International Journal of Multidisciplinary Educational Research

ISSN:2277-7881; IMPACT FACTOR -6.014; IC VALUE:5.16; ISI VALUE:2.286



VOLUME 8, ISSUE8(6), AUGUST 2019

A REVIEW ON CARBON-BASED ELECTRODE MATERIALS FOR SUPERCAPACITORS

Sonali Kokane

Satish Pradhan Dnyanasadhana College of Arts, Science and Commerce, Thane, India

Abstract

Electrode materials for supercapacitors are reviewed. Supercapacitors have gained a lot of attention due to their unique features like high power, long cycle life and environment-friendly nature. They act as a link for energy-power difference between a traditional capacitor (having high power) and fuel cells/batteries (having high energy storage). The focus has been on materials like carbon-based nanomaterials, metal oxides, conducting polymers and their nanocomposites.

Keywords: Supercapacitors, Faradaic reactions, capacitance, energy storage, composite materials

1. Introduction

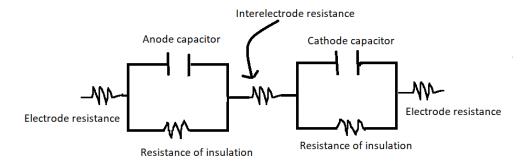
The capacitance which is a ratio of electric charge stored inside a capacitor to an electric potential difference between the two conducting plates can be increased by various ways: 1) By increasing the surface area of the two conducting plates or electrodes on which the charge is stored. Merely increasing the charge results in proportionate increase in the voltage so that the resulting capacitance remains same. Capacitance in Farads F= Q(Coulombs)/V(voltage). Hence physical alteration of the conducting plates is necessary. Capacitance can be varied by 1) altering the area of the electrode 2) By decreasing the distance between the plates which leads to decrease in the voltage between the plates. 3) By employing materials with improved dielectric constant. A similar equation to be considered is R = V/I (the Ohm's law). Just as resistance is a fixed constant for any material so is the capacitance. There is a linear relationship between current and voltage. In some Electrodes such as NiO/Ni(OH)₂, the current does not vary linearly with voltage and the capacitance is not constant. The physical alteration of electrodes and introduction of an electrolyte gives rise to many types of capacitors hereby referred to as supercapacitors due to increased value in capacitance. An ordinary parallel plate capacitor with the classical solid dielectric such as a paper has a capacitance of few microfarads while that of supercapacitor (with pseudocapacitance (faradaic reactions) and Electric double layer (nonfaradaic reaction or electrocapacitive behaviour) can go up to values of hundreds of farads. The earliest supercapacitors showed electro capacitive behaviour with activated carbon as electrodes; activated carbon being coated on aluminum sheets and dipped in an electrolyte such as Sodium sulphate and with a separator being a material such as Barium Titanate or polyvinylchloride felt. This supercapacitor gave capacitance up to few tenths of Farad.

The history of supercapacitors can be traced to early 1950s when engineers of General Electric motors used activated charcoal as electrodes. It can be traced through a series of US patents; the first of which was filed by The Standard Oil Company in 1972 (US patent 3648126). The basic mechanical design eventually evolved into a capacitor in which two aluminum foils are covered with chemically etched Carbon (to increase the surface area) dipped in an electrolyte and separated by thin, porous ion selective insulator. Supercapacitors were first used as back-up power in computer in 1978 during which period, the capacitance reached one Farad. From 1980 onwards there was a great deal of research with ruthenium oxide-based electrodes pioneered by Brians Evan Conway [1]. He first coined the term supercapacitor in 1999. Prior to the oxide-based electrodes, electrons were solely stored by the mechanism of Helmholtz double layer (as in activated carbons). The oxide electrodes were able to store charge by reversible surface redox reactions with faradaic charge transfer between electrodes and ions. This capacitance resulting from faradaic charge transfer is called as Pseudo-capacitance. The word pseudo distinguishes the classical electro-capacitance (non-faradaic) from other capacitances originating from faradaic redox reactions. In Figure 1.1 the electrodes are activated carbon exhibiting the electro-capacitance resulting from the Helmholtz double layer [2]. Transition metal oxides when



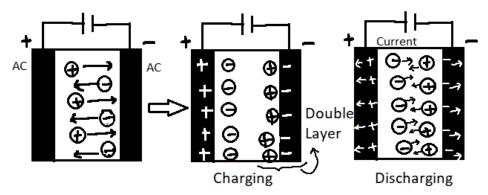
used as electrodes give both types of capacitances: that resulting from the electrical double layer and the redox faradaic reactions occurring at the surface and in the bulk of the electrodes. After such type of electrode is used, the resulting capacitor is called as Hybrid capacitor because the resulting capacitance is due to combination of faradaic and non-faradaic reactions [3]. The terms symmetric and asymmetric capacitors are used when both electrodes show similar capacitance in the former and dissimilar capacitance in the latter. Examples of asymmetric capacitors [4] may have these types of electrodes: 1) Redox//Redox: two different oxide materials or one oxide and one polymer for anode and cathode. 2) Redox//EDLC: Activated Carbon and an oxide 3) EDLC//EDLC: Graphene and Nitrogen – doped Graphene or Activated Carbon of two different weights.

The electric double layer is made up between the interface of two conducting media (solid-solid or liquid -liquid or solid -liquid) and consists of equal and opposite charge. For instance, an electric double layer is formed at the interface when p- and n-type conductors come together, when two metals with different work function are joined together or when a metal electrolyte is in contact with an electrolyte solution. Another way of creating a double layer is to apply potential difference across an interface of two electrodes which are dipped in an electrolyte creating two electric double layers giving a cathodic and anodic capacitor. The fat droplets of milk represent an electric double layer. A milk droplet is a heterogeneous system where fat droplets are dispersed in aqueous medium. At the interface is the double layer made up of positive charges on fat molecules and negative charges on the protein micelles. In a supercapacitor, the interface is the region between an electrode and the electrolyte (solidliquid type). A charge is induced on the electrode by applying a potential and equal and opposite charge is built up on its surface by adsorption of ions (of opposite polarity) from the electrolyte. Here the charge separation is of the order of few angstroms as compared to the charge separation in a conventional supercapacitor where it is of the order of few millimeters. The double layer replaces a conventional dielectric. Capacitance becomes proportional to the surface area of the double layer. Greater the surface area of an electrode, greater will be the area of the double electric layer and greater will be the capacitance. Any electrode with large porous structure will tend to have more surface area. Activated Carbon is the material of choice for electrodes in supercapacitors not only for their large surface area but also for their cheap availability [5-6]. The source of carbon can be various plants such as coconut shells [7], corn husk [8] or hemp fibers [9]. This biocarbon is converted to premium grade carbon by removing impurities. The abovementioned sources of biocarbon generates activated carbon for high performance supercapacitors. The charge – discharge cycles consist of adsorption-desorption of the ions from the electrolyte on the surface of activated electrode. There is no chemical reaction or electron transfer between the electrode and the electrolyte. Moreover, the ions from the electrolyte that form a double layer are solvated. There is no solid dielectric material as there is in a conventional parallel plate capacitor. Instead, the role of dielectric is played by the solvent molecules of the electrolyte. The separation between the two layers is only a few angstroms. A separator separates the two electrodes from touching each other. The anode and cathode capacitances are connected in series and the equivalent circuit is shown below.





The mechanism is shown schematically in Fig.2. The adsorption of ions leads to charging of the capacitor and desorption leads to discharging.



The electric double layer capacitors differ from Redox supercapacitors also called as Electrochemical pseudo capacitance in that the total capacitance in the latter come from the electrochemical pseudo capacitance and electric double layer capacitance. More often, the redox supercapacitors tend to give higher capacitance than EDLCs. The redox pseudo capacitors cover mostly these types: 1) Redox reaction occurring with metal oxide being used as cathode electrode and carbon as anode electrode or both electrodes are made up of two different metal oxides. 2) Redox reaction where one of the electrodes is made up of intercalating material such as a layered oxide or graphene sheets and the other electrode is a carbonaceous electrode: like Li-ion battery. The resulting capacitance is called as Intercalation pseudo capacitance. The layered metal oxides are used for cation intercalation and perovskites are used for oxygen anion intercalation. 3) Redox reaction occurs through underpotential deposition, for instance deposition of lead ions as lead on a gold electrode. The mechanism for electrochemical pseudo capacitance is the reversible faradaic redox reactions. The faradaic redox reactions can also occur on the surface of the electrode. The contribution to the total capacitance is from the surface faradaic redox reactions, the intercalation faradaic redox reactions and the electrical double layer.

2. Electrode material for Pseudo-capacitance and faradaic redox capacitance

The redox reactions that occur in supercapacitors are different from those that occur in batteries. Firstly, the redox reactions are not accompanied by phase changes in the electrode material. Secondly, there is no making or breaking of chemical bond. The de solvated ions are physically adsorbed on the surface of the electrode. The reactions with these physically adsorbed ions are faster and they leave only traces of by-products. The source of the electrons is always from the electrode material. In case of transition metal oxides, the electrons are the valence d orbitals of the transition metal ion. The electrode material must have affinity for the adsorbed ion. Just as in the case of EDLCs, here too there is no chemical reaction between the electrode and the electrolyte. The electrode preferably should have large surface area or a porous structure. The material of choice for the cathode are the transition metal oxides. They are intrinsically conducting and hence they need to be doped with a conducting material such as an activated carbon/graphene to increase the electrical conductivity. These oxides are very difficult to process into their nanostructures. Therefore, compositing them with activated carbon achieves greater porosity. Transition metal Oxides can show multiple oxidation states that favour redox reactions. The source of electrons is the partly filled d valence shells of these metals When the electrode material is a conducting polymer (for example, polyaniline, polypyrrole or polyacetylene), it is coated on the carbonaceous electrode surface. The polymer can also be doped with secondary dopants such as mcresol. Doping with polyethylene oxide has also been reported and the process is referred to as electrospinning. The transition metal oxides such as ruthenium oxide (RuO₂), manganese oxide (MnO₂), cerium oxide (CeO₂), vanadium pentoxide (V₂O₅), nickel oxide (NiO), and cobalt oxide (Co₂O₃) have



been examined as electrode materials for supercapacitors [10-13]. These TMOs are generally characterized with low conductivity and poor ion diffusion thereby reducing the cyclability of the electrodes. They are valued for their abundance, low toxicity as in MnO₂ and varied structural forms. For batteries, MnO₂ has been the most researched material as cathode for Li ion batteries. Activated carbon and MnO₂ are the representative materials for EDLCs and pseudocapacitors respectively. Lee and Goodenough began pioneering work on MnO₂ electrodes.

The reactions with these TM oxides are the intercalation and deintercalation of protons and alkali metal ions (from the electrolyte) in the bulk of the oxides. There is also the adsorption and de-adsorption of these ions on the surface of the electrodes. The intercalation and adsorption processes are the reduction reactions which take place during charging. The deintercalation and de-adsorption are the oxidation processes which take place during discharging. The valence state of the metal ion in these metal oxides undergo changes such that the valency is decreased during charging process. Examples are given below:

$$RuO_2 + xH^+ + xe^- \rightarrow RuO_{2-x}(OH)_x$$

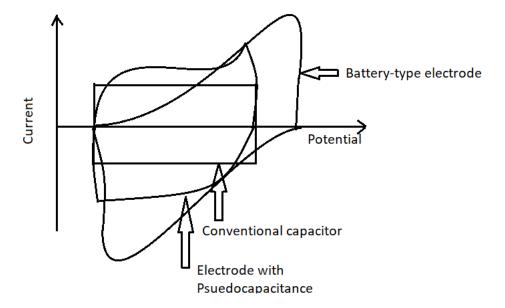
 $MnO_2 + C^+ + e^- \rightarrow MnOOC$

The charge-discharge cycles are accompanied by changes in the phase of the oxides. These phase changes may disturb the morphology and structure of an electrode and in turn the life of the device in terms of charge-discharge cycles. When two electrodes are made of the same material, they have the same resistance, and the potential of the capacitor varies symmetrically over both the electrodes. For a material to qualify as a redox electrode in a supercapacitor, it should show linear dependence on current versus voltage curve. Electrodes such as NiO or Co₃O₂ show non-linear relationship and are referred to as battery type electrode. The redox process occurs solely by faradaic charge transfer reactions between the electrode and the electrolyte and in the bulk of the electrode. There is no formation of double layer. There is a chemical reaction between electrode and electrolyte and there is a change in the oxidation state of the metal ion. The capacitance depends on the number of electrons that participated in the reaction between the electrode and the electrolyte. For this type of electrodes, capacitance is not reported because in these diffusion-limited faradaic processes (faradaic processes follow diffusion-controlled kinetics while non-faradaic processes follow surface-controlled kinetics), the capacitance is a meaningless quantity as it is changing constantly in the given potential window of charging and discharging. What is measured is the capacity or charge for these electrodes. Due to non-linear relationship between the voltage applied and the charge stored, the cyclic voltammograms will show distinct oxidation and reduction peaks. Integration is required to calculate the total amount of charge stored. On the other hand, a material such as activated carbon containing a double layer capacitor-like response will show a linear voltage versus time response in CV resulting in a rectangular curve where the oxidation and reduction peaks are clearly demarcated. These are categorised as capacitance electrodes [14-16]. The nature of peaks in the cyclic voltammograms will decide whether the electrode is capacitance or battery type. For electrodes which show capacitance (electric double layer) and surface/bulk faradaic redox capacitance, the CV curves will incorporate the features of both as shown below. CV curves are good indicators to categorise an electrode. With TMOs, a collector electrode is required to collect the current. This material can be an activated carbon or a metal such as Nickel.

International Journal of Multidisciplinary Educational Research ISSN:2277-7881; Impact Factor –6.014; IC Value:5.16; ISI Value:2.286

Volume 8, Issue8(6), August 2019





Graphene which are one atom thick sheets of graphite are light weight with very good mechanical strength and electrical conductivity [17-18]. Its theoretical capacitance is 550F/g. Since its electrical conductivity is better than that of Activated Carbon, there is no need to use a collector material with Graphene electrodes. The 2D structure of graphene sheets with vertical orientation helps the charge carriers to move in and out of the electrode material quickly. Graphene supercapacitors are already on the market. and several companies, including SkeletonTechnologies, CRRC, ZapGoCharger, and Angstron Materials are developing graphene based solutions. Materials that can compete with Graphene are: hemp which was used by Canadian researchers to develop hemp fibres that are at least as efficient as graphene ones in supercapacitor electrodes, Cigarette filters, which were used by Korean researchers to prepare a material for supercapacitor electrodes that exhibits a better rate capability and higher specific capacitance than conventional activated carbon and even higher than N-doped graphene or N-doped CNT electrodes. Supercapacitors based on graphene has the potential to be lighter and faster, but graphene comes with its own set of challenges. First and foremost, synthesis of pristine graphene sheets is extremely costly. There is no option which is commercially viable. Secondly, as Geim put it:" Graphene leaks like hell". It is so good as an electrical conductor that it still may leak electrons when we do not want it to.

Conducting polymers are an important class of electrodes [19-21]. Examples are polyaniline, polyacetylene, polypyrrole, polythiophene and PEDOT (poly 3,4-ethylenedioxythiophene). They are intrinsically conducting with a semiconducting bandgap of 2-3 electron volts: in the same range as that of inorganic semiconductors. They need to be doped (oxidised or reduced) to transform from semiconducting/insulating to conducting or metallic state. The conductivity can change from say 10⁻⁵ S cm⁻¹ to 10⁵ S cm⁻¹. The Dopant ions changes the properties of the conducting polymer. These properties are mechanical, optical, electrical, and chemical. During the doping process, deformation takes place around the charge (soliton, polaron, bipolaron) because the elastic energy and electronic energy will try to reach an equilibrium state. This lattice deformation can be 20 units long. A lattice deformation can accommodate a single charge called as polaron or two charges called as bipolaron. In a bipolaron the two charges repel each other but they are still bound by a single lattice deformation. This lattice deformation changes the spectroscopic properties and new bands at longer wavelengths appear in the electronic spectra. The deformation also leads to volume changes. The expansion and contraction during charging and discharging process hampers its cyclic stability by damaging the polymer structure. Conducting polymers offer the possibility of spin coating over large surface areas. This kind of



processability is not seen with other materials. During the synthesis, care must be taken that the conjugation in the polymer length is not affected. CVD (chemical vapour deposition) method ensures that the polymer film is one atom-thick and the conjugation is undisturbed. CVD on large scale is a very expensive method. Other cheaper methods such as thermal exfoliation, mechanical and chemical procedures introduce defects which disturb the conjugation and in turn, the conductivity. To compensate for these features which may reduce the conductivity of polymers, they are often composited with highly conducting carbon-based materials. Conducting polymers have higher theoretical specific capacity than most inorganic materials and activated carbon. Polymer based electrodes give pseudo-capacitance resulting from surface active redox reactions. In a typical set up, the polymer forms a cathode and a metal, or an activated carbon forms an anode. The polymer is p-doped and carries a positive charge while charging and accepts an electron while discharging. An example of an all conducting polymer-based supercapacitor would be PEDOT as anode and PANI as cathode. These are coated on collector electrode.

Carbon based materials are activated carbon, graphene, and carbon nanotubes. These are composited with Transition metal oxides, polymers, and small molecules. Examples of such electrodes are the following: RuO₂/graphene [22], RuO₂/CNT [23], MnO₂/Carbon composites [24], Co₃O₄/graphene [25], CNT/graphene [26], PANI/Graphene [27], PANI/AC [28], PEDOT/Graphene, PEDOT/AC and so on. Among Plant materials, Lignin is one such substance which contains high amount of redox active quinone groups. It is found in barks and woods and is the second most abundant organic material after cellulose. One disadvantage with Lignin is that it is electrically insulating. Graphite is added to make composite paste with Lignin and Polyprrole is polymerised with Lignin or its water-soluble form: Lignosulphonate (LS). Lignosulphonate is water soluble and obtained from paper mills as waste product. The resulting composite materials are composites of quinone/graphite or quinone/AC hybrid material and LS or quinone/polypyrrole [29-32]. Without going through the biomass route, quinonebased small molecules can directly be used to make hybrid electrodes. These small molecules are Hydroquinone, 1,4-Benzoquinone, 1,4-Naphthoquinone, 5-hydroxy-1,4-naphthoquinone (5-OH NO or juglone), 2-hydroxy-1,4-naphthoquinone (2-OH NQ or lawsone), 5-amino-1,4-naphthoquinone (ANQ), anthraquinone (AQ), 1-aminoanthraquinone (AAQ), 2,6-diaminoanthraquinone (Diamino AQ), alizarin, syringic acid, sinapic acid, and synthetic-lignin polymerized from phenolic functional groups (syringol and guaiacol) [33]. Composite materials allow for weight reduction of the supercapacitor with optimum surface area and conductivity of the electrodes.

An essential difference between ordinary parallel plate capacitors and supercapacitors is the presence of electrolyte. For critical analysis see the review of Pal et al [34]. These electrolytes are made up of cations and anions. The electrodes are porous with some pore size. The ions of the electrolyte should be able to fit into this pore size. This will increase the energy density of the capacitor. During discharging these ions should not be jammed in the pores. Instead, they should be able to smoothly return to the electrolyte. This will increase the current output and hence the power of the capacitor. For high power density, the internal resistance should be as low as possible. Commonly there are three types of electrolytes: Aqueous, Organic liquid and Ionic liquids. A good electrolyte will offer a wide voltage window, high conductivity, low viscosity, low toxicity, and non-flammability. Electrochemical stability of the decomposition potential of the electrolyte decides the working voltage of the capacitor. Aqueous electrolytes give a voltage window of 1.5 to 2.0 volts since water splitting will occur at potentials ranging from 1.5 to 2.0 volts. This is because at the cathodic limits water is oxidized to give oxygen gas, and at the anodic limits, water is reduced to give hydrogen gas. Aqueous electrolytes can be acidic such as H₂SO₄ solution), alkaline solutions (such as KOH solution) and neutral solutions (such as Li₂SO₄ and Na₂SO₄ solutions). For Organic liquids it is up to 2.5 to 3.0 volts. For instance, the electrolyte tetraethylammonium tetrafluoroborate (TEABF4) in acetonitrile has a voltage window greater than 4 V versus a platinum electrode or ~2.7 V versus a carbon electrode. This leads to realizable energy densities almost 5 times greater for organic electrolytes than aqueous electrolytes. The greatest range of voltage is offered by Ionic liquids which is 3.5 to 4.0 Volts. Unfortunately, they have high



viscosity, may be toxic and flammable. Using ionic liquid-based electrolytes has the benefit of further increasing the energy density.

3. Parameters in supercapacitors

Supercapacitors incorporates the functions of both – a battery and a capacitor. A battery stores energy and takes a long time to charge and discharge. A capacitor discharges (with consequent decrease in voltage) and charges rapidly but does not store energy as much as a battery. A battery runs over a constant voltage. Unlike a battery, a supercapacitor is light weight and since there are no chemical reactions, the charge-discharge cycles are greater. Unlike a capacitor, a supercapacitor holds a very large amount of charge due to increased electrode surface area and molecule-thin electrolyte. In essence, a supercapacitor seeks to include the features offered by a battery and a capacitor and at the same time, exclude their disadvantages. The parameters given below aids in quantifying the performance of a supercapacitor [35].

Supercapacitor Parameters.

- Charge/Discharge Time: Milliseconds to seconds
- Charge/Discharge cycles: about 1L to 10L cycles
- Operating Temperature: -40°C to +85C°
- Operating Voltage: Aqueous electrolytes ~1V; Organic electrolytes 2 3V
- Capacitance: 1mF to >10,000F
- Operating Life: 5,000 to 50,000 hrs (a function of temperature and voltage)
- Power Density: 0.01 to 10 kW/kg
 Energy Density: 0.05 to 10 Wh/kg
- Pulse Load: 0.1 to 100A
- Surface area: 500 to 2000 m² gm⁻¹
- Electrical Conductivity:

Commercial supercapacitors have life of 10-15 years after which their capacitance decreases, and internal resistance increases. A 30% increase in internal resistance signifies that the supercapacitor is nearing the end of its lifecycle. The charge-discharge cycles of an ordinary capacitor are unlimited. A supercapacitor can have a cycle of 1L to 10L cycles. The percentage amount of capacitance retained after say 1000 cycles is determined. This percentage goes down with loss in conductivity of the electrode material. For comparison, a laptop battery can be charged up to 500 times. The energy stored in a capacitor can be expressed in three ways: $E=QV/2=CV^2/2=Q^2/2C$, where Q is the charge, V is the voltage, and C is the capacitance of the capacitor. The energy is in joules when the charge is in coulombs, voltage is in volts, and capacitance is in farads. Energy density is energy stored per unit volume or per unit mass in each system and specific energy is used for energy density per unit mass. In case of capacitors, the energy is stored in the electrical field, and it needs an electrical reaction, namely, the displacement of the charges to release this energy. In an ideal Capacitor the energy stored is equal to QV. That is, all the work done on the charge in moving it from one plate to the other would appear as energy stored. Half of the energy (supplied by the battery in charging the capacitor) is dissipated as heat. The SI unit of specific energy is joules per kg or in case of batteries and capacitors, it is watt-hours per kg. It is abbreviated as kWh or kilowatt-hours. One must use 1 kilowatt of power for one hour to use 1 kWh. Suppose a light bulb has a power of 100 watts. To use 1 kWh of energy, the bulb would take 10 hours. 1kWh energy is equal to 1000 joules used for 3600 seconds, that is, 3,60,00,00 joules or 3.6 million joules. Hence 1kWh/kg = 3.6MJ/kg. Variations of the unit may be used. It could be Wh/g or kJ/kg. If the specific energy is per volume (volume between the parallel plates), the unit is Wh/L or kWh/L. Commercially available lithium-ion supercapacitors (anode: Carbon electrode pre doped with Li ions and cathode: Activated Carbon) offered the highest specific energy, reaching 15 Wh/kg (54 kJ/kg).





Commercial EDLCs with organic electrolytes have energy density between 5-10 Wh/kg. The power density refers to the amount of energy that can be discharged per unit of battery of capacitor. It is the rate at which energy is transferred or rate at which work is done. One watt is equal to one joule of work done per second. If P represents power in watts, E is the change in energy (number of joules) and t is the time taken in seconds, $P=\Delta E/\Delta t$. The Ragone plot above in Fig. 4 gives the big picture. A Li-ion capacitor will have a power output of 300 to 136000 W/kg. The capacitance is an important parameter and defines the application of that supercapacitor. For a parallel plate capacitor, the capacitance can be of the order of nano, micro or milli Farads. To have a capacitance any greater than these, the parallel plates would have to have an abnormally large surface area of the order of more than 10 kilometres x 10 kilometres (over 6 miles) square. That's practically impossible to design and that's why when capacitance exceed these values of milli, micro, nano and pico farads, we enter the regime of supercapacitors where the electrodes are designed with larger surface area to accommodate this huge amount of charge and nanomaterials which promise a larger surface area for greater storage of charge. Conductivity of electrodes based on activated carbon is about 0.003% of metals but it is enough for a capacitor.

Carbon can be sourced from agricultural waste, wood processing industry, petroleum residue, coal (lignite), forestry and food industry, carpentry etc. This source of waste biomass is sustainable both economically and ecologically. Examples could be bamboo, banana peel, cotton stalks, almond stone, olive stone, sugarcane, walnut shells, waste tea leaves, peanut shells, rice husk, oil palm shell, jatropha hull, corn cob etc. The biomass is washed with deionised water to remove soil impurities. It is then dried between 65 and 105 C. The biomass then undergoes milling to give uniform particles. Thereafter the biomass is subjected to carbonisation or pyrolysis, carried out in inert atmosphere at 500-1000 C. At this stage the existing vapours and gases form the basic pore structure giving a carbonized homogeneous mass. In the second stage of activation, the mass is heated at 800-1000 C in an oxidising atmosphere. To obtain high quality carbon, physical activation maybe carried out by chemical activation. The chemical agents are phosphoric acid, potassium hydroxide, zinc chloride and sodium amide. Even with chemical activating agents the temperature is required to be above 400C. The weight loss is between 10% to 40% and greater weight loss leads to greater development of pore structure in terms of completion of the pore forming process and smaller pore size. Biomass contains cellulose, hemicellulose, and lignin. Cellulose is straight-chain polysaccharides which are insoluble in water while hemicellulose is a cross linked polymer with water soluble sugars such as glucose, mannose, galacturonic acid, xylose, arabinose, O-methyl-glucuronic acid, and galactose. Lignin is a natural insoluble polymer and contains aldehydic and carbonyl groups. Lignocellulosic biomass such as coir, contains 10%–30% lignin and even up to 45%. It contains β-1,4-Glycosidic bonds and is highly



hydrophobic. Thermal decomposition of hemicellulose begins at 250 C while that of cellulose begins around 400 C. Lignin-rich biomass needs chemical activation. For production of AC for electrodes, the two-step activation procedure is followed.

4. Conclusion

With decreasing pore size of the activated carbon, the capacitance increases. Capacitance is maximised when the pore size matches with the ion size of the electrolyte. As pore size decreases surface area increases. Experiments have shown that smaller pore size does not guarantee higher capacitance. Rather the accessibility of the pores for the ions from the electrolyte is important [36]. Usually, electrodes with surface area around 2500m²/g and pore size around 2nm will give optimum performance for a given electrolyte. Decreasing the pore size below 2nm decreases the accessibility of the ions thus reducing the capacitance. The electrical energy stored can be effectively utilised and the capacitor can be charged and discharged at a higher current density if the carbon electrodes show a good conductivity. The intrinsic conductivity depends on the degree of graphitization of the activated carbon which in turn can depend on the feedstock and method of activation. Conductivity can be increased with, for instance, doping with 4% Silver nanowires which not only increased the conductivity but also imparted mechanical strength [37]. Surface morphology also determines the electrical conductivity. According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified as: macropore if the pore width is greater than 50 nm; mesopore, if the pore width is between 2 to 50 nm; and micropore, with a pore width is less than 2 nm. The surface area and porosity are influenced by the nature and quality of the precursor materials, the method and temperature of activation.

Competing Interests Statement

The author declare no competing interests.

Acknowledgements

This research did not receive any specific grant from funding agencies in the public, commercial or not-for-profit sectors.

References

- 1. Conway, Brian Evans (1999). Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications. Springer. doi:10.1007/978-1-4757-3058-6. ISBN 978-0306457364.
- **2.** Jayathu Fernando, Double-layer capacitors: fundamentals, characteristics, and equivalent circuits, Energy Storage Devices for Electronic Systems, Pages 149-186 (2015), https://doi.org/10.1016/B978-0-12-407947-2.00005-5
- 3. Malak, A., Fic, K., Lota, G., et al. (2010) Hybrid materials for supercapacitor application. Journal of Solid State Electrochemistry, 14(5), 811–816.
- 4. Asymmetric supercapacitors based on Graphene/ MnO_2 and activated carbon nanofiber electrodes with high power and energy density. Advanced Functional Materials, 21 (12), 2366–2375
- 5. Béguin, Francois; Raymundo-Piñeiro, E.; Frackowiak, Elzbieta (2009). ". Electrical Double-Layer Capacitors and Pseudocapacitors". Carbons for Electrochemical Energy Storage and Conversion Systems. CRC Press. pp. 329–375. doi:10.1201/9781420055405-c8. ISBN 978-1-4200-5540-5.
- 6. Qu, D.Y. (2002) Studies of the activated carbons used in double-layer supercapacitors. Journal of Power Sources, 109 (2), 403–411.
- 7. Jain, Amrita; Tripathi, S. K. Fabrication and characterization of energy storing supercapacitor devices using coconut shell based activated charcoal electrode. Materials Science and Engineering:B, Volume 183, 2014, pp 54-60
- 8. Wei Sun, Stephen M. Lipka, Christopher Swartz, David Williams, Fuqian Yang, Hemp-derived activated carbons for supercapacitors, Carbon 103 (2016) 181-192.



- 9. Su, L. et al. Sprinkling MnFe₂O₄ quantum dots on nitrogen-doped graphene sheets: The formation mechanism and application for high-performance supercapacitor electrodes. J. Mater. Chem. A 6, 9997–10007 (2018).
- 10. Lang, X.Y., Hirata, A., Fujita, T., and Chen, M.W. (2011) Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. Nature Nanotechnology, 6 (4), 232–236.
- 11. Lee, J.W., Ahn, T., Kim, J.H., et al. (2011) Nanosheets based mesoporous NiO microspherical structures via facile and template free method for high performance supercapacitors. Electrochimica Acta, 56 (13), 4849–4857.
- 12. Zhu, Y.W., Murali, S., Stoller, M.D., et al. (2011) Carbon-based supercapacitors produced by activation of graphene. Science, 332 (6037), 1537–1541.
- 13. Wang, Y., Shi, Z.Q., Huang, Y., et al. (2009b) Supercapacitor devices based on graphene materials. Journal of Physical Chemistry C, 113 (30), 13103–13107.
- 14. These New Graphene Supercapacitors could Finally Power an Electric Car, http://gizmodo.com/these-new graphene-supercapacitors-could-finally-power-1463259679 Fan, Z.J., Yan, J., Wei, T., et al. (2011) Hassan, F.M., Chabot, V., Li, J.D., et al. (2013)
- 15. Pyrrolic-structure enriched nitrogen doped graphene for highly efficient next generation supercapacitors. Journal of Materials Chemistry A, 1 (8), 2904–2912
- 16. Wang, H.L., Hao, Q.L., Yang, X.J., et al. (2009a) Graphene oxide doped polyaniline for supercapacitors. Electrochemistry Communications, 11 (6), 1158–1161.
- 17. Haihui Zhou, Hong Chen, Shenglian Luo, Gewu Lu, Wanzhi Wei, Yafei Kuang (2005) The effect of the polyaniline morphology on the performance of polyaniline supercapacitors. Journal of Solid-State Electrochemistry, 9 (8), 574–580
- 18. Takao Nagatomo, Chiaki Ichikawa and Osamu Omoto: All-Plastic Batteries with Polyacetylene Electrodes, Journal of The Electrochemical Society, Volume 134, Number 2, 1987, 305
- 19. Yang Huang, Hongfei Li, Zifeng Wang, Minshen Zhu, Zengxia Pei, Qi Xue, Yan Huang, Chunyi Zhi: Nanostructured Polypyrrole as a flexible electrode material of supercapacitor, Nano Energy, Volume 22, April 2016, Pages 422-438.
- 20. Murugesan Rajesh, C. Justin Raj, Ramu Manikandan, Byung Chul Kim, Sang Yeup Park, Kook HyunYu, A high performance PEDOT/PEDOT symmetric supercapacitor by facile in-situ hydrothermal polymerization of PEDOT nanostructures on flexible carbon fibre cloth electrodes, Materials Today Energy, Volume 6, December 2017, Pages 96-104 https://doi.org/10.1016/j.mtener.2017.09.003
- 21. Lingjuan Deng, Jianfang Wang, Gang Zhu, Liping Kang, Zhengping Hao, Zhibin Lei, Zupei Yang, Zong-Huai Liu, RuO₂/graphene hybrid material for high performance electrochemical capacitor, Journal of Power Sources, Volume 248, 2014, 407-415, https://doi.org/10.1016/j.jpowsour.2013.09.081
- 22. Jong Hyeok Park, Jang Myoun Ko and O. Ok Park Carbon Nanotube/ RuO2 Nanocomposite Electrodes for Supercapacitors, Journal of The Electrochemical Society, Volume 150, 2003, Number 7 DOI:10.1149/1.1576222
- 23. Shubin Yang, Guanglei Cui, Shuping Pang, Qian Cao, Ute Kolb, Xinliang Feng, Joachim Maier, Klaus Müllen Fabrication of Cobalt and Cobalt Oxide/Graphene Composites: Towards High-Performance Anode Materials for Lithium Ion Batteries, CHEMSUSCHEM, Volume3, Issue2, 2010, 236-239, https://doi.org/10.1002/cssc.200900106
- 24. Noel Díez, Cristina Botas, Roman Mysyk, Eider Goikolea, Teófilo Rojo and Daniel Carriazo, Highly packed graphene–CNT films as electrodes for aqueous supercapacitors with high volumetric performance, J. Mater. Chem. A, 2018,6, 3667-3673, https://doi.org/10.1039/C7TA10210K
- 25. Zhaoqi Huang, Le Li, Yufeng Wang, Chao Zhang, Tianxi Liu, Polyaniline/graphene nanocomposites towards high-performance supercapacitors: A review, Composites Communications, Volume 8, June 2018, Pages 83-91 https://doi.org/10.1016/j.coco.2017.11.005



- 26. Huseyin Zengin, Güllü Kalaycı, Synthesis and characterization of polyaniline/activated carbon composites and preparation of conductive films, Materials Chemistry and Physics, Volume 120, Issue 1, 15 March 2010, Pages 46-53, https://doi.org/10.1016/j.matchemphys.2009.10.019
- 27. Suvi Lehtimaki, Milla Suominen, Pia Damlin, Sampo Tuukkanen, Carita Kvarnström and Donald Lupo, Preparation of Supercapacitors on Flexible Substrates with Electrodeposited PEDOT/Graphene Composites, ACS Appl. Mater. Interfaces, 2015, 7 (40), 22137–22147
- 28. M. Selvakumar, D. Krishna Bhat, Activated carbon-polyethylenedioxythiophene composite electrodes for symmetrical supercapacitors, Journal of Applied Polymer Science, Volume 107, Issue 4, 2008, 2165-2170, https://doi.org/10.1002/app.27166
- 29. Sai Prasad Ega, Palaniappan Srinivasan, Quinone materials for supercapacitor: Current status, approaches, and future directions, Journal of Energy Storage, Available online 2 December 2021, https://doi.org/10.1016/j.est.2021.103700
- 30. Yilkal Dessie and Shimelis Admassie, Electrochemical Study of Conducting Polymer/Lignin Composites, Oriental Journal of Electrochemistry, 2013, Vol. 29, No. (4): Pg. 1359-1369 http://dx.doi.org/10.13005/ojc/290411
- 31. Lignin-Derived Materials for Supercapacitors Jesús Muñiz, Ana K. Cuentas-Gallegos, Miguel Robles, Alfredo Guillén-López, Diego R. Lobato-Peralta, and Jojhar E. Pascoe-Sussoni, Handbook of Supercapacitor Materials: Synthesis, Characterization, and Applications, Wiley Online Library, September 2021, Print ISBN:9783527346875 |Online ISBN:9783527824779, https://doi.org/10.1002/9783527824779.ch1
- 32. Shimelis Admassie, Ting Yang Nilsson, Olle Inganäs, Charge storage properties of biopolymer electrodes with (sub)tropical lignins, Phys. Chem. Chem. Phys., 2014,16, 24681-24684, https://doi.org/10.1039/C4CP03777D
- 33. Qiong Wu, Yiqing Sun, Hua Bai, Gaoquan Shi High-performance supercapacitor electrodes based on graphene hydrogels modified with 2-aminoanthraquinone moieties, Phys. Chem. Chem. Phys., 2011,13, 11193-11198, https://doi.org/10.1039/C1CP20980A
- 34. Stoller, M.D. and Ruoff, R.S. (2010) Best practice methods for determining an electrode material's performance for ultracapacitors. Energy & Environmental Science, 3 (9), 1294–1301
- 35. Endo, M., Takeda, T., Kim, Y.J., et al. (2001) High power electric double layer capacitor (ELDC's); from operating principle to pore size control in advanced activated carbons. Carbon Science, 1 (3 & 4), 117–128. Estes, A.C. (2013)
- 36. Hengyue Li, Hui Guo, Keqing Huang, Biao Liu, Chujun Zhang, Xiaohua Chen, Xiaowen Xu & Junliang Yang, Carbon electrode with conductivity improvement using silver nanowires for high-performance supercapacitor, Applied Physics A, volume 124, Article number: 763 (2018) DOI:10.1007/s00339-018-2182-4
- 37. Marcin Molenda, Michał Świętosławski, Marek Drozdek, Barbara Dudek, and Roman Dziembaj, Morphology and Electrical Conductivity of Carbon Nanocoatings Prepared from Pyrolysed Polymers, Journal of Nanomaterials, Volume 2014 Article ID 103418 https://doi.org/10.1155/2014/103418