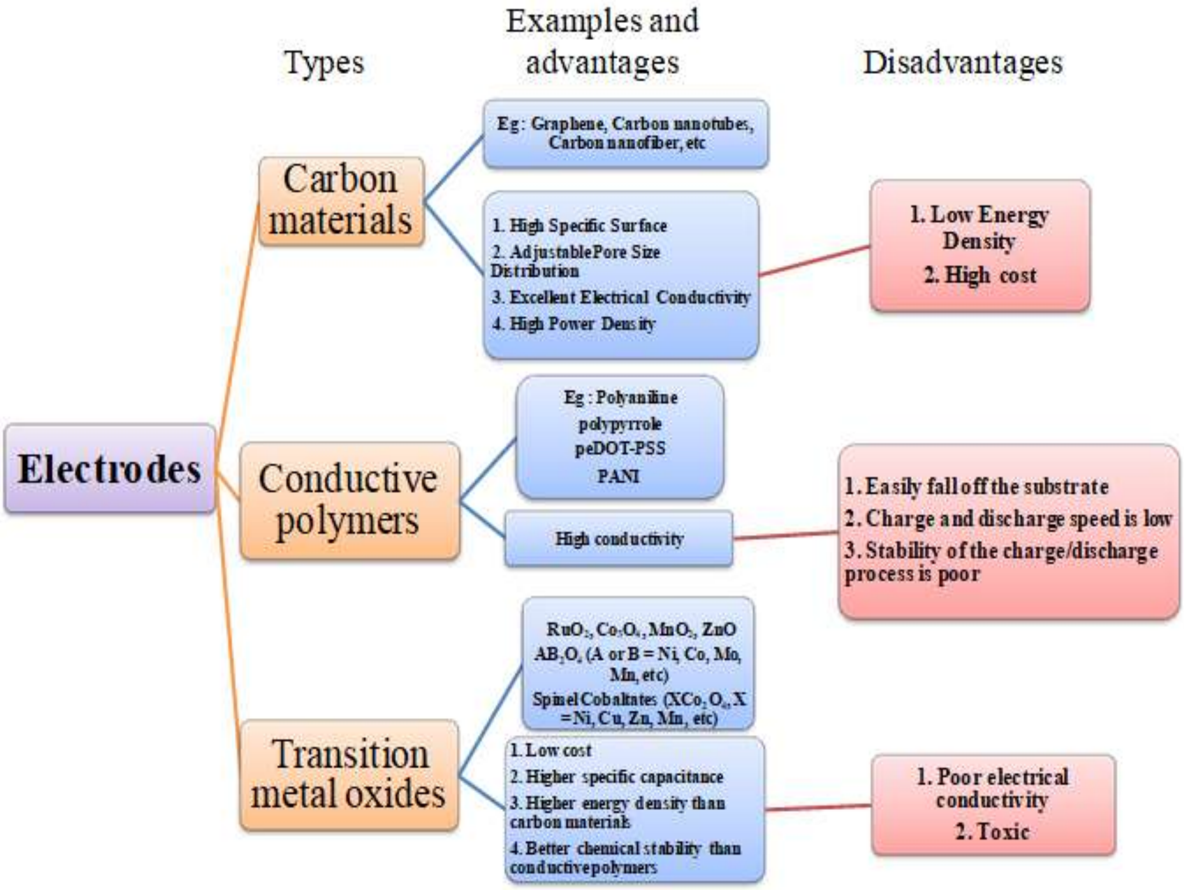

Figure 2: Classification of electrode materials with examples, merits, and demerits

The primary components that are employed for the polarizable negative electrode should ideally be nanostructured carbon materials because of their higher surface area, chemical and thermal stability, micro/nanoporous structure, and improved electrical conductivity [3]. Examples of these materials include activated carbon (AC), carbon aerogel, carbon nanotubes (CNT), and graphene. Additionally, pseudocapacitive materials such as metal oxides (such as Fe_2O_3, RuO_2, MnO_2, and V_2O_5) and conducting polymers (such as polypyrrole, peDOT-PSS, PANI), which offer a higher capacitance however comparatively smaller potential windows than EDLC materials, can be used as pseudocapacitive electrode materials. Co_3O_4, NiO, and its ternary compound [4], among other materials, are frequently employed as positive electrodes in batteries, etc.Figure 2. depicts the many types of electrodes, as well as instances of such electrodes and their benefits and drawbacks.

2. **Transition Metal Oxides:** Carbon compounds like carbon nanotubes, nanofibers, and graphene, have become extensively researched as electrode materials. Yet the lower specific capacitance of carbon materials confines the capability of double layer capacitors [5, 6], and their applications are constrained by their expensive nature. Conductive polymers have high conductive in nature and they have pseudocapacitive characteristics, but their durability is low, and they rapidly slide off their supporting material [7, 8]. Polyaniline, for example, has a low charge and discharge rate and poor charge/discharge stability in the process[9, 10].Transition metal oxides have greater specific capacitance (100-2000 F/g), higher energy density, and greater chemically stable characteristics over conductive polymers[11, 12].

Ruthenium oxide (RuO_2) is believed to be the best pseudo-capacitive electrode material. Fortunately, its high cost and environmental toxicity severely limit its use in super capacitors[9, 13]. Other metal oxide electrodes, such as cobalt oxide (Co_3O_4) [14-16], manganese oxide (MnO_2), and zinc oxide (ZnO), can also be used as electrodes, as they are cheap and widely available. These metal oxides can be used instead of RuO_2.

Spinel cobaltates and metal molybdates have piqued the interest of researchers because of their inexpensive cost, improved electrochemical activity, and abundant availability as natural resources. Simple metal oxides also have disadvantages; they have poor electrical conductivity. Therefore, the composite materials received great interest. To further enhance the capacitance of transition metal oxides and their composites, they are made on a nanoscale by creating oxygen vacancies and also modifying them into quantum dots. It is also noted that metal sulfide and metal oxide composite materials have also been created to enhance the electrochemical characteristics.

Asim et al.,[17] prepared the carbon nanotube-grown carbon cloths with RuO_2 nanorods. The electrode produced possesses the properties of in cooperation Li-ion batteries and supercapacitors. The specific capacitance was found to be 176 F/g. Metal oxides can also be modified using carbon nanotubes, other nanotubes, and nanorods. This modification increases the capacitance due to its unique characteristics, such as an enlarged surface area and increased active sites, as well as the synergic effect of metal oxide. More interest has been created in preparing ternary composites to further increase the specific capacitance. Metal oxides can be decorated with carbon nanotubes along with conductive polymers.

Zhu et al., [18] prepared ternary nanocomposites, single-walled carbon nanotubes/RuO_2/polyindole (SWCNT/RuO_2/PIn) and got a specific capacitance of 1283 F/g. Metal oxides and their composites at the nanoscale can also be easily synthesized using various wet chemical methods.

Cobalt oxide is also a member of the best transition metal oxides as it has a high theoretical specific capacitance. Cobalt oxide has made electrodes with durability and chemical stability due to its affordable price and environmental friendliness. It's an interesting active substance. However, due to its lower conductivity and particle aggregations, it shows variations from the theoretical value. The cycling performance of cobalt oxide also has some limitations.When Cobalt oxides are synthesized in nanoscale dimensions, their morphology changes, which improves their electrochemical characteristics.

Using a diversity of applications of nanotechnology by creating nanofibers, nanoparticles, nanowires, nanotubes, and nanosheets, one can alter the specific capacity of this metal oxide. In that case, doping of them is also done to enhance their capacitance. For some metal oxides, binders are necessary in order to prepare the electrode; hence, along with them, PVDF as a Binder has been used [16, 19], and the procedure involves the coating of their slurry on the surface of metal surfaces such as nickel foam. However, it decreases the specific capacitance due to the binder's resistance properties. Also, it decreases active sites. Instead of using binders, directly growing metal oxides on the substrates of stainless steel,carbon cloth, Carbon fiber, metal forms, and any conductive additives is beneficial.

Binary metal oxides metal molybdates ($AMoO_4$; A = Ni, Zn,Co, Mn, etc) are in more demand. They also have pseudo capacity behaviors, and they have high specific capacitance as a result of more redox reactions on the surface of the electrode. Ternary metal oxides also have more active sites along with quicker redox reactions than single and binary metal oxides[20].Because of their natural resources, high theoretical specific capacitance, and inexpensive expenses, mixed transition metal oxides and transition metal molybdates have received a lot of interestThe efficiency of the super capacitors is heavily influenced by the arrangement of their atoms and their structure; as a result, it is critical to generate electrode materials with distinct spatial and structural features

IV. ELECTROLYTES FOR SUPERCAPACITORS

Electrolytes are also significant in this case. Organic electrolytes have several drawbacks: they can cause flammability at higher temperatures and are hazardous to the environment. Ionic liquids can be employed as electrolytes to circumvent these drawbacks. When compared to organic liquids, they have higher working voltages. They are also non-toxic, have a low vapor pressure, and are thermally stable. However, these ionic liquid super capacitors have a drawback in that they only work at temperatures around or above 60 °C.

Ionic liquids have a low ionic diffuse capacity due to their viscosity, making diffusion of these ions difficult at the required scan rates. Furthermore, the size of the cations and ions restricts the utility of these ionic liquids. Electrolytes alter the electrochemical properties of materials. The electrolyte that increases the cell voltage also has a greater effect on the capacitance. Some unique electrolytes enable the cell voltage to rise and increase the capacitance [21]. Protic electrolytes are one form of electrolyte that improves the capacitance owing to their rapid redox reactions. Electrolyte plays a crucial role in ion diffusion in double-layer capacitors; it must carry the ions towards the surface of electrode. The relative permittivity of the dielectric electrolyte is critical in determining capacitance.

Electrolyte's resistance, such as ionic resistance also affects the specific power. Its resistance was used to compute the equivalent series resistance. The electrolytes can be aqueous, organic, or ionic liquids, commonly known as 'liquid salts'. The electrolyte influences the level of ionic conductivity and stability window. Voltammogram characteristics are entirely affected by the electrolyte used. Acetonitrile and propylene carbonate are the top examples of organic electrolytes. In comparison to these organic electrolytes, acid and base in water systems, namely sulfuric acid and potassium hydroxide, have more mobility and hence conductivity, can be exploited to provide improved power performance and capacitance in super capacitors. The electrical conductivity of aqueous solutions of potassium hydroxide was proven to be around 1 S/cm. This aqueous solution has several restrictions as well. They possess a smaller potential window, which implies that the performance stability is relatively limited to low voltages, namely 1.23 V, and the operational voltage is likewise quite low (1 V).

Electrolytes, which generate the high working voltage, improve the super capacitor's performance. Acid electrolytes have drawbacks as well; they undergo corrosive reactions, necessitating usage of neutral pH electrolytes. These electrolytes work up to 2 V. Electrolytes with a neutral PH have a long charge-discharge cycle life. In asymmetric capacitors with a negative AC electrode and a positive electrode consisting of transition metal oxides, sodium sulfate (Na_2SO_4) and lithium sulfate (Li_2SO_4) are utilized.

In comparison to aqueous solutions, a salt that is dissolved in the organic solvent gives a more stable potential window of 2.7 to 2.8 V. However, the specific capacitance and conductivity are lower than those of the aqueous electrolytes. Organic electrolytes, on the other hand, produce higher cell voltages and specific energy than aqueous systems; thus, organic electrolytes, namely acetonitrile and propylene carbonate, are employed in industrial systems. Propylene carbonate has the resistance to undergo hydrolysis; nevertheless, it is more susceptible to temperature changes due to its viscosity. The salts that are used in organic electrolytes are often quarterly ammonium salts like Tetra ethyl ammonium and tetra fluoroborate, which are commonly used in commercial super capacitors. The ability to conduct electricity of each salt varies, and salt concentration is also essential. Once the greatest conductivity point is reached, the salt no longer makes an impact to electrolyte's conductivity. Ionic liquids at room temperature have recently seen considerable and promising use in super capacitors. A solvent is not required for these types of electrolytes. These ionic liquids have higher temperature stability than organic electrolytes; they also have electrochemical stability; however, the disadvantage of these ionic liquids is their conductivity, which is generally lower than organic electrolytes and reduces super capacitor performance. The size of the ions in the electrolyte is also essential. Typically, electrode materials have some pore sizes, and if the size of the electrolyte ions is larger than that of the electrode pore size, then diffusion of electrolyte ions is also difficult, results decrease in current capacity. The best examples of improved aqueous electrolytes are Li2SO4 and Mg2Cl2[22]. Because the lithium and chloride ions are small and the sulfate and magnesium ions are large, adsorption of smaller ions is easier and adsorption of larger ions is harder. It should also be noted that the capacitance is also influenced by electrode's average pore size.

With the variation in scan rates, larger ions can move inside the smaller pore sizes. Sometimes, the disappearance of capacity in the current was observed. Therefore, it is necessary to consider the sizes of both the dimensions of electrode’s pore and also the dimensions of the ions, and they should be matched to each other.

V. CONCLUSION

In conclusion, with varying electrode types and electrolytes, one can design the supercapacitor by incorporating the pseudo-capacitance behavior in the double-layer capacitor electrodes by using materials with high surface area and porosity, which increases the capacitance. As well as making composites of metal oxide materials with the carbon derivative material, this also increases the specific capacitance. The electrolytes can be altered to increase the specific capacitance by altering them, employing unique and advanced electrolytes, and also for special needs. The capacitance of the super capacitor can be improved by changing the designs and morphology of the electrodes. Optimizing the electrode design and electrolyte composition can also improve capacitance. In terms of energy storage and power distribution, the electrode and electrolyte work together to determine the performance and efficiency of super capacitors.

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