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Recent advancement on different electrode materials for next generation energy storage devices

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ABSTRACT

Renewable energy sources has drawn attention around the world due to the rapid industrial development and growing population .In order to make the effective use of renewable energy to meet the global energy consumption, it is important to develop high performance, low cost and economically friendly energy storage devices. Since conventional capacitors have some inadequacies such as small energy density (i.e., <0.05 Wh/kg) for many applications which require a large amount of energy storage or delivery,supercapacitors has emerged as new storage device due to their high durability during its long charge – discharge cycles. Supercapacitors are governed by the same fundamental equations as conventional capacitors, but utilize higher surface area low resistance electrodes and thinner dielectrics to achieve greater capacitances. Properties of supercapacitors depend both on the technique used to prepare the electrode and on the current collector structure. Carbon Materials in different forms such as carbon fibers, carbon aerogels, activated carbon, carbon nanotubes and graphene are the attractive electrode materials for supercapacitors. The incorporation of nanomaterials as electrodes help to control the surface area as well as porosity which results in improved performance, greater efficiency and life time of the super capacitors .This recent technology improvement enabled supercapacitors as an alternative to pulsed batteries for applications in industry and telecommunication equipment. This review focuses on the taxonomy of supercapacitors, explores principle and theory of operation, dependence on different electrode materials on supercapacitor output and their application in the present world.

Introduction

Electrostatic capacitors have been used as energy storage elements in the order of micro farads and assist in filtering. Capacitors have two main applications; one of which is a function to charge or discharge electricity. This function is applied to smoothing circuits of power supplies, backup circuits of microcomputers, and timer circuits that make use of the periods to charge or discharge electricity. The other is a function to block the flow of DC. This function is applied to filters that extract or eliminate particular frequencies. This is indispensable to circuits where excellent frequency characteristics are required [1]. Due to low capacitance values have traditionally limited them to low power applications as component in analogue circuits and in short term memory back up supplies. Recent developments in manufacturing technology with help of electrode material with high surface area and low resistance. This has combined with an understanding of the charge transfer that occur in the electro-double layer to make high power electrochemical capacitor possible.

Electric double layer capacitors (EDLC) represent new class of technology that store greater amount of energy than convectional capacitor and deliver more power than batteries. The current position of the Electric double layer capacitors (EDLC) is easily visualized by means of a Ragone plot (fig 1.1) which graphically represents a device's energy and power capabilities [2].

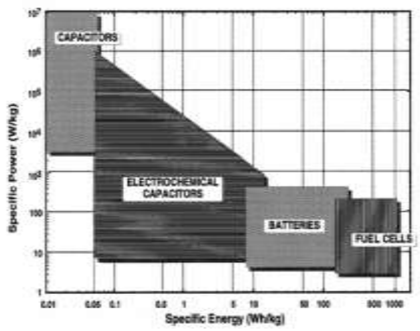

Fig.1.Ragone plot for various energy devices

Super capacitors are one of the important new sustainable energy standards. Supercapacitors, also called ultracapacitors, store electrochemical energy by accumulating the charge from electric double layer, which is caused by electrostatic attraction. The capacity of supercapacitor is proportional to the electrode surface, i.e., the electrochemically active surface, where how much ions are attracted [3]. Electrochemical capacitors (EC) are possible to be fully charged and discharged in seconds. Supercapacitor energy density (about 5-10 Wh/kg) is lower compared fuel cell and batteries, but higher power density (10 kW/kg) [4].The advantage of electrochemical capacitors are follows non toxic materials, good durability, fast charge /discharge rate and safety against short circuit [5].

Comparison between Capacitors, Supercapacitors and Batteries [6].

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Factors	Conventional Capacitors	Supercapacitor (Ultracapacitors)	Conventional Batteries
Charge Time	$10^{-6} \sim 10^{-3}$ s	$1 \sim 30$ s	$0.3 \sim 3$ h
Discharge Time	$10^{-6} \sim 10^{-3}$ s	$1 \sim 30$ s	$1 \sim 5$ h
Specific Power (W/kg)	10,000	1000 ~ 2000	50 ~ 200
Specific Energy (Wh/kg)	<0.1	1 ~ 10	20 ~ 100
Cycle Life (cycle)	> 500,000	> 100,000	500 ~ 2000
Charge/Discharge Efficiency (%)	~ 100%	90% ~ 95%	70% ~ 85%

Structure and taxonomy of supercapacitors

The basic structure of a super capacitor consists of two electrodes immersed in or impregnated with an electrolyte solution with a semi-permeable membrane serving as a separator that prevents electrical contact between the two electrodes, but which allows for ionic diffusion. When an electric potential is applied to the electrodes, a potential difference is created at the electrode-electrolyte interface. This electrostatic interface consists of a double layer between ions in the electrolyte and the electronic charges on the electrode [7-8].

Taxonomy of supercapacitors can be divided into three general classes: (i) Electrochemical Double Layer Capacitors (EDLCs), (ii) Pseudocapacitors, and (iii) Hybrid capacitors [10].There is unique storage mechanism for each class such as faradaic processes, non-Faradaic and a combination of both. Faradaic processes (such as oxidation-reduction reactions), involves chemical or composition changes that results in the transfer of charge between electrode and electrolyte where as non-Faradaic processes does not use any chemical mechanism. A graphical taxonomy of the different classes and sub class of supercapacitors is shown in fig.2.

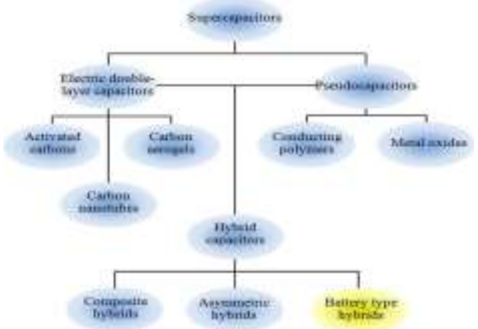

Fig.2.Taxonomy of Supercapacitors

Electric double layers capacitors

Electric Double layers capacitor (EDLC) consists of two based carbon electrodes, an electrolyte and a separator between them. Electric Double layers capacitors store the charge electrostaticaly by the process of reversible adsorption – desorption of electrolyte ions onto active electrode materials. The active materials should be chemically stable and have large accessible area. The large surface storage area allows very fast energy uptake and delivery, and better performance [11-12]. The electrolyte is an essential component for charge transport between the positive and negative electrodes and plays an important role in determining the performance, safety, and lifetimes of an EDLC. An EDLC can utilize either an aqueous or organic electrolyte.Aqueous electrolytes most commonly used are H_2SO_4 and KOH, and organic electrolyte include propylene carbonate (PC) and acetonitrile (ACN) electrolytes. Aqueous electrolytes have the advantage of high ionic conductivity but the disadvantage of small electrochemical window (~ 1.2 V), i.e., the potential over which the electrolyte is neither reduced nor oxidized at an electrode.__Organic electrolytes are advantageous over aqueous ones mainly due to their larger electrochemical windows, resulting in a larger cell voltage (2 ~ 3 V). Organic electrolytes suffer from serious health and safety problems as they are inherently volatile, flammable, and toxic, leading to a narrow operational temperature range and potential for explosion during outlying circumstances [13-16]. The electrodes are an essential component for charge storage / delivery and play an important role in determining energy and power densities of supercapacitor.Carbon materials are used as electrode material due to its attractive features such as high surface area, low cost and easier fabrication techniques. Different forms of carbon materials that can be used to store charge in EDLC electrode are activated carbon, carbon aerogels and carbon nanotubes (CNT's) [17-18].

Pseudocapacitors

Pseudocapacitors store charge through the process of electron transfer between the electrode and solution species knows as Faradaic process .This transfer is obtained through electrosorption, reduction oxidation reactions, and intercalation processes [19-21].Greater capacitance properties and energy densities are obtained in pseudocapacitor by faradaic process. Basically there are two types of electrodes used in Pseduocapacitors to store charge are as follows :(1) metal oxides and (ii) conducting polymers .Researches are focusing on various types of cheap transition metal oxides such as vanadium oxide (V_2O5), manganese oxide (MnO_2), and nickel oxide because of their high conductivity[22-24]. Conducting polymers are used as electrode material for supercapacitors due to their good electrical conductivity, large capacitance and relatively low cost. The most frequently used conducting polymer consists of polyaniline (PANI), polypyrrole (PPy), and poly[3,4-ethylenedioxythiophene] (PEDOT) [25-30].

Hybrid capacitors

Hybrid capacitor works on the principle of both physical and chemical storage mechanism to improve the merits and minimize the demerits that exist in EDLCs and pseudocapacitors. In other words they utilize both faradaic and non-faradaic process to store charge. They offer greater energy and power densities compared to other types of capacitors. Depending upon electrode configuration, there are three types of hybrid supercapacitors (i) composite capacitors (ii) Asymmetric capacitors and (iii) Battery capacitors Composite capacitors are prepared using carbon based material with either metal oxides or conductive polymer together in a single electrode. Asymmetric hybrid supercapacitors couple EDLC electrode with a pseudocapaciotr electrode

Unlike the other two types of capacitors, battery type capacitors are unique in coupling a supercapacitor electrode with a battery electrode. . The higher maximum operating voltage and the lower equivalent series resistance are additional beneficial factors which significantly improve the performance of supercapacitors [31-32].They are widely used in hybrid power system due to their combined utilization of double layer electrode along with the pseudocapacitance electrode which are charged in two different mode [33].

Activated carbon for supercapacitors

Carbon materials in different forms such as carbon fibers, carbon aerogels, activated carbons and carbon nanotubes are attractive materials for supercapacitors .They exhibit striking physical and chemical properties such as high conductivity, high surface area, high temperature stability, good corrosion resistance, high porosity, easy processability and good compatibility in composite materials and relatively low cost[Activated carbon is the oldest, extremely cheap and readily available forms of porous carbon. Commercial activated carbon productions depend on fossils fuel such as petroleum coke and coal. But due to the depletion of fossils fuel, led to the production of activated carbon from sustainable and renewable resources .Activated carbons are found in variety of form as small hexagonal rings organized into graphene sheet [34-35]. Both Physical and Chemical activation are used for the synthesis of activated carbon. In physical activation, carbon precursor is pyrolyzed at temperatures in the range 600–900 ^{0}c in absence of oxygen (usually in inert atmosphere of N_2) to remove non-carbon species, and followed by exposing to oxidizing atmospheres (CO_2, steam, or a mixture of both) at temperatures above 450 ^{0}C, usually in thin chemical activation prior to carbonization the carbon precursor is impregnated with certain chemicals (such as KOH, NaOH, H_3PO_4, ZnCl and H_2SO_4,), then the precursor is Carbonized at slightly lower temperatures of 450–900^{0}C. It is believed that the carbonization/activation step proceeds simultaneously with the chemical activation. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating materials. Moreover, chemical activation generally results in more uniform pore size distribution and higher specific capacitance in both aqueous and organic electrolytes temperature range of 600–1200 ^{0}C to develop porosity by partial etching of carbon . There are three type of pore size distribution classified by IUPAC46 micropores (diameters less than 2nm), mesopores (diameters between 2 and 50nm) and macropores (diameters greater than 50nm). The size of the electrolyte has an adverse effect on pore size electrochemical accessibility. Larger size of electrolyte ion than pore size limits the ability of the electrolyte to form double layer [36]. Fig shows the schematic diagram of the pore size network of an activated carbon [37].

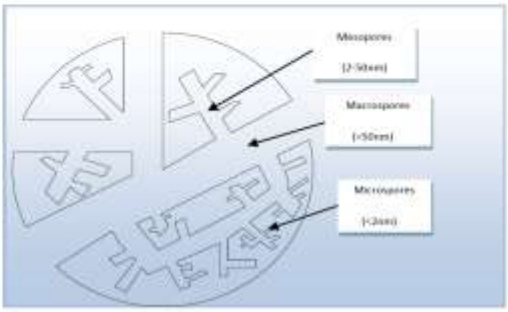

Fig 3: shows the schematic diagram of the pore size network of an activated carbon [37]

There are different kinds of electrolytes have been used in Electric double layer capacitors with activated carbon electrode. aqueous (solution of acids, bases and salts), organic (most commonly solution of tetraethylammonium tetrafluoroborate (TEATFB) salt either in anhydrous acetonitrile (AN) or propylene carbonate (PC) solvents), and Ionic liquid (IL) [38] . Due to their high surface area, activated carbon are used as an active material for negative electrode .The value of supercapacitor of activated carbon ranges from 100 to 200 Fg^{-1} in aqueous medium , and from 50 to 150 Fg^{-1}. The larger values in aqueous media are due to their smaller size of solvated ions and higher dielectric constant compared to organic media [39]. Fig is typical CVs of activated carbon in three different electrolytes [40].

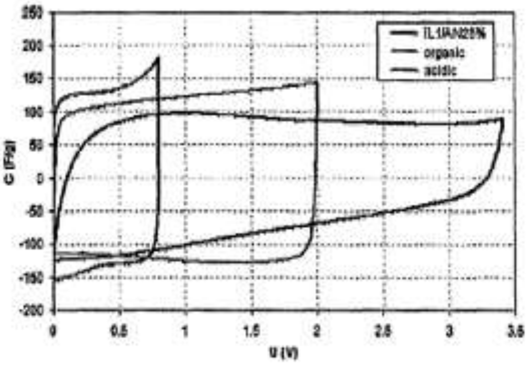

Fig4: is typical CVs of activated carbon in three different electrolytes [40].

Wu Zhang et al found that hybrid supercapacitor with PbO2/activated carbon electrode exhibits excellent energy and power performance, with specific energy of 43.6 Wh/kg at a power density of 654.2 W/kg[41]. Shao-yun et al studied about the effect of activated carbon and electrolyte on properties of supercapacitor.They concluded that super capacitors working voltage depend upon the compatibility of the activated carbon and electrolyte[42]. Anbao Yuan et al made comparative studies on Manganese dioxide / activated carbon with Lithium hydroxide electrolyte and Manganese dioxide / activated carbon with potassium hydroxide electrolyte prepared by solid state reaction route. The results of the experiment indicated that rate dischargeability and cyclic stability of MnO_2/AC capacitor with 1 M LiOH electrolyte is excellent and better than with 1 M KOH electrolyte [43]. K. Karthikeyan et al reported Li_2FeSiO_4 and activated carbon electrodes (LFSO/AC) cell reported excellent cycleability and greater efficiency over 1000 cycles [44].Haijie Shen *et al*. reported that a heteroatom-containing activated carbon prepared by simple carbonization and activation of phenol–melamine–formaldehyde resin and synthesized by the condensation polymerization method showed better capacitive behavior and delivers a high specific capacitance, as high as 210 F g−1[45]. S.R.S. Prabaharan *et al*. reported that symmetrical carbon/carbon double layer capacitors (EDLCs) were fabricated employing nanostructure mesoporous non- graphitized carbon black (NMCB) powders as electrode have BET surface area (469m^2 g−1) that can be used for Electric Double Layer Capacitor(EDLC) applications[46]. Sook-Keng Chang et al found that incorporation of activated carbon in o nickelecobalt oxide composite synthesized by co precipitation method did not altered the spinel structure of nickel cobalt oxide. NickeleCobalt oxide/activated carbon composite (NCAC) obtained maximum capacitance of 59 Fg^{-1} as the pseudocapacitor . Good electrochemical stability was obtained by retaining 86.7% of initial capacity over 1000 cycles. The benefits for using activated carbon as electrode materials are as follows :(1) easy and fast synthesis; (2) commercially available and very cheap raw materials; (3) high electrochemical performances; (4) environmental benignity. All these characteristics give evidence that activated carbon can be used as an electrode material for Electric Double Layer Capacitors applications [47].

Carbon nanotube for supercapacitors

Carbon nanotubes, long and thin cylinders of carbon, are a unique quasi one-dimensional nanomaterial. They were first reported by Iijima in 1991 when he discovered multi-walled carbon nanotubes (MWNTs) in carbon-soot made by an arc-discharge method [48]. Later, he also reported the single-walled carbon nanotubes (SWNTs) [49]. Carbon nanotube has been used as a new electrode for supercapacitors due to its attractive features. The activated carbon electrodes are easier to fabricate but the poor mesoporosity of activated carbons limit their capacitance. In case of carbon based electrode materials, the mesopores in CNTs electrode are interconnected allowing a continuous charge distribution that serves almost all the surface area .Because of the electrolyte ion can diffuse easily into the mesopores network, CNTs electrodes have lower Equivalent Series Resistance (ESR) than activated carbon [50]. Electro active polymers (e.g.polyaniline, polypyrrole, polythiophene) have attracted considerable attention as a family of novel organic electrochemical materials. Electro active polymers possess the advantages of low cost, light weight and high energy storage capability over high-surface-area activated carbons [51]. Polypyrrole can be combined with CNTs [52, 53, 54, 55, and 56, 57-60] to form composite for positive electrode. Zhou et al prepared positive electrode using pyrrole combined with treated functionalized single walled CNTs obtained a performance of 350 F g−1 at 0.4 A g−1 and 200 F g−1 at 30 A g−1[57].M.Hughes et al co deposited polypyrrole with carbon nanotubes by oxidizing monomer in the presence of negatively multiwalled carbon nanotubes (MWNT).The experimental result showed that low specific capacitance but high electrode specific capacitance due to more open or porous structure resulting from MWNT backbone[54]. Chen et al combined polypyrrole with carbon nanotubes resulted in a linear capacitance versus deposition to the same film thickness (10 C cm^{-2}) allowing majority of internal sites to be accessed by ions [58]. K.Lota et al prepared polythiophene with carbon nanotubes composite by three different mechanism (i) direct polymerization on ultrasonically dispersed CNTs (130 F g−1),(ii) mixing of polymer with carbon nanotubes (composite capacitance of 120 F g−1) (iii) electrochemical deposition of polymer onto the CNTs (up to 150 F g−1) results in improved in improved cycleability and stability[61] . They also prepared composite by combining PEDOT with carbon nanotube improved the conductivity in the undoped state and increased the cycle life [62]. Zhen et al identified various noble metal oxides such as RuO_2 and IrO_2 as electrode material due to their amazing specific capacitance, good electrical conductivity and high chemical stability [63]. Lee, J.Y. et al reported that current researchers are focusing on cheap transition metals (e.g., vanadium oxide (V_2O_5), manganese oxide (MnO_2), and nickel oxide [64]. Passerini et al fabricated V_2O_5 with CNTs nanocomposite electrodes with high-capacity and high –rate that can be utilized for supercapacitor applications [65]. Sakamoto & Dunn developed V_2O5 / SWNT nanocomposites electrode showed high specific capacity of 452 mAh/g and retains up to 65% of this capacity when the discharge rate is increased from 112 mA/g (0.2C) to 2800 mA/g (5C) [66]. There are several methods to enhance the supercapacitors storage properties .CNT thin film electrode are fabricated by growing or depositing CNTs directly on the current collector (Ni,Al,alloy or other metals) as electrode , reducing the contact resistance and improving its electrochemical performance [67,68,69,70-72]. Some researchers are focusing on the design of dense CNT networks as both the current collector and the activated electrode material for ECs[73]. A second method is by developing hybrid composite consisting of two hybrid materials together to gain the largest capacitance by dual storage mechanisms (EDLC and pseudocapacitance)[74]. In a hybrid system, conducting polymers or some metal oxides have a very large specific capacitance (e.g. 775 F/g for PANI, 480 F/g for PPy, theoretical value of MnO2 1100 F/g) [75-77], contributing to the overall capacitance. Third method is by integrating both the advantages of ECs and Li- ion batteries to form a new hybrid EC [78]. CNTs play the role of a perfect backbone and a good conductor for the composite during long cycling.

Graphene as supercapacitors

Graphene based supercapacitors are attracting a lot of research attention due to its fabulous properties such as large surface area (2630 $m^2/g^)$ [79], good thermal [80] and electrically conductivity (484 ~ 5300 W/mk, $2*10^2$ S/m) [81], theoretical capacitance (~ 21 μ/cm^2) [82].There were several methods used by the researchers to enhance the electrochemical properties of supercapacitors. One way is to prevent single or few layered graphene sheets from agglomeration, so as to obtain higher effective surface area. Another way to enhance the storage capacity is to combine graphene with other nanomaterials and fabricate hybrid composite electrodes [83].In addition to this , other composite were prepared using graphite with other electrode materials such as activated carbon [84] , metal oxides [85,86] and conducting polymer [87,88]. J.J.Yoo et al prepared graphene by Chemical Vapor Deposition (CVD showed specific capacitance of 80 F/cm^2[89]. C. Liu et al found that curved morphology rGO caused by convection drying measured an energy density 85.6 (kW/kg) and the power density of 9.8 (kW/kg). The electrode showed the specific capacitance around 250 (F/g) [90]. Q. Du et al reported that functionalized GO material obtained by the thermal exfoliation treatment of graphite oxide has the specific capacitance of 230 (F/g) at an energy density of 28.5 (Wh/kg) [91]. Choi et al dope nitrogen into the graphene basal planes by nitrogen plasma treatment .The N-Graphene displayed maximum specific capacitance of 282 (F/g) at a energy density 48(Wh/kg) and power density 800 (kW/kg) [92].Various hybrid composite were synthesized , such as Carbon black-graphene [93] , CNT-graphene [94], Carbon sphere-GNS [95] , PANi-graphene[96] RuO2-grapheneraphene [97] , PPy-Graphene [98], PEDOT-graphene [99], MnO_2-exfolitated graphite [100], graphene–Sn_3S_4 [101], RuO_2-graphene [102], NiO-graphene [103] and Fe_3O_4-graphene [104].The new hybrid composite exhibited better electrochemical reaction and excellent stability than each individual component .

Application

When high power is requested for short time, a bank of ultracapacitors releases a burst of energy to help a crane to lift load. They capture the released energy during discharge to recharge. Super capacitors are used in buses, trams, and garbage trucks recovers energy released during braking using it when peak power is demanded. Ultracapacitors are more effective regenerative storage devices than batteries because no chemical reactions are involved .Super capacitors provide backup power for the memory used in microcomputers and cell phones. They also supply brief bursts of energy to numerous consumer products such as cameras containing batteries. . Supercapacitors are investigated as replacement for batteries in hybrid cars cause capacitors function well in temperatures as low as -40^0 C; they can give electric cars a boost in cold weather, when batteries are at their worst. They can be subjected to high-current pulses and charged or discharged too quickly [105]. Thin film based super capacitors with in plane fabrication can be extended to various structural and hybrid design for energy storage. Carbon nanotube thin film-based supercapacitors fabricated with printing methods provide flexible and light weight displays such as laptops, cordless tools and toys [106]. Self assembled graphene /carbon nanotube hybrid films supercapacitors with well defined architecture, tunable thickness and variable separator for energy storage application [107]. There is a rapid advancement made in the field of printable electronics with paper supercapacitors that is used to power other paper electronics devices [108].

Summary

Graphene , a class of two –dimensional allotrope of carbon - based material ,are considered as best suitable base-materials for developing alternative energy sources for next generation energy storage device due to its high specific surface area, good chemical stability and outstanding electrical properties. There is a fast growing demand for electrochemical applications using graphene and graphene- based material.

Transparent Graphene thin films are used as transparent electrodes in solar cells and light emitting diodes Graphene Nanoribbons (GNRs) are used in the semiconductor industries for manufacturing graphene field-effect transistors (FETs) Graphene nanosheets have widespread applications in the field such as optoelectronics, photocatalysis [,direct methanol fuel cell, electrochemical cells, and electrochemical biosensing.They also provide platforms for sensing TNT and studying charge transport .

They are used in analyzing small molecules by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. In this review a comparative studies is made on activated carbon, carbon Nanotube and graphene as electrode material and their overall performance. The hybrid graphene composite supercapacitor has great potential for commercialization. However, it is important to keep in mind that graphene need further improvement in terms of cost and performance to compete with traditional carbon and graphite. This review can provide valuable insights to the researchers to gain further knowledge to speed up graphene way for new energy storage devices.

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