Supercapacitors as Energy Storing Device: A Review

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Abstract: Supercapacitors are the efficient energy storing devices with advanced properties like high power density, better cycle life, and high durability. But due to less energy density they cannot be used in commercial sector. In order to remove this barrier graphene based electrodes are used in supercapacitors which results in high stability but lacking in high value of specific capacitance. In series of research, it has been suggested that graphene along with conducting polymers and metal oxides can be used as electrode material for supercapacitors in order to provide both high value of specific capacitance and stability. So, this review paper summarizes the recent studies of incorporation of graphene with conducting polymers and metal oxides based supercapacitors as efficient energy storing device.

Keywords: Supercapacitor, graphene, metal oxide, conducting polymer, energy density

Introduction

In today's era, the demand for smart energy storage devices is on the peak. At present, lithium-ion batteries are used to store energy in electronic applications based on electrochemical reactions within them to store the charge. That means for releasing the energy from lithium-ion batteries, firstly lithium will shuffle into the electrolyte and then shuffle back for releasing it which is very time consuming. i.e. taking so much time for charging/discharging. These batteries also degrade with short period of time due to the presence of chemicals in it and are not environmental friendly too. On the other hand capacitors stores electricity directly, charged instantly and also delivers the energy at very fast rate due electrostatic mechanism of charge storage. They can also provide more power than batteries, much more durable than li-ion batteries with less degradation. But conventional capacitors are lacking in terms of much less energy density than batteries. Now supercapacitors are the upgraded version of capacitors with advance design, moderate energy density, high power density, storing much more energy, long cycle life, quick charge and discharge, can withstand in extreme temperatures, environment friendly [1,2]. Thus supercapacitors are bridging a gap between conventional batteries and conventional capacitors. Supercapacitors will be able to replace the batteries if their fabrication would be accurate [3,4].

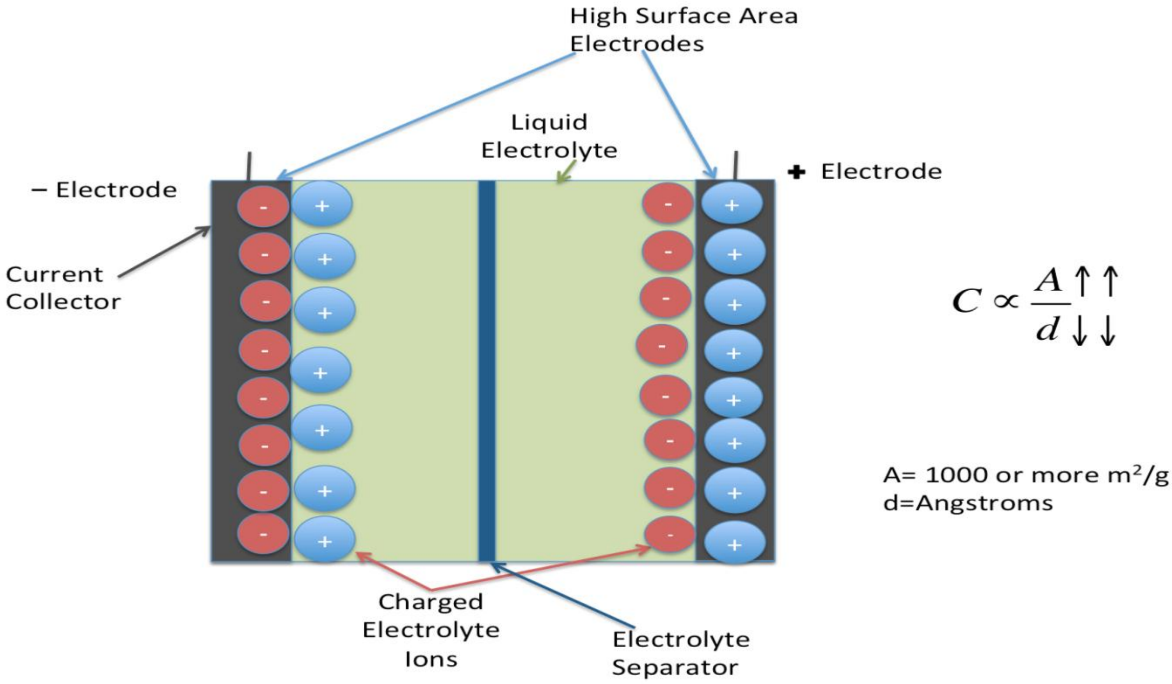

Fig. 1: Schematic Diagram of Supercapacitors

Background of Supercapacitors

Based on current scenario in the field of research, although supercapacitors are not having that much energy density than lithium-ion batteries but they do have much more power densities in comparison of batteries [4].

Indeed, because energy is stored in the supercapacitors at the electrochemical interface between electrode and the electrolyte by simple charge separation mechanism allowing them to store and deliver energy at much faster rates than batteries [4]. From previous research it has been observed that supercapacitors are lacking in operating voltage i.e. they cannot stand with high voltage condition. Also self-discharging in supercapacitor is a cause of their declined performance. With agreement for the above mentioned properties of supercapacitors, it becomes a great interest of research among scientists for the potential utilization in hybrid and electric automobiles for energy recovery in regenerative braking, backup system, wearable and portable devices, and such a like [5].

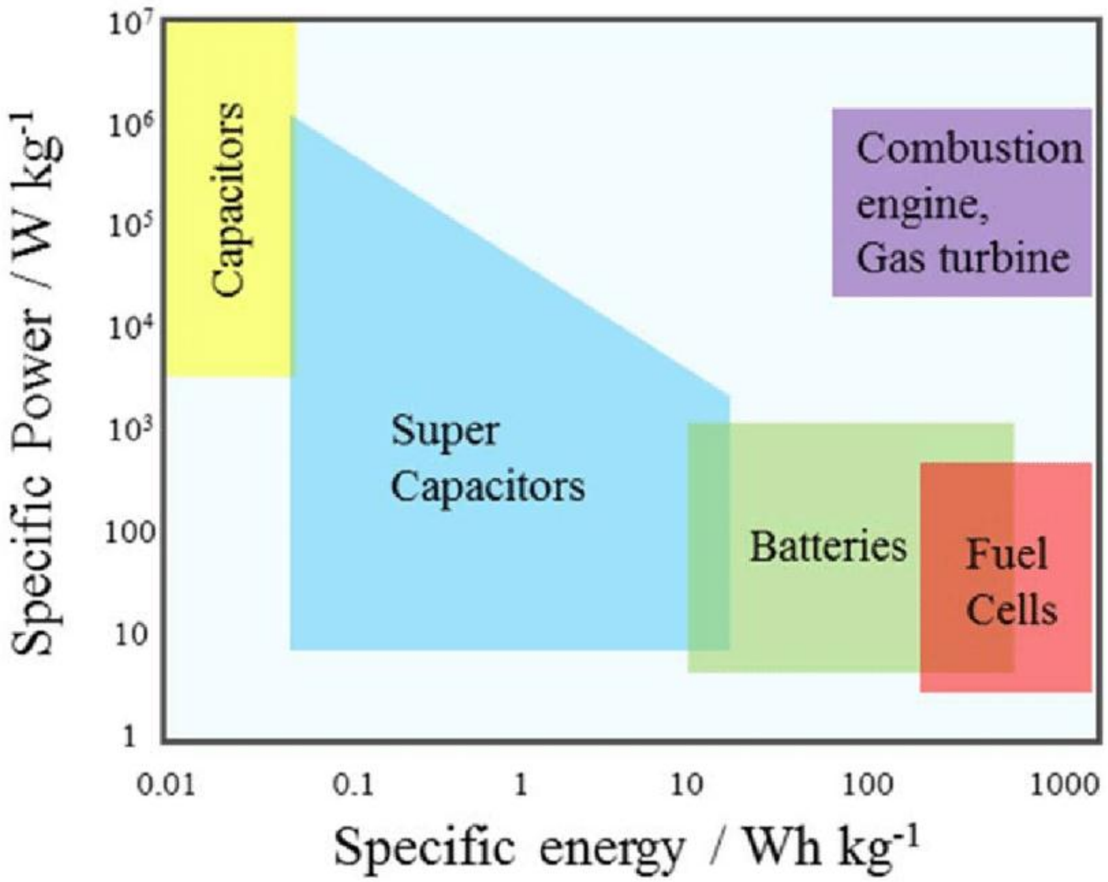

Fig. 2: Simplified Ragone plot for the various electrochemical energy conversion systems.

Classification of Supercapacitor

Depending on energy storage mechanism and active material used, supercapacitors are classified into three categories: Electric Double Layer Capacitors (EDLCs) and Pseudo-capacitors (PCs) and hybrid supercapacitors [6].

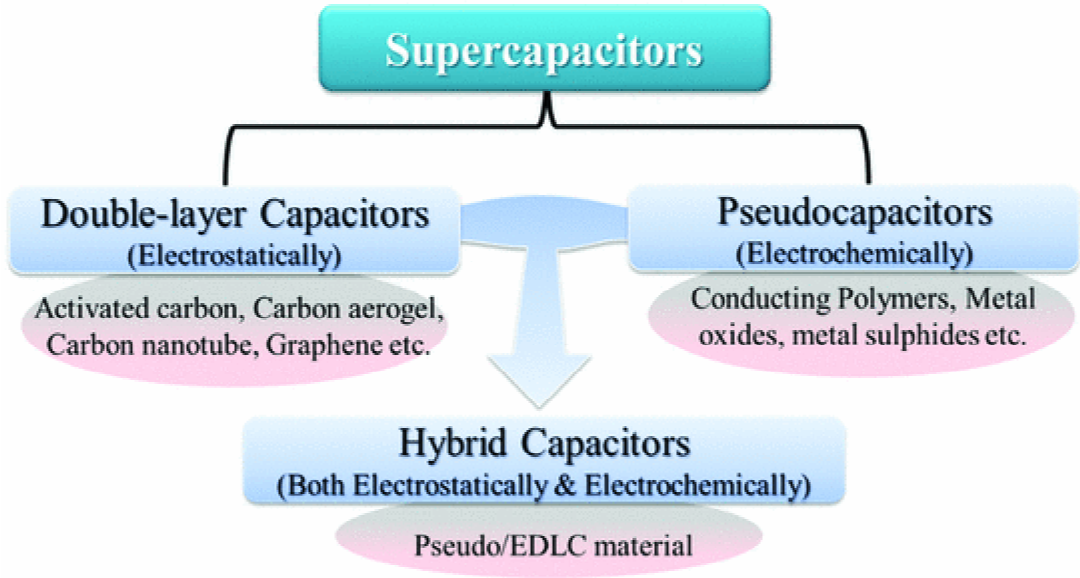

Fig.3: Taxonomy of Supercapacitor

In EDLCs, electrostatic charge accumulation is done at the interface of electrode and electrolyte and the material of electrode is usually fabricated by using electrically conductive materials (e.g. carbon based active materials). Whereas in pseudocapacitors, capacitance achieved by transferring the faradic charges between electrode and electrolyte [5]. On comparing these two, it was observed that EDLCs owning high power density and long cycle life but due to small surface area, fails to deliver high energy density and high specific capacitance. On the other hand, PCs possesses higher value of energy density and specific capacitance than EDLCs but having much less power density and poor cycle life. So far utilizing the potential of supercapacitors, simultaneous enhancement of energy density without loss in its power density and cycle life is the major challenge [6]. Third type supercapacitor i.e. hybrid supercapacitor is the combination of these two above mentioned supercapacitors combining the properties of both in order to achieve high value of specific capacitance along with high energy and power densities. It can be possible to design a hybrid supercapacitor by choosing right material for the fabrication of the electrodes simultaneously with incorporation of the electrolyte used in the device. Several combinations were already tested and several combinations are on the list. Presently researchers are focused on three types of hybrid supercapacitors: composite, asymmetric and battery type [6].

Graphene Based Electrode for Supercapacitor

Graphene, a supernatural material discovered in 2003 emerges as a promising material for novel potential application for electrochemical energy storage devices. Graphene is a single layer of graphite, a carbon based material found in pencil leads. It is a two-dimensional material consisting sp^2 bonds between carbon atoms and having honey-comb like structure. Owning unique properties like high electrical and thermal conductivity, 200 times stronger than steel, million times thinner than piece of paper, high transparency, excellent mechanical flexibility, large theoretical value of specific surface area (~2600 $m^2\ g^{-1}$), it becomes the wonder material for the scientists for utilizing its properties in supercapacitors application in order to minimize the drawbacks faced by them [1-5].

With the chain of simultaneous experiments and research over using graphene based electrodes for supercapacitors, one of the review paper summarized the various forms of graphene-based material used in supercapacitors on the bases of structural complexity such as: zero-dimensional (0D) which includes free-standing dots and particles made of graphene, one-dimensional (1D) which consists of fiber/yarn type structures, two-dimensional (2D) includes nanocomposites films and papers based on graphene, three-dimensional (3D) like foams and hydrogels based on graphene. To design a supercapacitor using free standing dots of graphene, polymer binders and conductive additives are used to connect electrode with current collectors but these binders and additives normally doesn't contribute much to the overall capacitance and results in the degradation of both gravimetric and volumetric capacitance of a supercapacitor. Further, 1D and 2D type graphene-based material came into play providing a promising electrical conductivity and high mechanical flexibility but due to their aggregation and surface modification results in the moderate stability rate and poor power density. In contrast to these 3D porous graphene based electrodes can provide more ease to the electrolyte ions to diffuse within the surface which cannot be achieved due to aggregation of 2D and 1D graphene based materials therefore provide improved stability and more power density in accordance [4]. Self-charging flexible supercapacitor were designed using electrode of graphene-Ag-3D graphene foam, which was highly conductive with areal capacitance (38 $mF\ cm^{-2}$) which was three times higher than other reported flexible supercapacitors. Also, it had 65% capacitance retention after 2500 charge/discharge cycle. Paper also reported high value of power density and moderate value of energy density. Overall work provided a great idea for using flexible supercapacitors in wearable electronics [7]. Jang et al. synthesized porous graphene sphere having controlled pH by environmentally

friendly method. Synthesized material at pH 2 showed porous structure with 150 m^2/g specific surface area while material at pH 10 showed porous structure with 216 m^2/g specific surface area with higher specific capacitance of 182 F/g than graphene sphere fabricated at pH 2 [8].
Wide researches were conducted on supercapacitors based on graphene electrodes but due to some lacking, research took further direction.

Graphene/Conducting Polymer Based Electrode for Supercapacitor

Although graphene is the preferred electrode material for supercapacitor but several modifications in its properties are entertained time to time in order to enhance the device performance such as doping of nitrogen onto graphene, graphene oxide, reduced graphene oxide, etc. In general for ideal supercapacitor device, preferred electrode should have high value of specific capacitance together with high stability. Considering this aspect, it was observed that pure/modified graphene based electrodes provides good stability but fails in providing high value of specific capacitance. In addition to this it was observed that graphene and conductive polymer/metal oxide composites can be used to provide high value of specific capacitance along with stability provided by graphene. Commonly used conductive polymers are: Polyaniline (PANI), Polypyrrole (PPy) and Poly (3, 4-ethylenedioxythiophene) (PEDOT) [6, 9].

One of the paper summarized the use of different polymers with graphene in order to enhance the properties of the electrode material in supercapacitors, came with the conclusion that PANI has been used most prominently than other conducting polymers because it possesses high theoretical capacitance value (750 F/g), excellent process ability, easy to synthesize and also it is cost effective [6]. Guevara et al. reported fabrication of reduced graphene/polyaniline composite based supercapacitors using infrared laser having specific capacitance value 442 F g^{-1} and 84% of capacitance retention after 2000 cycles [10]. Adam et al. reported synthesis of PANI/reduced graphene oxide composite electrodes for supercapacitors assisted by hydrothermal treatment having specific surface area of 228 m^2g^{-1}, with specific capacitance from 420 to 239 F g^{-1} at current densities of 0.2 to 20 A g^{-1}. Also having 80% capacitance retention after 6000 cycles [11]. Ji et al. recorded the highest specific capacitance value (1217.2 F/g at 10 mV/s and 865.6 F/g at 1 A/g) till now using graphene/polyaniline (PANI) composites in the presence of graphene oxide with the assistance of phytic acid. High value of capacitance and long cycle life is due to the synergistic effect of graphene and PANI respectively [12].

PPy and PEDOT composites are also used with graphene but due to low specific capacitance value, their use is limited till date.

Graphene/Conducting Polymer/Metal Oxide Based Electrode for Supercapacitor

Although the binary composites of some metal oxides with conducting polymers and graphene has also been studied and yields good results. But from last few years this research has been shifted towards ternary composites for electrode material. Considering ternary metal oxides like $ZnCo_2O_4$, $CoMoO_4$, $MnCo_2O_4$, and $NiCo_2O_4$ are the rising materials from recent studies with enormous properties like high electrochemical activity and electrical conductivity together with high abundance, low cost and environment friendliness [13-16]. From past few years, researchers are focused on making ternary composites using metal oxide/conducting polymer with graphene in order to improve overall performance of supercapacitor device.

Combination of $NiCo_2O_4$ with PANI results in large electrode surface area which increases the cycling stability and provides better accommodation of mechanical stress as well as decreases the length of electron transport [16]. On the other hand, composite of $NiCo_2O_4$ with carbon based material gives much higher values of specific capacitance along with large surface area resulting in the better performance of energy storing device [15].

Therefore, when these two profound materials (PANI and spinal metal oxides) combined together with incorporation of graphene as stability holder using suitable synthesis method, then a novel product will result with the properties of these three materials.

Challenges/Limitation for the Commercialization of Supercapacitor Devices

Although several advances and research grown successively on graphene/conductive polymer based electrode material for supercapacitors in order to incorporate with the various drawbacks but still there is a room for improvement in the enhancement of these properties. There are many challenges which can be overcome with time. Some of the challenges are:

- Feasible and cost effective method for the production of such electrochemical energy storage devices. Several methods used today are very expensive which resist the mass production of the device. There is a need to find such method by which cost of the production reduces, making commercialization possible in future [4-6].
- There is a need to access more porous 3D structure using different fabrication method in order to achieve more pore size so that it can provide more surface area to electrolyte ions to diffuse into the electrode hence resulting in high capacitance value with increased energy density [6].
- Some techniques yet to be determined for utilization of whole surface area provided by the graphene material so that specific capacitance value should increase more dominantly [7, 17].
- From previous researches, it is observed that the volume of fabricated supercapacitor devices increases effectively which will degrade the quality of the device as well as the energy density. This is one of the biggest challenges during the fabrication of any supercapacitor device. Future work should focus on this limitation as device fabrication should be done by considering all those factors increasing the volume of the device [17, 11].
- Last and the most important challenge for the commercialization of supercapacitors and which lack them from batteries is low energy density value, i.e. they cannot hold much amount of charge at a time, which is the main requirement for any energy storage device to be liable in electronic application [5, 11].

Despite of several challenges, researchers are trying various ways to overcome all these problems. Also with some sort of time some challenges are already taken in hand.

Future Scope for Supercapacitor

Supercapacitors have tremendous applications due to their advance property. They replaced the lithium-ion batteries in various potential applications and are on the surge of new development with a promising future. Some future aspects may follow:

- Supercapacitor potential application can also be utilized in other electronic devices such as solar cells to directly store the electricity and deliver it at instant of time.
- There is a high demand for flexible supercapacitors for wearable and portable electronics like sports watches with measuring sensor or for monitoring heartbeat. Due to high mechanical strength and environment friendly properties of these supercapacitors it is possible to utilize their worth in such application.
- Making a promising self-energy storage device using graphene/conductive polymers/metal oxide composite with promising high power density and high energy density [18-29].

By doing so, one day supercapacitors will fully replace batteries on commercial scale and will help in advancement of technology.

Conclusion

After reviewing several research papers, it is easy to conclude that supercapacitors are having wide applications but they need advance research for the commercialization in the market. In the series of researches, firstly several carbon materials were used as the electrode material for supercapacitors then invention of graphene disclose new ways for the advanced properties of these energy storing devices [24-26]. Several graphene based supercapacitors were constructed and tested showing high stability but the somehow lacked in the high specific capacitance value as well as high energy density. So, after various experiments it was found that conducting polymers can be used with graphene to make composite electrode which gave high stability with high specific capacitance value. With due sort of time, ternary combination using carbon material with conducting polymer and metal oxide were used for the electrode material for supercapacitor due to the achievement of better results than before [27, 28-33].

From that time to till now research has been going to find a suitable method from which supercapacitors can achieve high value of energy density without compromising other advanced properties in order to replace the batteries. Therefore, several researches are focused in this field of energy storing devices in order to provide a renewable energy storing device.

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