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Short Review

A Brief Review on Electrode Materials for Supercapacitor

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One of the issues recently faced in electrostatic field is storage. With recent advances in this area it has become necessary to find an alternative which lead to emergence of supercapacitor. Supercapacitor shares the same fundamental equations as conventional capacitors; to attain higher capacitances supercapacitor uses electrodes having high specific surface area and thinner dielectrics. With these properties it makes them have power densities greater than those of batteries and energy density greater than those of conventional capacitors. Since supercapacitor is mainly a pulse current device it is best used with devices that require high current for short duration of time. Researchers being carried out now are on how to improve the energy density so that they can be used in wider range of applications. The performance of supercapacitor relies on factors such as electrochemical properties of electrode materials used, electrolyte and voltage range. However, most researches are focused on the development of new electrode materials that will yield better performances. In this review paper, storage principle and characteristics of electrode materials such as carbon based materials, metal oxides and conducting polymers in supercapacitors have been reported.

Keywords: Supercapacitors, EDLC, Pseudocapacitors, CNTs, Graphene, Ruthenium oxide, PANI.

1. INTRODUCTION

The discovery of the possibility of storing an electrical charge in surface arose from phenomena associated with rubbing of amber during the ancient times. In the mid eighteen century that was when the effect of such phenomena was understood during the period when physics of so-called ‘’static electricity’’ was being investigated and various ‘’electrical machines’’ were being developed.

In 1957 a group of General Electric Engineers were experimenting with devices using porous carbon electrode when they noticed electric double layer capacitor effect. Their observation at the time was that energy was store in the carbon pores and it showed an exceptionally high capacitance. Later in 1966, a group of researchers at Standard Oil of Ohio accidently rediscovered the effect while working on fuel cell designs. Their cell design was made up of two layers of activated charcoal separated by a thin porous insulator, and the mechanical design remained the same for most electric double layer capacitors to date. In 1978 NEC finally introduce the term Supercapacitor and its application was used to provide backup power for maintaining computer memory [1].

Due to its application, many researchers delved into supercapacitor which led to trying of other composite as electrode material such as Metal Oxides and Conducting Polymer etc.

Among the challenges faced in this century is unquestionably energy storage. Therefore it is important that new, environmentally friendly and low-cost energy storage systems be found, in response to the needs of emerging ecological concerns and modern society [2].

Supercapacitors (also called electric double-layer capacitors or ultracapacitors) are energy storage devices with very high capacity and a low internal resistance, that are able to store and deliver energy at relatively higher rates as compared to batteries due to the mechanism of energy storage which involves a simple charge separation at the interface between the electrode and the electrolyte [3, 4]. A supercapacitor consists of two electrodes, an electrolyte, and a separator which isolates the two electrodes electrically. Electrode material is the most important component of a supercapacitor [5, 6]. Some of the benefits of supercapacitors when compared with other energy storage devices are long life, high power, flexible packaging, wide thermal range ($-40^{o}C$ to $70^{o}C$), low maintenance and low weight [7]. Supercapacitors can best be utilized in areas that require applications with short load cycle and high reliability, for example energy recapture sources such as forklifts, load cranes and electric vehicles, power quality improvement [8]. Among the promising applications of supercapacitors is in fuel cell vehicles and low emission hybrid vehicles [9, 10]. Supercapacitors with its unique qualities when used with batteries or fuel cells they can serve as temporary energy storage devices providing high power capability to store energy from braking [11, 12].

Due to its high power capability a bank of supercapacitors, can bridge the short time duration between a power failure and the start up of backup power generators. Even though energy density of supercapacitor is greater than that of conventional capacitors; it is considerably lower than batteries or fuel cells. Electrochemical performances of an electrode material strongly rely on factors like surface area, electrical conductivity, wetting of electrode and permeability of electrolyte solutions [13].

Passive components are required in all electronic applications to store electrical energy in volume and weigh as small as possible. The power needed by an application as well as the speed of storage process determines the type of energy storage device to be used.

Essentially, when it comes to applications the ones that need faster discharge rate go for capacitor while the slower ones go for batteries. From figure 1, it can be seen that a batteries are capable of attaining up to 150 Wh/kg of energy density, around 10 times what an electrochemical capacitor is capable of. In terms of power density batteries don’t have the capability of reaching the values of electrochemical capacitors. Batteries hardly reach 200 W/kg which is about 20 times less than the expected electrochemical capacitor performance. Batteries experience weaknesses like rapid decrease in performances due to fast charge discharge cycles or cold environmental temperature, they are expensive to maintain and have a limited life time [14].

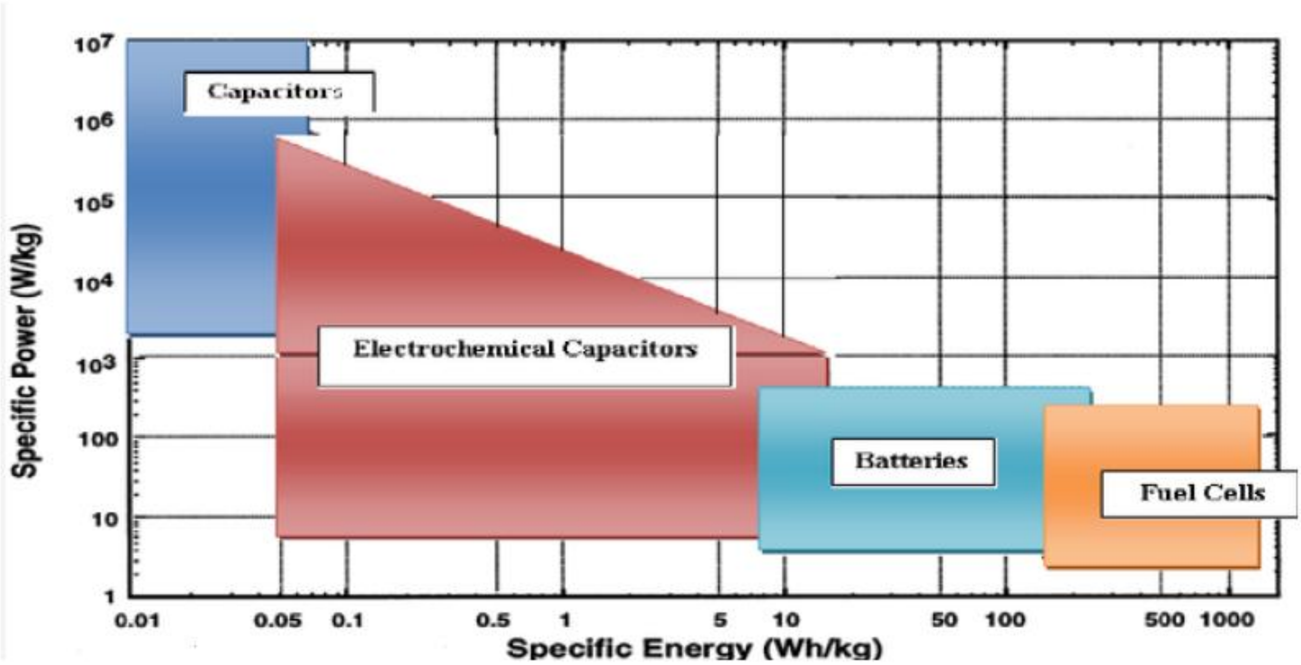

Figure 1. Specific Energy Vs Specific Power plot for various energy storage devices.

In general, considering energy storage mechanism, supercapacitors are grouped into three (3) different categories. The first being electrical double layer capacitor (EDLC), in this group capacitance is achieved due to pure electrostatic charge accumulated on the electrode electrolyte interface, this group strongly relies on electrode surface area that is available to electrolyte ions. Second is the pseudocapacitor, in this case a fast and reversible faradic process take place due to electro active species [15, 16]. The third group is hybrid which combines the properties of both EDLC and Pseudocapacitors. Selection of electrode material is of paramount importance in supercapacitors as it determines the electrical properties [17]. Double layer charge storage is a surface process therefore surface property of electrode material greatly influences capacitance of the cell.

Among the challenges faced by supercapacitors include low energy density, production cost, low voltage per cell and high self discharge. One of most intensive approaches of overcoming the obstacle of low energy density is by developing new electrode materials for supercapacitors.

Most popular today are carbon materials, metal oxides and conducting polymers are used as electrode materials. From the beginning of supercapacitor fabrication carbon materials have been used due to their high surface area. Metal oxides offer attractive options as electrode material due to high specific capacitance and low resistance, making it easier to construct high energy and power supercapacitors. In the case of conducting polymers reduction-oxidation process is used to store and release charge [18].

One of the frequently asked question is how can the electrochemical supercapacitor technology compare to the battery technology? At the moment, these supercapacitors cannot be used to substitute for the battery technology but could work as a supplement in terms of momentary and temporary power outage by providing instantaneous current required thereby reducing battery current. In large scale battery units, electrochemical supercapacitors can be installed in parallel to compensate for momentary and temporary interruptions. This would greatly repress the undue stress put on batteries from short term interruptions [19].

Currently, all the researches focused on supercapacitors are on how to improve the energy density while maintaining high power density, fast charge/discharge and cycling stability [20, 21]. The storage principle and characteristics of different electrode materials in supacapacitor have been reviewed and presented in this paper. This paper is organised as follows: Section 1 consists of the introduction of supercapacitors. Section 2 describes the different types of supercapacitors in terms of energy storage mechanism. Different types of electrode fabrication materials like Activated Carbons, Carbon Nano tubes, graphene, Ruthenium oxide, Nickel Oxide, Manganese Oxide and Polyaniline have been presented in section 3. Section 4 consists of nano composite materials obtained by combining carbon materials with either metal oxides or conducting polymers. Finally, in the section 5 and 6 consists of conclusion and future works respectively.

2. ENERGY STORAGE MECHANISM

The principle of operation of supercapacitor is based on energy storage and distribution of the ions coming from the electrolyte to surface area of the electrodes. Based on the energy storage mechanism supercapacitors are classified into three classes: Electrochemical double-layer capacitors, pseudocapacitors, and hybrid supercapacitors as shown in figure 2 below.

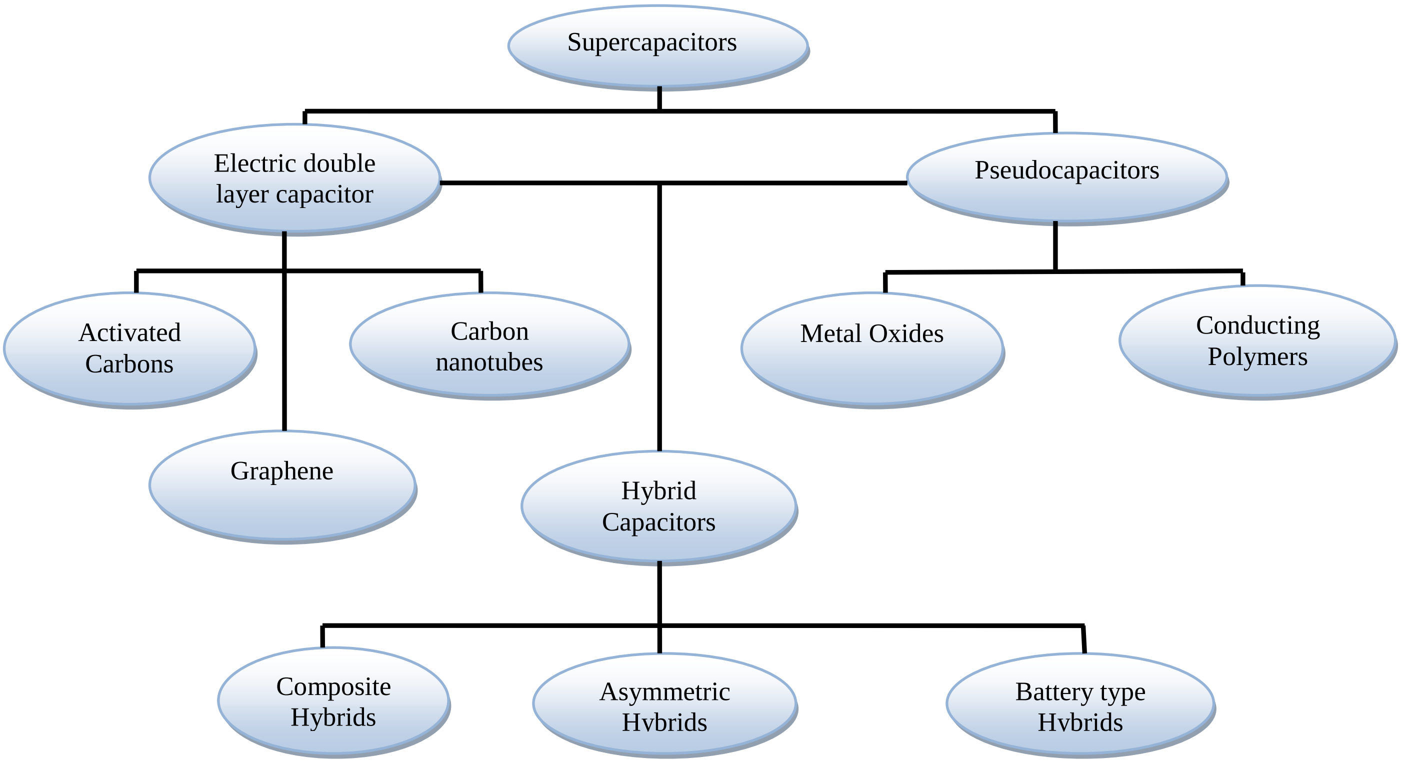

Figure 2. Taxonomy of supercapacitors.

2.1. Electrochemical double layer capacitors (EDLCs)

EDLCs are constructed using two carbon based materials as electrodes, an electrolyte and a separator. EDLCs can either store charge electrostatically or via non faradic process, which involves no transfer of charge between electrode and the electrolyte [22, 23]. The principle of energy storage used by EDLCs is the electrochemical double layer. When voltage is applied, there is an accumulation of charge on electrode surfaces, due to the difference in potential there is an attraction of opposite charges, these results to ions in electrolyte diffusing over the separator and onto pores of the opposite charged electrode. To avoid recombination of ions at electrodes a double layer of charge is formed. The double layer, combined with the increase in specific surface area and distances between electrodes decreased, allows EDLCs to attain higher energy density [24, 25].

Additionally, due to the EDLCs storage mechanism this allows for very fast energy uptake, delivery and better power performance. Due to non-faradic process, that is no chemical reaction. It eliminates swelling observed in active material which batteries demonstrate during charging and discharging. A few differences between EDLCs and batteries can be noticed as (i) EDLCs can withstand millions of cycles unlike batteries that can withstand few thousands at best. (ii) Charge storage mechanism does not involve solvent of the electrolyte; in Li-ion batteries it contributes to solid electrolyte inter phase when high-potential cathodes are used or graphite anodes [26, 27]. However, due to the electrostatic surface charging mechanism, EDLCs devices experience a limited energy density, which is why today’s EDLCs research is mainly focused on increasing energy performance and improving temperature range where batteries cannot operate. Performance of EDLC can be adjusted depending on the type of electrolyte used.

2.2. Pseudocapacitors

Compared to EDLCs, that store charge electro-statically. Pseudocapacitors store charge via faradic process which involves the transfer of charge between electrode and electrolyte [28]. When a potential is applied to a pseudocapacitor reduction and oxidation takes place on the electrode material, which involves the passage of charge across the double layer, resulting in faradic current passing through the supercapacitor cell. The faradic process involved in pseudocapacitors allows them to achieve greater specific capacitance and energy densities compared to EDLCs. Examples are metal oxides, conducting polymers. Which leads to interest in these materials but due the faradic nature, it involves reduction-oxidation reaction just like in the case of batteries; hence they also suffer lack of stability during cycling and low power density [29-31].

2.3. Hybrid

As we have seen EDLCs offer good cyclic stability, good power performance while in the case of pseudo capacitance it offers greater specific capacitance. In the case of hybrid system it offers a combination of both, that is by combining the energy source of battery-like electrode, with a power source of capacitor-like electrode in the same cell [32, 33]. With a correct electrode combination it is possible to increase the cell voltage, which in turn leads to an improvement in energy and power densities.

Several combinations have been tested in the past with both positive and negative electrodes in aqueous and inorganic electrolytes. Generally, the faradic electrode results in an increase of energy density at the cost of cyclic stability, which is the main drawback of hybrid devices compared to EDLCs, it is imperative to avoid turning a good supercapacitor into an ordinary battery [34]. Currently, researchers have focused on the three different types of hybrid supercapacitors, which can be distinguished by their electrode configurations: Composite, Asymmetric and Battery-type.

2.3.1 Composite

Composite electrodes combines carbon based materials with either metal oxides or conducting polymer in a single electrode, this means a single electrode will have both physical and chemical charge storage mechanisms. Carbon based materials offer capacitive double-layer of charge and high specific surface area which increases the contact between pseudocapacitive materials and electrolyte. Through Faradaic reaction, pseudocapacitive material increases capacitance in composite electrode [24]. Currently there are two different types of compsites: Binary and Ternary composites. Binary composites involves the use of two different electrode materials, while in the case of ternary it uses three different electrode materials to form single electrode.

2.3.2 Asymmetric

Asymmetric hybrids combine Non faradic and Faradic processes by coupling and EDLC with a Psuedocapacitor electrode. They are set up in a way that the carbon material is used as a negative electrode while either metal oxide or conducting polymer as positive electrode [24].

2.3.3 Battery Type

Battery type hybrid combines two different electrodes, like in the case of asymmetric hybrids but in this case they are made up by combining a supercapacitor electrode with battery electrode. This configuration was set up so as to utilize both properties of supercapacitors and batteries in one cell [24].

3. ELECTRODE MATERIALS

Among the parameters that rely on the type of electrode materials used in supercapacitors are capacitance and charge storage.

3.1. Carbon materials

Carbon materials in their various forms are the most used electrode materials in the fabrication of supercapacitors. Reasons are due to its (i) high surface area (ii) low cost (iii) availability (iv) established electrode production technologies. The storage mechanism used by carbon materials is electrochemical double layer formed at the interface between the electrode and electrolyte. Hence, the capacitance mainly relies on the surface area accessible to electrolyte ions. Important factors which influence electrochemical performance are specific surface area, pore shape and structure, pore size distribution, surface functionality and electrical conductivity [35-37]. Having a high specific surface area in the case of carbon materials, results in a high capability for charge accumulation at the interface of electrode and electrolyte. When improving specific capacitance for carbon materials, apart from pore size and high specific surface area, surface functionalization must be considered. Examples of carbon materials used as electrode materials are activated carbon, carbon aerogels, carbon nanotubes, graphene etc.

3.1.1 Activated carbon (AC)

The most widely used electrode material is AC and that is due to its large surface area, good electrical properties and moderate cost [38]. AC can be produced by either physical or chemical activation from various types of carbonaceous materials (e.g. wood, coal nutshell etc.). The physical activation involves the treatment of carbon precursors at a high temperature (700-1200 ^{o}C) in the presence of oxidizing gases like steam, CO_2 and air. In the case of chemical activation it is carried out at a lower temperature (400-700 ^{o}C) using activating agents such as sodium hydroxide, potassium hydroxide, zinc chloride and phosphoric acid [39]. Depending on the activation methods and the carbon precursors used, AC possess numerous physiochemical properties with well developed surface areas of up to 3000 m^2/g. Porous structure of AC obtained using activation processes had a broad pore size distribution that consists of micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) [40].

Numerous researchers have tested the relationship between specific capacitance and specific surface area (SSA) of AC and it seems there is a discrepancy between them. Having a high SSA of around 3000m^2/g, a relatively small capacitance was obtained. This shows not all pores are effective during charge accumulation. Hence, even though the SSA in EDLC is an important parameter when it comes to performance, some other aspects are also considered in carbon materials that influence electrochemical performance to great extent like pore size distribution [41, 42]. Additionally, excessive activation results in large pore volume, which in turn leads to drawbacks like low conductivity and material density, which will lead to a low energy density and loss of power capability.

Efforts have been made to see the effect of different electrolytes on the capacitance performance of AC. It was observed that the capacitance of AC is higher in aqueous electrolytes (ranging from 100 F/g to 300 F/g) as compared to organic electrolytes (<150 F/g) [10].

3.1.2 Carbon nanotubes (CNT)

With the discovery of CNT there has been a significant advancement in the science and engineering of carbon materials. The factor that determines the power density in a supercapacitor is the overall resistance of the components. A great deal of attention is been given to CNT as supercapacitor electrode material due to its unique pore structure, good mechanical and thermal stability and superior electrical properties [43-45]. Carbon nanotubes are produced via catalytic decomposition of some hydrocarbons and byy carefully manipulating different parameters, it becomes possible to generate nano structures in various conformations and also control their crystalline structure [39]. carbon nanotube unlike other carbon based electrodes, have mesopores that are interconnected, this allows for a continuous charge distribution that utilizes almost all of the accessible surface area. CNTs have a lower ESR than activated carbon because the electrolyte ions can diffuse into the mesoporous network [24].

CNT can be categorized as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), both are generally explored as supercapacitor electrode materials [46]. When it comes to high power electrode materials CNT are regarded due to their good electrical conductivity and readily accessible surface area. Additionally, they provide a good support for active materials due to their high mechanical resilience and open tubular network. Generally, CNT have small SSA (<500 m^2/g) which in turns leads to a low energy density as compared to AC. CNT can be chemically activated with potassium hydroxide, in order to improve its specific capacitance. The above method can substantially lead to an increase in the surface area of CNT (by a factor two to three times) and still maintain its nanotubular morphology [39].

3.1.3 Graphene

Graphene has enjoyed significant recent attention [47]. Graphene a one atom thick layer 2D structure has emerged as a unique carbon material that has potential for energy storage device applications because of its superb characteristics of high electrical conductivity, chemical stability, and large surface area [48-50]. Recently, it was proposed that graphene can be used as a material for supercapacitor applications, because when graphene is used as supercapacitor electrode material it doesn’t depend on the distribution of pores at solid state, as compared to other carbon materials such as activated carbon, carbon nanotube etc [51, 52].

Among all carbon materials used as electrode materials electrochemical double layer capacitors, newly developed graphene has higher specific surface area (SSA) around $2630m^2/g$ [53, 54]. If the entire SSA is fully utilized graphene is capable of achieving a capacitance of up to 550 F/g [48]. Another benefit of using graphene as electrode material is that both major surfaces of graphene sheet are exterior and are readily accessible by electrolyte. There are many different methods currently being researched for the production of different types of graphene such as chemical vapour deposition, micromechanical exfoliation, arch discharge method, unzipping of CNTs, epitaxial growth, electrochemical and chemical methods and intercalation methods in graphite [55-58].

In order to utilize the highest intrinsic surface capacitance and specific surface area of single-layer graphene measures were taken to prevent graphene sheets from restacking themselves during all phases of graphene preparation and subsequent electrode production procedures, these can be ensured by preparing curved graphene sheets and that will not restack face to face. Energy density of 85.6

Wh/kg at room temperature and 136 Wh/kg at 80 °C measured at a current density of 1 A/g were obtained. The energy densities obtained can be compared to that of the Ni metal hydride battery [48]. There are various methods of obtaining graphene from graphite. Chemically modified graphene (CMG) was obtained and it was tested on both aqueous and organic electrolyte and capacitances of 135 and 99 F/g was yielded respectively [2]. Graphene suffers agglomeration that is it tends to restack back to graphite. Graphene material used in supercapacitor electrodes yielded a high capacitance of 205 F/g at 1.0 V using an aqueous electrolyte, having an energy density of 28.5 Wh/kg, the results obtained are significantly higher than those of carbon based supercapacitors electrode. The experiment involved a single layered graphene oxide sheet reduced via gas-based hydrazine at room temperature. Graphene obtained from this method had a lesser degree of agglomeration compared to chemically modified graphene prepared using aqueous solution [6]. To find a more a suitable method for using graphene as supercapacitor electrode material, three different methods were researched. The first method was thermal exfoliation of graphitic oxide, in the second method graphene was obtained by heating nano-diamond at 1650 ^{o}C in a helium atmosphere, and in the last method camphor was decomposition over nickel nano-particles. Highest specific capacitance of 117F/g and an energy density of 31.9 Wh/kg were obtained from thermal exfoliation of graphitic oxide [59]. Among the applications of supercapacitors is in the area of high power applications, hence it’s important to produce supercapacitors with high specific capacitance and fast charging time at high current density. Such was possible by synthesizing grapheme from modified hummer’s method and tip sonication. Different charging current were experimented on 2.5 A/g, 5 A/g to 7.5 A/g. Even at a high current of 7.5 A/g the energy and power density obtained were 58.25 Wh/kg and 13.12 kW/kg respectively, thus making it possible to be used for electric vehicle applications [60]. Chemical exfoliation of graphene is done at a high temperature. A novel approach was researched which uses low temperature for exfoliation of graphene, due to the unique surface chemistry that was exhibited by low temperature exfoliated graphene showed good energy storage performance, capacitance obtained is higher compared to high temperature exfoliated graphene [61]. Several methods are being researched on how to reduce the issue of agglomeration and restacking facing graphene. Highly corrugated grapehene sheets were synthesized by thermal reduction of graphite oxide at a high temperature followed by rapid cooling using liquid nitrogen. A high specific capacitance of 349 F/g was obtained [62].

3.2. Metal oxide

Metal oxides present another alternative for materials used in electrodes fabrication in supercapacitor because they exhibit high specific capacitance and low resistance, making it simpler to construct supercapacitors with high energy and power. The commonly used metal oxides are nickel oxide (NiO), ruthenium dioxide (RuO2), manganese oxide (MnO2), iridium oxide (IrO2). The lower cost of production and use of a milder electrolyte make them a feasible alternative [63-65].

3.2.1 Ruthenium oxide (RuO_2)

RuO_2 in both amorphous and crystalline forms is essentially important in both theoretical as well as practical purposes, due to its unique combination of characteristics, like catalytic activities, metallic conductivity, electrochemical reduction-oxidation properties, high chemical and thermal stability and field emitting behaviour. Having these properties RuO_2 finds way in various applications such as, electronic applications, thick or thin resistors, ferroelectric films and integrated circuit development. The most recent application of RuO_2 is as an electrode material in supercapacitors [66].

Among the many metal oxide that are used as electrode materials e.g RuOx, NiOx and IrOx. RuO_2 has had the most success given its advantages of long cycle life, wide potential window of high specific capacitance, highly reversible reduction-oxidation reaction, and metallic type conductivity. For supercapacitor application RuO_2 was electrochemically produced using electrodeposition method. The resulting electrodes were stable for large number of cycles yielding a specific capacitance of 498 F/g at a scan rate of 5mV/s [67].

3.2.2 Nickel oxide

Nickel oxide is among the promising electrode material for supercapacitor because of its environmental friendliness, easy synthesis and low cost. Among the benefits of electrochemical strategy include reliability, simplicity, accuracy, low cost and versatility. Using electrochemical strategy nickel hydroxide was transformed into nickel oxide.. The resulting method produced an ultra high specific capacitance of 1478 F/g in 1 M KOH aqueous solution electrolyte [68].

3.3.3 Manganese oxide

Recently, manganese oxide has attracted a lot of research interest because of its unique physical and chemical properties with a wide range of applications in ion exchange, catalysis, biosensor, energy storage and molecular adsorption. A special interest is given to manganese dioxide MnO_2 as an electrode material for supercapacitors due to its low cost, excellent capacitive performance in aqueous electrolytes and environmental benignity [69-72].

3.3 Conducting polymers

Different conducting polymers have been widely researched as supercapacitor electrode material due to easy production and low cost [73]. Conducting polymers have a relatively high conductivity and capacitance and equivalent series resistance when compared with carbon based electrode materials. There are different electrode configurations that can be used for conducting polymers, the n/p type configuration, having one negatively charged (n-doped) and one positively charged (p-doped) electrodes, offers a high energy and densities, although due to lack of n-doped conducting polymer electrode materials have limited psuedocapacitors from reaching their potential [24].

In conducting polymers reduction-oxidation process is used to store and release charge. If oxidation occurs also known as doping, ions are been transferred to the polymer back bone. If reduction occurs also known as de-doping, in that case ions are released back into the solution [18]. Due to the reduction-oxidation in conducting polymers these causes a mechanical stress which in turn limits the stability through many charge-discharge cycles [74].

3.3.1 Polyaniline (PANI)

Considering the different types of conducting polymer, PANI is considered as the most promising supercapacitor electrode material because of its high conductivity, easy synthesis, excellent capacity for energy storage and low cost [75]. However, due to repetitive cycles (charge/discharge process) swelling and shrinkage, PANI is susceptible to rapid degradation in performance. To avoid this limitation, combining PANI with carbon materials has proved to reinforce the stability of PANI as well as maximize the capacitance value [76, 77].

4. NANO COMPOSITES BASED ELECTRODE MATERIALS

Composite electrodes integrate carbon based material with either metal oxide or conducting polymer materials, which in turn offers both physical and chemical charge storage mechanism together in a single electrode [78].

4.1 Carbon-Carbon composites

In carbon materials a high capacitance is obtained based on the effective specific surface area (SSA) that is accessible to the electrolyte ions. By enhancing the effective SSA in carbon materials this will lead to a higher energy and power density in supercapacitor. Graphene faces dispersion problem, to come up with a solution non-covalent functionalized graphene was prepared [79]. One of the disadvantages of using chemical reduction of graphene oxide is that it tends to aggregate and restack through van der Waals interactions during the reduction process, hence making surface area less accessible to electrolyte. In order to avoid the restacking is to use single walled carbon nanotubes (SWCNT) as spacers. By inserting CNTs leads to creation of intra-pores for the electrolyte. A capacitance of 261 F/g and energy density of 123Wh/kg were obtained for the graphene supercapacitors at potential 3.7 V using ionic liquid electrolyte [80].

4.2 Carbon-Metal oxides composites

A research was carried out were a comparison was made between CNT, pure MnO_2 and a composite of MnO_2/CNT. The composite was prepared using simple hydrothermal treatment. The MnO_2/CNT nanocomposite electrode exhibited a higher specific capacitance and rate capability compared to CNT and pure MnO_2 electrodes. High specific capacitance obtained in the composite can be attributed to high porous structure and high specific surface area of MnO_2 [69]. An assemtric supercapacitor was was assembled using graphene and MnO_2. The prepared composite of MnO_2-coated/graphene was used cathode while pure graphene was used as anode. The process of electro-activation was used on graphene electrode, and a capacitance of 245 F/g at a charging current of 1 mA was obtained. When MnO_2 was deposited the capacitance increased to 328 F/g at same charging current, an energy density of 11.4 Wh/kg and a power density of 25.8 kW/kg was obtained [81].

Among the benefits of CNT is their ability to have their surface functionalized by metal oxide, polymers or oxidizing to overcome the presence of some impurities. A research was carried out using CNT/MnO_2, certain observations were made, the first was vertically aligned CNTs had a higher capacitance as compared to random ones, this shows that morphology affects capacitance significantly. Secondly, water plasma treatment was used on the surface and it was observed that it gave higher results due to clearer and larger active surface of nanotubes. Lastly, with the addition of MnO_2 via electrochemical deposition technique yielded highest specific capacitance of 475 F/g was obtained [82]. Another research was carried out using a composite of molybdenum sulfide (MoS_2) with reduced graphene oxide (rGO). The composite was obtained using a simple process of one pot hydrothermal. The resultant composite yielded a specific capacitance of 253 F/g at a current density of 1 A/g with a good cycling stability [83].

Activated carbon having good properties such as large surface area, good electrical properties and moderate cost was used in this experiment. Three different metal oxides Nickle (Ni), Cobalt (Co) and Manganese (Mn) where used to see which combination will produce highest specific capacitance. In this work AC was used as anode and a combination of two of the metal oxides as cathode. The degree of inversion was varied by a factor 0.2 to see the effect it will have on performance. 12 different samples were prepared and the highest specific capacitance was 78 Fg^{-1} from ($Mn_{0.6}Co_{0.4}$) and this was due to large pores that were observed from the SEM images which allowed easy diffusion of electrolyte and the minimum value was 5Fg^{-1} for ($Mn_{0.8}Co_{0.2}$) because the sample showed non uniform crystalline image with hairy surface which made it difficult for electrolyte to pass [84].

4.3 Carbon-Conducting polymer composites

A high SSA (1976 m^2/g), narrow pore size distribution (<3nm) and short diffusion length were obtained when activated carbon was synthesized from carbonization of PANI and then subsequently activated with KOH. The resulting composite exhibited excellent performances. A high specific capacitance of 455 F/g in 6M KOH was obtained. Graphene was further added to PANI and after 2000 cycles there was an increase in specific capacitance retention ration from 88.7% to 94.6% [85]. Conventional polymer like Poly (3-methylthiophene) pMeT was chosen because it can be easily produced from low cost commercial monomer. Although, the pMeT application in the n/p type supercapacitors cannot be envisioned, mainly because a high polymer content in the composite, such as 80%, is not viable for the negative electrode. A hybrid configuration of pMeT and activated carbon as positive and negative electrodes respectively yielded a supercapacitor with better performance and cost as compared to double-layer carbon supercapacitors [86]. A research was carried out involving a composite of GNS/PANI. The composite was synthesized using in situ polymerization, due to the presence of GNS in the composite provided a high conductivity as well as relatively large area where the PANI particles were deposited. A high specific capacitance of 1046 F/g at 1mV/s was obtained with energy density of 39Wh/kg and power density of 70kW/kg [87]. Three different composites where synthesized using in situ polymerization, involving graphene nansheet/carbon nanotube/polyaniline (GNS/CNT/PANI). The highest specific capacitance was recorded for GNS/PANI with 1046 F/g, then GNS/CNT/PANI with 1035 F/g and CNT/PANI with 780 F/g. After 1000 cycles the capacitance decreases only 6% for GNS/CNT/PANI, 52% GNS/PANI and 67% for CNT/PANI [88].

5. RECOMMENDATIONS AND OBSERVATIONS

- As it can be seen from the reported paper, supercapacitors still have a long way to go in order for them to replace batteries.
- Current supercapacitors in the market can be used for applications that require a combination of high power delivery for a short time, high cycling stability, short charging time and long shelf life.
- Discovery of graphene opened a lot of doors in the research of supercapacitors.
- The way forward in the fabrication of supercapacitors should pay more effort in the area of improving hybrid supercapacitors.
- Find a more efficient method of reducing equivalent series resistance and optimization of electrolytes.
- Work on better methods that will curb the issue of self discharge in supercapacitors.
- Research on simpler and less cost effective methods for the synthesis of graphene.

6. CONCLUSIONS

With the invention of supercapacitors an important alternative energy storage device emerged offering high electrochemical properties, high power density and good stability. As it was reported supercapacitors have the quality that makes them suited for a number of applications including being able to compliment the strengths of batteries, used in electric vehicles hybrid power systems and emergency power supplies. As it can be seen from the review presented here, there is still room for improvement in the design and fabrication of supercapacitors for them to able to be used in more applications needing high energy density. Researchers are still focusing on the different electrode materials like carbon materials, metal oxide and conducting polymers. With carbon materials, a high specific surface area and rational pore distribution were achieved, even though their capacitances and energy density are still low. Conducting polymers show high specific capacitance, but the major challenges faced are their swelling and shrinking when charging and discharging, leading to short lifetime. In the case of metal oxides, they also posses high specific surface area and favor diffusion of ions onto the bulk of material. With the discovery of graphene as electrode material for supercapacitor, it has opened a lot of research opportunities being carried out. Future work efforts should focus more on the effect graphene might have on other electrode materials, which is by combining it with either metal oxides or conducting polymers to form composites. In doing so it can minimize particle size, induce porosity, enhance specific surface area, prevent particles from agglomerating, expanding active sites, improving cycling stability and providing extra pseudocapacitance. Now researchers are focused on ternary composite which has been reported.

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References

1. B.E. Conway *Electrochemical Supercapacitors Scientific Fundamentals and Technological Applications*, Plenum Press, New York (1999).
2. A.S. Arico, P. Bruce, B. Scrosati, J.M. Tarascon and W.V. Schalkwijk, *Nature Mater.*, 4 (2005) 366.
3. M.D. Stoller, S. Park, Y. Zhu, J. An and R.S. Rouf, *Nano lett.*, 8 (2008) 3498.
4. H.P. Wu, D.W. He, Y.S. Wang, M. Fu, Z.L. Liu, J.G. Wang and H.T. Wang, *IEEE*, (2010) 465.
5. M.H. Ervina, B.S. Miller, B. Hanrahan, B. Mailly and T. Palacios, *Electrochim. Acta*, 65 (2012) 37.
6. M. A. Pope, S. Korkut, C. Punckt and I.A Aksay, *J. Electrochem. Soc.*, 160 (2013) A1653.
7. Y. Wang, Z. Shi, Y. Huang, Y. Ma, C. Wang, M. Chen and Y. Chen, *J. Phys. Chem. C*, 113 (2009) 13103.
8. J.R. Miller and P. Simon, *Mater. Sci.*, 321 (2008) 651.
9. N.L. Wu, Mater. *Chem. Phys.*, 75 (2002) 6.
10. Y.M. Cai, Z.Y. Qin and L. Chen, *Progress Nat. Sci: Mater. Int.*, 21 (2011) 460.
11. L.L. Zhang and X. S. Zhao, *Chem. Soc. Rev.*, 38 (2009) 2520.
12. A.K. Mittal and M.J. Kumar, *Nanosci. and Nanotech.*, 13 (2011) 263.
13. B. Rajagopalan and J.S. Chung, *Nanoscale Research Lett.*, 9 (2014) 1.
14. A. Schneuwly and R. Gallay, *PCIM*, (2000) 1.
15. L.L. Zhang, R. Zhou and X. S. Zhao, *J. Mater. Chem.*, 20 (2010) 5983.
16. Q. Du, M. Zheng, L. Zhang, Y. Wang, J. Chen, L. Xue, W.Dai, G. Ji and J. Cao, *Electrochim. Acta*, 55 (2010) 3897.
17. Y. Li, M.V. Zijll, S. Chiang and N. Pan, *J. Power Sources*, 196 (2011) 6003.
18. P. Sharma and T.S. Bhatti, *Energy Conversion and Management*, 51 (2010) 2901.
19. S.C. Smith and P.K. Sen, *IEEE*, (2008).
20. G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Lett.*, 11 (2011) 4438.
21. Y. Zhu, S. Murali, M.D. Stoller, K. J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle and R.M. Wallace, *Science*, 332 (2011) 1537.
22. M.V. Kiamahalleh, S.H.S. Zein, G. Najafpour, S.A Sata and S. Buniran, *Nano*, 7 (2012) 1.
23. M. Jayalakshmi and K. Balasubramanian, *Int. J. Electrochem. Sci.*, 3 (2008) 1196.
24. M.S. Halper and J. C.Ellenbogen, *Mitre Nanosystems Group*, (2006).
25. H. Choi and H. Yoon, *Nanomaterials*, 5 (2015) 906.
26. P. Simon and Y. Gogotsi, *Nature Mater.*, 7 (2008) 845.
27. M.S. Ata, McMaster University, (2012).
28. S. Mohapatra, A. Acharya and G. S. Roy, *Lat. Am. J. Phys. Educ.*, 6 (2012) 380.
29. S.M. Chen, R. Ramachandran, V. Mani and R. Saraswathi, *Int. J. Electrochem. Sci.*, 9 (2014) 4072.
30. M. Beidaghi, Florida International univeristy, (2012).
31. T. Chen and L. Dai, *Materials Today*, 16 (2013) 272.
32. A. Burke, Z. Liu and H. Zhao, Institute of transportation studies, (2014).
33. A. Burke, *Electochim. Acta*, 53 (2007) 1083.

34. P. Simon and K. Naoi, *Electrochem. Soc.*, (2008) 34.
35. H. Yang, S. Kannappan, A.S. Pandian, J.H Jang, Y.S. Lee and W. Lu , p. 1.
36. Z. Bo, Z. Wen, H. Kim, G. Lu, K. Yu and J. Chen, *Carbon*, 50 (2012) 4379.
37. A.P. Singh, P. B. Karandikar and N.K. Tiwari, *IEEE*, (2015) 669.
38. N. Syarif, I. Tribidasari A and W. Wibowo, *Int. Transaction J. Eng., Management, & Applied Sci. & Tech.*, 3 (2012) 21.
39. A.G. Pandolfo and A.F. Hollenkamp, *J. Power Sources*, 157 (2006) 11.
40. P. Sabatier, l'institut Carnot Cirimat, (2012).
41. K. Lota, A. Sierczynska and I. Acznik, *Chemik*, 67 (2013) 1138.
42. F. Lufrano and P. Staiti, *Int. J. Electrochem. Sci.*, 5 (2010) 903.
43. Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya and L.C. Qin, *Phys. Chem. Chem. Phys*, 13 (2011) 17615.
44. P. Tamilarasan, A.K. Mishra and S. Ramaprabhu, *IEEE*, (2011).
45. C. Du and N. Pan, *Nanotech. Law & Business*, 4 (2007)569.
46. J. Li, X. Cheng, A. Shashurin and M. Keidar, *Sci. Res.*, 1 (2012) 1.
47. D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu and J.M. Tour, *Acsnano*, 4 (2010) 4806.
48. C. Liu, Z. Yu, D. Neff, A. Zhamu and B.Z Jang, *Nano lett.*, 10 (2010) 4863.
49. H. M. Cheng, *IEEE*, (2010) 49.
50. H. Wang, Q. Hao and X. Yang, *Electrochem. Commun.*, 11 (2009) 1158.
51. P. Karthika, N. Rajalakshmi and K.S. Dhathathreyan, *Soft Nanosci. Lett.*, 2 (2012) 59.
52. T.Y. Kim, G. Jung, S. Yoo, K.S. Suh and R.S. Rouff, *Acsnano*, 7 (2013) 6899.
53. T.Y. Kim, H.W. Lee,M. Stoller, D. R. Dreyer, C.W. Bielawski, R.S. Ruoff and K.S. Suh, *Acsnano* 5 (2011) 436.
54. K. Moon, Z. Li, Y. Yao, Z. Lin, Q. Liang, J. Agar, M. Song, M. Liu and C.P. Wong, *IEEE*, (2010) 1323.
55. R. Ramachandran, V. Mani, S.M. Chen, R. Saraswathi and B.S. Lou, *Int. J. Electrochem. Sci.*, 8 (2013) 11680.
56. R. Ramachandran, M. Saranya, V. Velmurugan,B.P.C. Raghupathy, S.K. Jeong and A.N. Grace, *Applied Energy*, (2015) 1.
57. S.M. Selverston, San Jos´e State University, (2011).
58. T. Kuilla, S. Bhadra, D. Yao, N.H. Kim, S. Bose and J.H. Lee, *Progress Polymer Sci.*, 35 (2010) 1350.
59. S. Kannappan, K. Kaliyappa, R.K. Maniand, A.S. Pandian, H. Yange, Y.S. Lee, J.H Jang and W. Lu , p. 1.
60. S.R.C Vivekchand, C.S. Rout, K.S. Subrahmanyam, A. Govindaraj and C.N.R. Rao, *J. Chem. Sci.*, 120 (2008) 9.
61. W. Lv, D.M. Tang, Y.B. He, C.H. You, Z.Q. Shi, X.C. Chen, C.M. Chen, P.X. Hou, C. Liu and Q.H. Yang, *Acsnano*, 3 (2009) 3730.
62. J. Yan, J. Liu, Z. Fan, T. Wei and L. Zhang, *Carbon*, 50 (2012) 2179.
63. A.O. Mary, University of Nottingham, (2012).
64. A. M. Jiwo, University of Nottingham, (2012).
65. A.M. Namisnyk, University of Technology, Sydney, (2003).
66. C. Zhao and W. Zheng, *Frontiers Energy Research*, (2015) 1.
67. T. P. Gujar, W.Y. Kim, I. Puspitasari, K.D. Jung and O.S. Joo, *Int. J. Electrochem. Sci.*, 2 (2007) 666.
68. H.Y. Wu and H.W. Wang, *Int. J. Electrochem. Sci.*, 7 (2012) 4405.
69. H. Xia, Y. Wang, J.i Lin and L. Lu, *Nanoscale Res. Lett.*, (2012) 1.
70. I. Acznik, K. Lota, A. Sierczynska and G. Lota, *Int. J. Electrochem. Sci.*, 9 (2014) 2518.
71. S. Chen, J. Zhu, X. Wu, Q. Han and X. Wang, *Acsnano*, 4 (2010) 2822.

72. C. Liu, D. Gui and J. Liu, *IEEE*, (2014) 177.
73. D.W. Wang, F. Li, J. Zhao, W. Ren, Z.G. Chen, J. Tan, Z.S. Wu, I. Gentle, G.Q. Lu and H.M. Cheng, *Acsnano*, 3 (2009) 1745.
74. M. Mastragostino, C. Arbizzani and F. Soavi, *Solid State Ionics*, 148 (2002) 493.
75. Q. Cheng, J. Tang, N. Shinya and L.C Qin, *J. Power Sources*, 241 (2013) 423.
76. J. Li, H. Xie, Y. Li, J. Liu and Z. Li, *J. Power Sources*, 196 (2011) 10775.
77. X. Feng, R. Li, Z. Yan, X. Liu, R. Chen, Y. Ma, X. Li, Q. Fan and W. Huang, *IEEE*, 11 (2012) 1080.
78. M. Vangari, T. Pryor and L. Jiang, *J. Energy Eng*., 139 (2013) 72.
79. Y. Chen, X. Zhang, H. Zhang, X. Sun, D. Zhang and Y.Ma, *Rsc Adv*., 2 (2012) 7747.
80. 80 F. Zhang, J. Tang, N. Shinya and L.C. Qin, *Chem. Phys. Lett.*, 584 (2013) 124.
81. Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya and L-C. Qin, *Carbon*, 49 (2011) 2917.
82. A.T. Mutlu , p. 1.
83. M. Mandal, D. Ghosh, S.S. Kalra and C.K. Das, *Int. J. Latest Research in Sci. and Tech*., 3 (2014) 65.
84. Z.S. Iro, C. Subramani, H.Y. Hafeez*, Indian J. Sci. and Tech*. 9 (2016) 1.
85. J. Yan, T. Wei, W. Qiao, Z. Fan, L. Zhang, T. Li and Q. Zhao, *Electrochem. Commun*., 12 (2010) 1279.
86. M. Mastragostino, C. Arbizani and F. Soavi, *J. Power Sources*, (2001) 812.
87. J. Yan, T. Wei, B. Shao, Z. Fan, W. Qian, M. Zhang and F. Wei, *Carbon*, 48 (2010) 487.
88. J. Yan, T. Wei, Z. Fan, W. Qian, M. Zhang X. Shen and F. Wei, *J. Power Sources*, 195 (2010) 3045.