ENERGY STORAGE MATERIALS FOR SUPERCAPACITORS

[1]L.Malleswara Rao, [1]A P V Appa Rao, [1]J Rama Mohan, [2]K Ramnarayana and [3]Ch. Sundar Singh
[1]Lecturers in Physics, Sri.Y.N.College, Narsapur
[2]Lecturer in Physics, ASNM Govt. Degree College, Palakol
[3]Lecturer in Physics, DNR Degree College for Women, Palakol.

Abstract: *Supercapacitors or EDLCs (i.e. electric double-layer capacitors) or ultra-capacitors are becoming increasingly popular as alternatives for the conventional and traditional battery sources. 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. Electrochemical capacitors use the double-layer effect to store electric energy; however, this double-layer has no conventional solid dielectric to separate the charges. EDLCs can either store charge electro statically or via non faradic process, which involves no transfer of charge between electrode and the electrolyte. Pseudocapacitors store charge via faradic process which involves the transfer of charge between electrode and electrolyte. The CNT as supercapacitor electrode material due to its unique pore structure, good mechanical and thermal stability and superior electrical properties. 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. Supercapacitors may emerge as the solution for many application-specific power systems. In particular; supercapacitors have great potential for applications that require a combination of high power, short charging time, high cycling stability and long shelf life.*

Index Terms: Super capacitors, Energy Storage Materials, EDLC, Pseudo capacitors, CNTs, Graphene.

I. INTRODUCTION:

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. A supercapacitor consists of two electrodes, an electrolyte, and a separator which isolates the two electrodes electrically. They typically store 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerate many more charge and discharge cycles than rechargeable batteries. Electrode material is the most important component of a supercapacitor. Some of the benefits of supercapacitors when compared with other energy storage devices are long life, high power, flexible packaging, wide thermal range (-40ºC to 70ºC), low maintenance and low weight. 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. Among the promising applications of supercapacitors is in fuel cell vehicles and low emission hybrid vehicles. 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.

Supercapacitors are used in applications requiring many rapid charge/discharge cycles rather than long term compact energy storage: within cars, buses, trains, cranes and elevators, where they are used for regenerative braking, short-term energy storage or burst-mode power delivery.

II. BASIC DESIGN:

Electrochemical capacitors (supercapacitors) consist of two electrodes separated by an ion-permeable membrane (separator), and an electrolyte ionically connecting both electrodes. When the electrodes are polarized by an applied voltage, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity. For example, positively polarized electrodes will have a layer of negative ions at the electrode/electrolyte interface along with a charge-balancing layer of positive ions adsorbing onto the negative layer. The opposite is true for the negatively polarized electrode. Additionally, depending on electrode material and surface shape, some ions may permeate the double layer becoming specifically adsorbed ions and contribute with pseudocapacitance to the total capacitance of the supercapacitor.

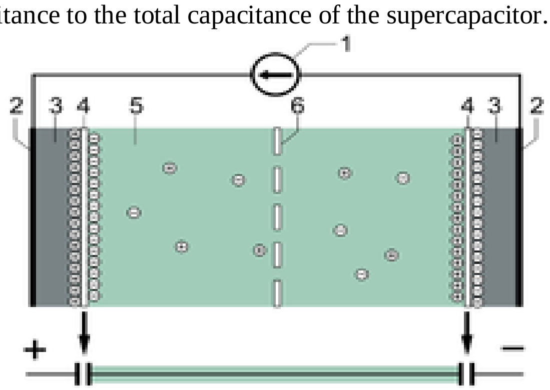

Fig. 1: Typical construction of a supercapacitor

III. STORAGE PRINCIPLES:

The two key storage principles behind the supercapacitor theory are: • Double-layer capacitance – Electrostatic storage achieved by separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte. The separation of charge is of the order of a few angstroms (0.3–0.8 nm), much smaller than in a conventional capacitor. • Pseudo capacitance – Faradic electrochemical storage with electron charge-transfer, achieved by redox reactions, intercalation or electro sorption **(Fig 2& Fig 3)**.

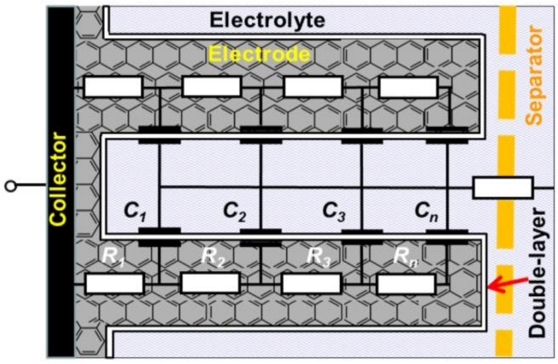

Fig. 2: Simplified View of EDLC

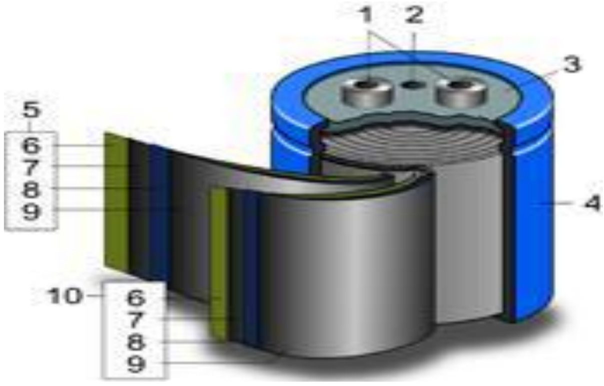

Fig. 3: Schematic construction of a supercapacitor

IV. EARLY DISCOVERIES:

Early Batteries: Volta discovered in 1800 that certain fluids would generate a continuous flow of electrical power when used as a conductor. This discovery led to the invention of the first voltaic cell, more commonly known as the battery. Invention of the Rechargeable Battery: In 1836, John F. Daniel, an English chemist, developed an improved battery that produced a steadier current than earlier devices. Until this time, all batteries were primary, meaning they could not be recharged. In 1859, the French physicist Gaston Planté invented the first rechargeable battery. It was based on lead acid, a system that is still used today. In 1899, Waldmar Jungner from Sweden invented the nickel-cadmium battery (NiCd), which used nickel for the positive electrode (cathode) and cadmium for the negative (anode). High material costs compared to lead acid limited its use and two years later, Thomas Edison produced an alternative design by replacing cadmium with iron. Low specific energy, poor performance at low temperature and high self-discharge limited the success of the nickel-iron battery. It was not until 1932 that Shlecht and Ackermann achieved higher load currents and improved the longevity of NiCd by inventing the sintered pole plate. In 1947, Georg Neumann succeeded in sealing the cell. For many years, NiCd was the only rechargeable battery for portable applications.

V. CLASSIFICATION OF SUPERCAPACITORS:

1. **Double-layer capacitors (EDLC)**:

These ones with activated carbon electrodes or derivates with much higher electrostatic double-layer capacitance than electrochemical pseudocapacitance.

EDLCs are constructed using two carbon based materials as electrodes, an electrolyte and a separator. EDLCs can either store charge electro statically or via non faradic process, which involves no transfer of charge between electrode and the electrolyte. 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 (**Fig.4)**.

2. **Pseudo capacitors**:

These are capacitors with transition metal oxide or conducting polymer electrodes with a high amount of electrochemical pseudocapacitance Compared to EDLCs, that store charge electro-statically. Pseudocapacitors store charge via faradic process which involves the transfer of charge between electrode and electrolyte.

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.

3. **Hybrid capacitors**:

These are capacitors with asymmetric electrodes one of which exhibits electrostatic and the other mostly electrochemical capacitance, such as lithium-ion capacitors.

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. 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.

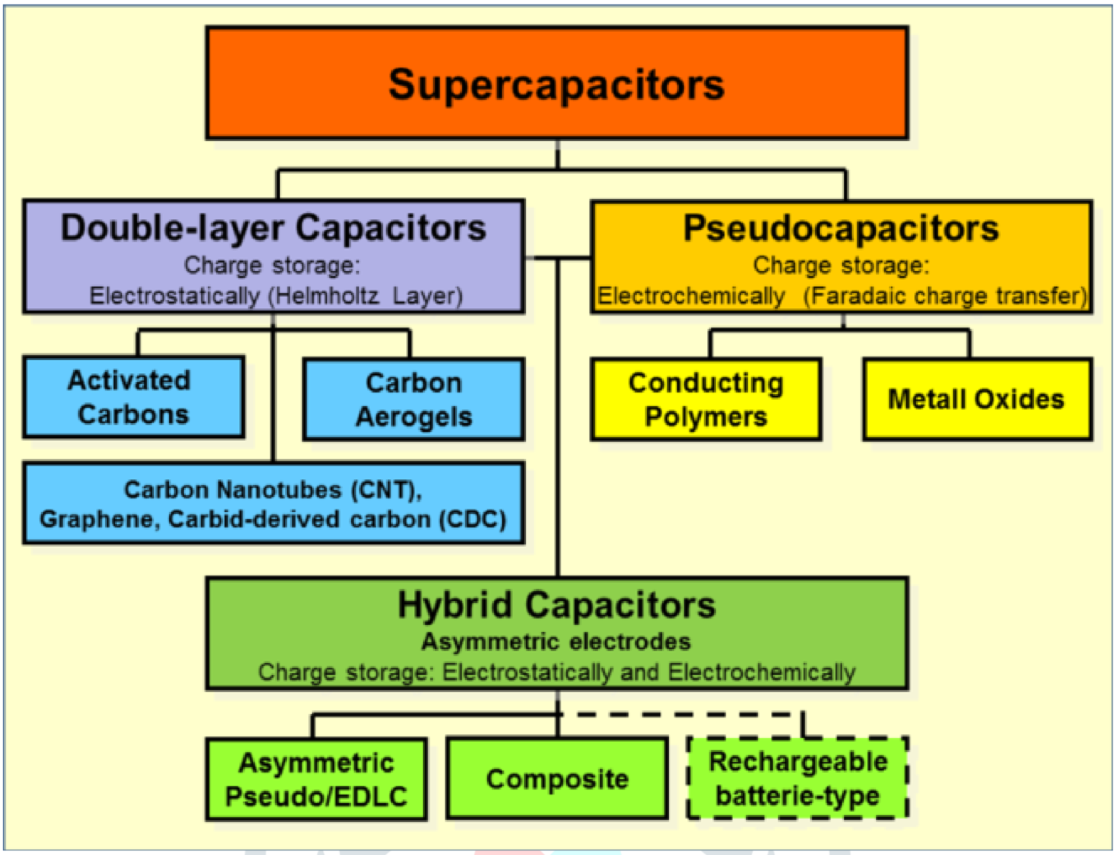

Fig.4: Classification of Supercapacitors

VI. ENERGY STORAGE MATERIALS:

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. 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.

2. CARBON NANOTUBES (CNT):

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. The CNT as supercapacitor electrode material due to its unique pore structure, good mechanical and thermal stability and superior electrical properties. Carbon nanotubes are produced via catalytic decomposition of some hydrocarbons and by carefully manipulating different parameters, it becomes possible to generate nano structures in various conformations and also control their crystalline structure. 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.

CNT can be categorized as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), both are generally explored as supercapacitor electrode materials. 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 m2/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.

3. GRAPHENE:

Graphene has enjoyed significant recent attention. 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. 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.

Among all carbon materials used as electrode materials electrochemical double layer capacitors, newly developed graphene has higher specific surface area (SSA) around 2630m2/g. If the entire SSA is fully utilized graphene is capable of achieving a capacitance of up to 550 F/g. 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.

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. 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. They are environmentally safe. The various materials that can be used for supercapacitors are activated carbon, activated charcoal, activated carbon fibers, carbon nanotubes, carbon aerogel, carbide-derived carbon, graphene, conductive polymers, metal oxides, etc.

VII. METAL OXIDES:

Oxides of transition metals are commonly used in redox electrochemical capacitors. The most popular types are ruthenium oxides (RuOx) [5,7] for which x value varies from 1.9 to 2.0. Specific capacitance for ruthenium oxide capacitors can even reach 720 F/g. This is the highest value of specific capacitance achieved for any known electrode material; however, RuOx applications are limited due to the high cost of this material. Promising alternatives include oxides of manganese, iron, indium, tin, vanadium and their combinations. For these, specific capacitance is around 150 F/g. A supercapacitor composed of Fe3 O4 as a negative electrode and MnO2 as a positive electrode is characterized by an operating voltage up to 1.8 V in aqueous electrolyte. Specific capacitance of such a device is 21.5 F/g, actual specific power – 405 W/kg and specific energy – 8.1 Wh/kg.

VIII. SUPERCAPACITOR APPLICATIONS:

Electrochemical capacitors are increasingly reliable devices which can work with wind turbines or photovoltaic cell systems [17]. Very fast charging/discharging rates offered by supercapacitors allow them to promptly adapt to load changes. Supercapacitors have found applications in household appliances, electronic tools, mobile telephones, cameras etc. They are also used in the power supply systems of electrically driven cars. In the automotive industry the main purpose of supercapacitors is to provide support for classic batteries – they act as an additional buffer during acceleration and braking. Such an arrangement lowers operational costs of the vehicle, as it extends battery lifetime. Supercapacitors protect the battery from harmful effects of peak loads. Recovery of braking energy by supercapacitors also allows reducing operational costs by decreasing energy consumption.

IX. CONCLUSION:

Supercapacitors are dynamically entering the power engineering market. Legal regulations concerning environmental protection and sustainable development foster installation of renewable energy sources, and this in turn generates the demand for reliable energy storage and conversion systems.The invention of Supercapacitors an important alternative energy storage device emerged offering high electrochemical properties, high power density and good stability. Supercapacitors have some intrinsic characteristics that make them ideally suited to specialized roles and applications that complement the strengths of batteries. In particular, Supercapacitors have great potential for applications that require a combination of high power, short charging time, high cycling stability, and long shelf life. With carbon materials, a high specific surface area and rational pore distribution were achieved, even though their capacitances and energy density are still low. With the discovery of graphene as electrode material for supercapacitor, it has opened a lot of research opportunities being carried out. Thus, supercapacitors may emerge as the solution for many application-specific power systems. So, it can be concluded that supercapacitors are indeed the very near future for all of us on globe.

X. REFERENCES:

[1] Zaharaddeen S. Iro, C. Subramani, S.S. Dash, *Int. J. Electrochem. Sci.*, 11 (2016) 10628 – 10643
[2] en.wikipedia.org/wiki/Supercapacitor
[3] en.wikipedia.org/wiki/Electric_double-layer_capacitor
[4] batteryuniversity.com/learn/article/whats_the_role_of_the_supercapacitor
[5] M.V. Kiamahalleh, S.H.S. Zein, G. Najafpour, S.A Sata and S. Buniran, *Nano*, 7 (2012) 1
[6] M. Jayalakshmi and K. Balasubramanian, *Int. J. Electrochem. Sci.*, 3 (2008) 1196
[7] M.S. Halper and J. C.Ellenbogen, *Mitre Nanosystems Group*, (2006)
[8] H. Choi and H. Yoon, *Nanomaterials*, 5 (2015) 906

[9] S. Mohapatra, A. Acharya and G. S. Roy, *Lat. Am. J. Phys. Educ*., 6 (2012) 380
[10] S.M. Chen, R. Ramachandran, V. Mani and R. Saraswathi, *Int. J. Electrochem. Sci.*, 9 (2014) 4072
[11] M. Beidaghi, Florida International univeristy, (2012)
[12] T. Chen and L. Dai, *Materials Today*, 16 (2013) 272
[13] A. Burke, Z. Liu and H. Zhao, Institute of transportation studies, (2014).
[14] A. Burke, *Electochim. Acta*, 53 (2007) 1083
[15] P. Simon and K. Naoi, *Electrochem. Soc*., (2008) 34
[16] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya and L.C. Qin, *Phys. Chem. Chem. Phys*, 13 (2011) 17615. P. Tamilarasan,
[17] A.K. Mishra and S. Ramaprabhu, *IEEE*, (2011).
[18] C. Du and N. Pan, *Nanotech. Law & Business*, 4 (2007)569
[19] J. Li, X. Cheng, A. Shashurin and M. Keidar, *Sci. Res*., 1 (2012) 1.
[20] 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.
[21] P. Karthika, N. Rajalakshmi and K.S. Dhathathreyan, *Soft Nanosci. Lett*., 2 (2012) 59.
[22] T.Y. Kim, G. Jung, S. Yoo, K.S. Suh and R.S. Rouff, *Acsnano*, 7 (2013) 6899.
[23] 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.
[24] K. Moon, Z. Li, Y. Yao, Z. Lin, Q. Liang, J. Agar, M. Song, M. Liu and C.P. Wong, *IEEE*, (2010) 1323.
[25] Anna Lisowska-Oleksiak et.al, Supercapacitors as Energy Storage Devices, pp: 71-76.