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Mesoporous Materials for High-Performance Electrochemical Supercapacitors

Ranganatha Sudhakar

Abstract

Supercapacitors are very important kind of electrochemical energy storage devices. It differs from those of batteries and exhibit high power density. The energy storage in supercapacitors is influenced by many parameters like nature of electrode material, current collector, electrolyte, etc. among which most crucial is the morphology of the electrode. This makes most of the research works are targeting in designing suitable and high performing electrode materials by adopting new routes of synthesis, modifying the regular methods so on. Herein we discuss the fundamentals of supercapacitors, their design and approaches to obtain high-performance electrode materials.

Keywords: supercapacitors, porous, mesoporous, specific capacitance, carbon materials

1. Introduction

Materials with diverse structural and consequent physicochemical properties can be successfully evaluated for their electrochemical methods. Especially porous materials, which can be synthesized, modified or functionalized electrochemically or via other synthetic routes, exhibit good electrochemical properties. There is a direct link between porosity and electrochemistry and can be connected to following aspects like, composition and structural information by electroanalytical methods, electrosynthetic routes to design suitable porous materials, designing electrocatalysts for synthesis and sensing applications, magnetochemical, photochemical, electrochemical, photovoltaic etc [1–8] (**Figure 1**).

Generally there are many methods to analyze porous materials and electrochemical methods can be used to have analytical data on porous materials. Especially voltammetric techniques are extensively adopted as they provide information on reaction mechanisms. Also, AC impedance measurement aids to have information on corrosion and other metal surface related studies. This methodology, conceived as the recording of the voltammetric response of a solid material mechanically transferred to the surface of an inert electrode, provides information on the chemical composition, mineralogical composition, and specification of solids. Application of these porous materials especially intersecting with electrochemistry involves important concerns like transduction, sensing, gas production and its storage, energy production and storage and pollutant degradation. Application of porous materials is very significant in electrochemical energy generation and

storage along with advanced dielectric materials for integrated circuits suitable for microelectronics industry.

Different electroanalytical techniques can be made use for getting information on the composition as well as structure of microporous materials. Generally, we can divide these techniques into two classes. Firstly, conventional electrochemical methods like cyclic voltammetry (CV), chronoamperometry, chronopotentiometry, and coulometry, and secondly, electrochemical impedance spectroscopy (EIS). We do have other additional methods namely, differential pulse- and square-wave voltammetries, electrochemical quartz crystal microbalance (EQCM), electrochemical atomic force microscopy which can efficiently characterize microporous solids. There is a possibility of having these techniques coupled with ultraviolet-visible spectrometry, Fourier-transform infrared spectroscopy, X-ray diffraction. Electrochemical phenomena involve electron transfer processes through a two-dimensional boundary (interface) separating the metal type electrode and the ionically conducting electrolyte. Such kind of phenomena can be characterized by electrochemistry, focused on the heterogeneous electrode/electrolyte charge transfer process, and ionics, which throw light on ionically conducting liquid/solid phases. As far as porous materials are concerned, ionic conductivity being a general property, can be varied successfully by doping, defects and temperature. Astonishingly, some porous materials like hydrated aluminosilicates, behave as liquid electrolyte-like conductors, and as solid ionic conductors when dry. The classical model for describing the electrode-liquid electrolyte junction considers a formation of dense accumulation of oppositely charged species at the interface of electrode, double layer with dipole-oriented solvent molecules and a double layer of charge-separated ions, which results in a capacitive effect. Next to this, away from double layer, there is a less structured region, the diffuse layer, reducing randomly organized bulk-electrolyte solution. The earlier formulation, according to Helmholtz, distinguished between the inner (Helmholtz) layer, which composed all species that are specifically adsorbed on the electrode surface, and the outer (Helmholtz) layer, which comprises all ions closest to the electrode surface but are not specifically adsorbed. As area and geometry of the electrode surface affect

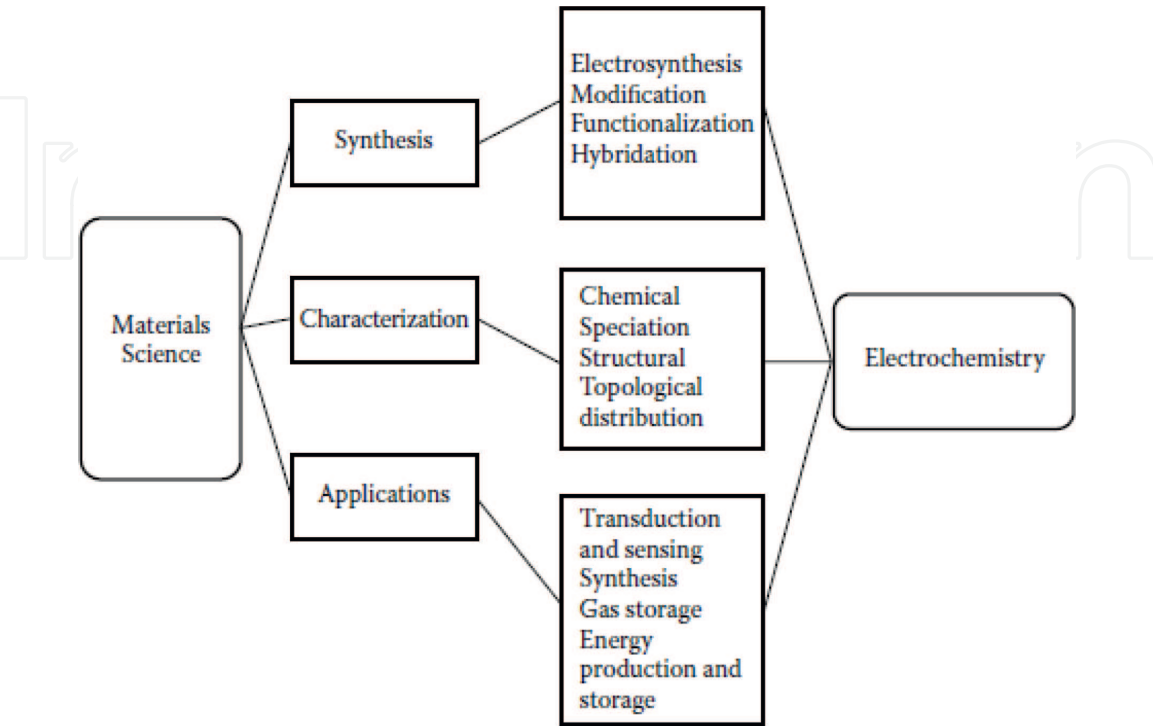


Figure 1.
Chart depicting link between diverse materials, their syntheses, characterizations and electrochemistry.

the double-layer capacitance, porous materials having large effective surface areas can lead to high capacitance effects, which will severely influence the electrochemical process. In the case when there is an establishment of some potential difference between electrode and electrolyte, some phenomena can be observed at the interface; charge transfer through electrode and electrolyte interface and concomitant charge transfer process in the electrolyte and electrode in particular involving ion restructuring in the double-layer zone. Resulting current flow can be described in terms of the summation of faradaic current which is associated with ion restructuring in the vicinity of the electrode surface. Let us consider an electroactive specie and its corresponding redox reaction or either a reduction or an oxidation reaction at an inert electrode surface. Faradaic current's magnitude is significantly influenced by mass transfer of these species from bulk of the solution to the surface of electrode. There are some particular ways how mass transport can occur. They are, diffusion where concentration difference makes transport happen, convection where momentum gradient drives and migration wherein electric field is the driving force. When solution is stirred or undergoes some vibrations, convection occurs. Ionic migration is diminished at highly concentrated supporting electrolyte. Under planar, semi-infinite diffusion conditions (*vide infra*), the faradaic current, i , for the reduction of a species whose concentration in the solution bulk is c , and its diffusion coefficient is D , at a plane electrode is then given by:

$$i = nFAD \left(\frac{\partial c}{\partial x} \right)_{x=0} \quad (1)$$

where A represents the electrode area, n is the number of transferred electrons per mole of electroactive species, and x is the distance from the electrode surface. This current is proportional to electroactive species concentration at the interface. Considering electron transfer phenomena across at the interface a heterogeneous one, heterogeneous electron transfer rate constant is applied to account the same.

The kinetics can be described via the Butler-Volmer equation:

$$i = -nFAk^0 \left[C_{red}^0 \exp \left[\frac{nF(1-\alpha)(E-E^{0'})}{RT} \right] - C_{ox}^0 \exp \left[-\frac{\alpha nF(E-E^{0'})}{RT} \right] \right] \quad (2)$$

Here, concentrations of redox species are represented by C_{ox}^0 and C_{red}^0 , standard rate constant for the electron transfer (heterogeneous) corresponding to the reaction is k^0 and symmetry for the energy barrier is α . Also, E and $E^{0'}$ are applied and formal electrode potentials and $E - E^{0'}$ being overvoltage which represents the additional energy provided beyond equilibrium potential value. It is to be noted that, we obtain the Nernst equation from Butler-Volmer condition whenever system reaches equilibrium or current becomes zero and reaction will be very fast. Electrochemical reactions can be regarded as multistep as may be a reaction could be associated with reactions in solution phase or gas evolution or deposition. Electrochemical methods can provide mechanistic information of the processes by the aid of kinetics of interfacial reactions and coupled chemical reactions [9–15].

2. Mesoporous materials in energy storage and conversion

In current society, we are encountering energy crisis and consequently production, storage of electrical energy and its conversion to various other forms are most in must demand. Batteries are electrical power sources where chemical energy is converted into electrical energy via spontaneous electrochemical reactions. These

power sources may be composed of one or several individual sets of electrodes making cells wherein reduction and oxidation reactions occur at specific electrode system which is separated by a diaphragm. These batteries are classified as primary and secondary which are characterized as chargeable and non-chargeable. There is a clear contrast between these batteries and capacitors which store electric energy with two conducting elements separated by a dielectric. With the application of potential difference between the two electrodes, capacitor acquires charge and stores. These capacitors in addition to be used in electronic circuitry, rectifiers, frequency filters, etc., can be also find application in energy storage especially for shorter periods. The charge/discharge processes in batteries goes with interconversions of electrode materials involving phase changes. Also, this process will be irreversible to some extent which restricts its cycle life which is a crucial parameter to decide whether battery is efficient or not. As achieving high stability and cyclability in energy storage devices along with the usage of environment friendly and inexpensive materials are the focus of considerable research efforts. In this context, the use of porous materials with high surface area plays an essential role.

Conventional capacitors are composed of nonpolarized dielectric materials such as ceramics or polymers, with picofarad to microfarad capacitance range. Polarized which are electrochemical capacitors involve generally anodic oxides of Al, Ta, or Nb, with the capacitance in microfarad to millifarad range. In recent past, new class of capacitors called supercapacitors are devised. These follow two probable mechanisms for charge storage: double layer and charge transfer reactions, the latter resulting in the so-called pseudocapacitances. Double-layer capacitance results from the separation of charge at the interface between a solid electrode and an electrolyte, whereas pseudocapacitance arises from fast, reversible faradaic reactions taking place at or near a solid electrode surface over an appropriate range of potential. Such redox reactions can go beyond the surface area and penetrate into the bulk of these materials. Metal oxides such as RuO_2 and IrO_2 offer the highest specific capacitance values (750 F/g), with the limitation that they are toxic and expensive. Hence, porous transition metal oxides such as CoO_x , NiO_x , and MnO_2 are currently under massive research as electrode materials for supercapacitors [16–20].

Electrochemical evaluation of their performance is usually conducted by preparing electrodes by pressing a mixture of the powdered material with a conducting material and binder i.e., acetylene black plus polytetrafluorene correspondingly, onto metal strip as current collectors (typically $1 \times 1 \text{ cm}^2$). Cyclic voltammetric analysis of electrodes prepared from such materials allows researchers to differentiate between a purely capacitive behavior and a pseudocapacitance response. The purely capacitive response results in box-shaped voltammograms. The specific capacitance, C_{sp} (F/g), can be evaluated from CVs as the quotient between the “box” current, I , and the product of the potential scan rate and the mass of the composite layer, m :

Analogously, the specific capacitance can be calculated from charge/discharge curves at a given current rate by using the relationship:

$$C_{xp} = \frac{I}{m \Delta V_d} \quad (3)$$

where I represents the discharge current density, m is the mass of the composite, Δt is the total time of discharge, and ΔV_d is the potential drop during discharge.

$$C_{xp} = \frac{I \Delta t}{m \Delta V_d} \quad (4)$$

The discovery of storing an electrical charge on surface arose from process associated with mechanical rubbing of amber in ancient times. Later in mid eighteenth

century the phenomenon was understood as “static electricity” and various “electrical machines” were being developed.

Scientists of General Electric Company were experimenting with devices using porous carbon electrode in 1957 and they found electric double layer capacitor effect. They observed carbon pores can store energy and it exhibited an exceptionally high capacitance. A research group in 1966 at Standard Oil of Ohio accidentally rediscovered the same phenomenon while working on fuel cells. The cell was composed of two layers of activated charcoal sandwiched thin insulator, and the mechanical design remained the same for most electric double layer capacitors to date. In 1978 NEC introduce the term Supercapacitor and its application was used to supply backing up computer memory. Due to its application, many scientists delved into supercapacitor which led to trying of other composite as electrode material such as metal oxides and polymers especially conducting polymers, etc. Among the challenges faced in this century, energy storage is unquestionably significant. It is a challenge to search for environmentally friendly and low-cost energy storage material combination be found, in response to the needs of emerging ecological concerns and modern society. Supercapacitors are energy storage systems with very high capacity and a low internal resistance which are capable 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. This is an alternate energy storage device with high power density and long cycle life. Supercapacitors are characterized with higher energy densities of about 5 Wh kg^{-1} in contrast to conventional capacitors. Although supercapacitors have the lower energy densities than secondary or chargeable batteries like Li ion batteries wherein their ultrafast charged and discharged capability lead to high power densities of about 10 kW kg^{-1} . The principle of energy storage in a supercapacitor is the ion adsorption on an electrode/electrolyte interface forming electric double layer leading to electrical double layer capacitors, EDLC or due to electron transfer between the electrolyte and electrode through fast Faradic redox reaction which is termed pseudocapacitors. These can find applications in electronics, transportation, communication and aviation. It can also be used in a wide range of energy capture and storage applications either by themselves as a primary power source or in combination with batteries and fuel cells. Supercapacitors can be used as back-up supplies used to protect against power disruption and load-levelers as back-up power for memories, microcomputers, clocks, system boards, etc. In the case of electric vehicles they are being used in combination with batteries and fuel cells. A supercapacitor consists of two electrodes, an electrolyte, and a separator which isolates the two electrodes electrically. Electrode material is the most important constituent of a supercapacitor. Key advantages of supercapacitors in comparison with other energy storage devices in terms of long life, high power, flexible packaging, wide thermal range of -40 to 70°C , low maintenance and low weight. Supercapacitors can best be made use in areas requiring applications with short load cycle as well as high reliability. Energy recapture sources such as forklifts, load cranes and electric vehicles, power quality improvement mostly utilize supercapacitors. Most promising application is in fuel cell vehicles and low emission hybrid vehicles. High power capability of supercapacitors can bridge the short time duration between a power failure and the startup of backup power generators. Though energy density of supercapacitor is greater than that of conventional capacitors which is considerably lower than batteries or fuel cells. Electrochemical performances of an electrode material strongly depend on parameters like surface area, electrical conductivity, wetting of electrode and permeability of electrolyte solutions which are very significant. The power needed by an application as well as the speed of storage process decides the kind of device to be applied. Indeed, when

it comes to applications the ones that need faster discharge rate go for capacitor while the slower ones go for batteries. From **Figure 2**, it can be noted that batteries are capable of attaining up to 150 Wh/kg of energy density, around 10 times what an electrochemical supercapacitor is capable of. In terms of power density batteries do not possess the capability of having capacities of electrochemical capacitors. Batteries hardly reach 200 W/kg which is about 20 times less than that of expected electrochemical capacitor performance. Batteries experience shortcoming like rapid fall in performances due to fast charge discharge cycles or cold environmental temperature, they are expensive to maintain and have a limited cycle life [3–8].

2.1 Electrochemical supercapacitors

Based on the working principle, supercapacitors can be classified into three different groups. The first being electrical double layer capacitor EDLC where in capacitance is achieved due to pure electrostatic charge accumulates at the interface. This class of set up strongly depends on electrode surface area that is exposed to ions of electrolyte. Second is the pseudocapacitor, which considers a fast and reversible faradic process taking place due to electro active species. The third group is hybrid which combines the properties of both EDLC and pseudocapacitors. Selection of electrode material is of very high importance as it determines the resultant output. As charge storage in EDLC type is a surface phenomenon, surface property of electrode greatly affects capacitance of the capacitor. There are few challenges faced by supercapacitors include low energy density, production cost, low voltage per cell and high self-discharge. Most reliable way to overcome the shortcoming of low energy density is to design new electrode material. Popularly carbon materials, metal oxides and conducting polymers are used as electrode materials. Carbon materials have been used due to their high surface area. Metal oxides offer attractive choices as electrode material due to high specific capacitance with low resistance, making easier to construct high energy and power supercapacitors. Conducting polymers store and release charge based on reduction-oxidation processes. Supercapacitors cannot substitute batteries but could work as a supplement in terms of momentary and temporary power outage by providing instantaneous current required thereby reducing battery current. Electrochemical supercapacitors can be installed in parallel to compensate for momentary and

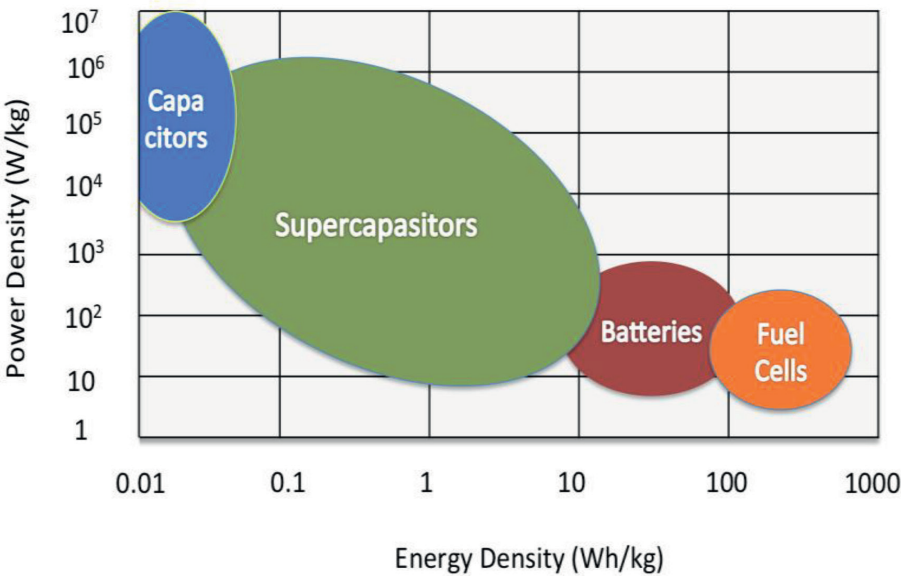


Figure 2. Ragone plot showing energy density and power density for different kind of energy storage devices.

temporary interruptions in large scale battery units. Currently, all the researches focused on supercapacitors are on how to improve the energy density while maintaining high power density, fast charge/discharge and cycling stability.

Designing an EDLC involves two carbonaceous materials as electrodes, an electrolyte and a separator. The mechanism of charge storage in this case is through non-faradaic reactions that is via electrostatic one. There will be a creation of electrochemical double layer and voltage is applied there one can see accumulation of charges onto the porous surface of electrodes and ions in the electrolytic solution will diffuse towards opposite poles. The energy density at the electrode is proportional to specific surface area of the electrodes directly and their distance indirectly. Fast energy uptake, delivery and better power performance can be achieved by maintaining these parameters constructively. This principle of charge storage which is non-faradaic one is beneficial in contrast to that of batteries wherein electrode swelling is obvious because of charge and discharge processes. One can list out major differences between EDLC and battery. They are basically, wrt very long cycle life of EDLC compared to that of battery because of non-faradaic type of charge storage and non-involvement of solvent of electrolyte in charge storage (**Figure 3**).

Energy storage capacity and output of EDLCs strongly dependent on the type of electrolyte adopted. Reversible adsorption of ions from the electrolytes on the electrode surface drives the energy storage in double layer capacitors. Here there will be no electrochemical reactions and only physical absorption is considered and consequently no charge transfers hence no net ion exchanges across the interface of electrode and electrolyte. As strength of the electrolyte solution is constant and electrodes are intact throughout, this class of double layer capacitors are capable of sustaining millions of continuous charge/discharge cycles. The model of energy storage could be defined by the relation.

$$E = 0.5 CV^2 \tag{5}$$

where E is the entire energy delivered, C is the capacitance and V is the working potential range [1–3].

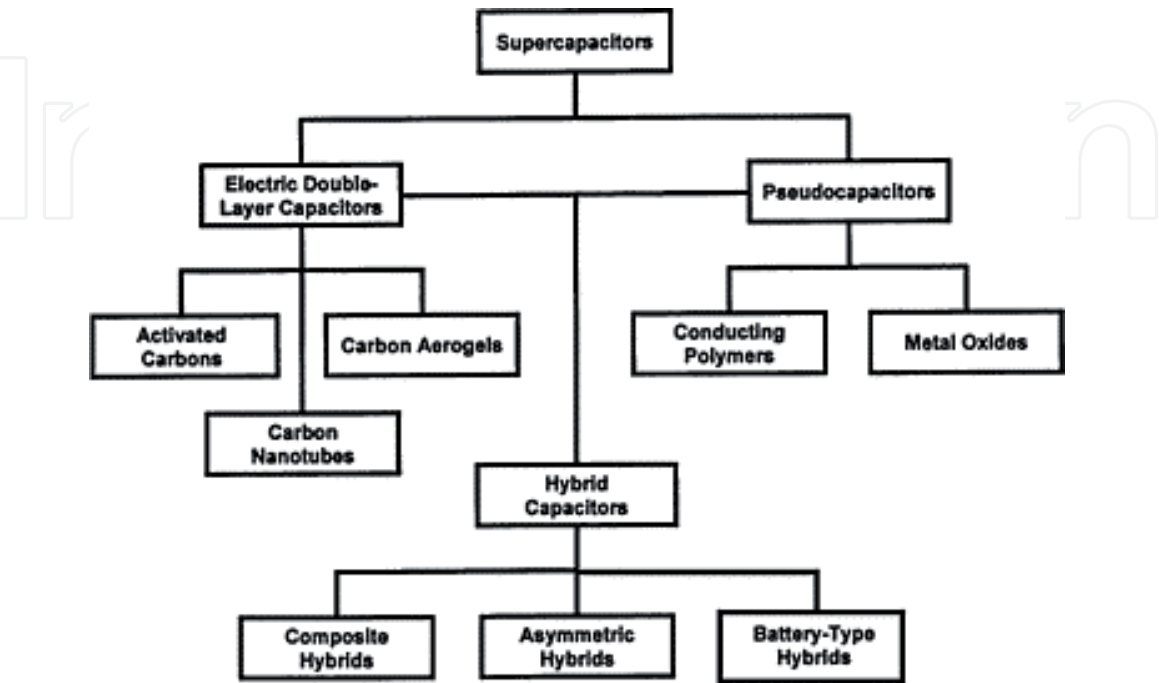


Figure 3.
Taxonomy of supercapacitors.

In contrast, charge storage in pseudocapacitors is dependent on faradaic process involving charge transfer at electrode electrolyte interface. Due to redox reactions between electrode and electrolyte when potential is applied makes to pass faradaic current through the supercapacitor cell. This makes them to exhibit higher specific capacitance compared to EDLCs. Frequently employed materials for this class faradaic materials are metal oxides, conducting polymers. As these involve in strong redox reactions as like battery materials, suffer lack of stability and cycle life. The pseudocapacitive class of capacitors, can be either surface phenomenon or bulk storage based on the location of the reactions. Pseudocapacitors involving multiple stable oxidation states, will be able to deliver higher energy density, however these suffer from relatively lower power density than EDLC types as Faradaic reactions are usually slower than those of non-faradaic processes. Also, it is to be noted that, because of redox reactions and corresponding physical changes in the electrodes, these show poor cycling stability compared to EDLCs.

The electrode materials mainly determine the performance of supercapacitors. Depending on the charge storage mechanism and active materials used, electrode materials for supercapacitors can be classified into three categories: (i) carbon materials, (ii) metal oxides/hydroxides and (iii) conducting polymers.

To compare and contrast EDLCs and pseudocapacitors, key parameters to be considered are cycle stability, energy and power densities. In the case of EDLCs, cycle stability and power performance will be very good, whereas, specific capacitance will be greater with pseudocapacitors. Hybrid systems combine benefits of both the mechanisms and offer extremely good power and energy characteristics, cycle life, cell voltage. Also, some advantages can be added, if one can play with different organic and inorganic electrolytes. Current research is focused on different configurations of these hybrid systems like composites, asymmetric and battery type (**Figures 4 and 5**).

2.1.1 Mesoporous materials as electrode materials for supercapacitors

Research and innovations on complex and hierarchically organized porous materials has made tremendous progress and findings in the last decades and the area is still evolving. There has been many synthetic approaches developed towards designing porous materials that exhibit interconnected pore dimensions on several length scales, from molecular (0–2 nm) via nano- (2–100 nm) to macroscopic (4100 nm). Pores smaller than 2 nm are characterized micropores, pores with sizes between 2 and 50 nm mesopores and pores larger than 50 nm are macropores. Such multilevel porous architectures confer unique properties and features to materials depending on the combination of pore sizes, e.g., micro- and mesopores impart high surface areas and pore volumes providing size and shape selectivity and large interfacial areas, while larger pores of about 450 nm reduce transport limitations in the material and facilitate mass transport to the active sites. Diverse techniques and routes have already been reported for the preparation of micro-macroporous, micro-mesoporous, meso-macroporous or micro-meso-macroporous materials with great potential for applications in the fields of catalysis, sorption, separation, energy storage and conversion, sensing and biomedicine, i.e., medical diagnostics or therapies. Structural characteristics such as the total amount of pores, the accessibility of the pores (ratio of closed to open pores), tortuosity and inter connectivity, gradients, etc., and very importantly, the chemical composition as well as the processability in terms of shaping (films, fibers, monoliths, etc.) make materials suitable for specific applications. As an example, for the importance of structure and morphology of the materials, highly porous, hierarchically organized macroscopic monolithic material, can give lower backpressures, a higher permeability and better performance in flow-through catalytic or separation systems [13–18].

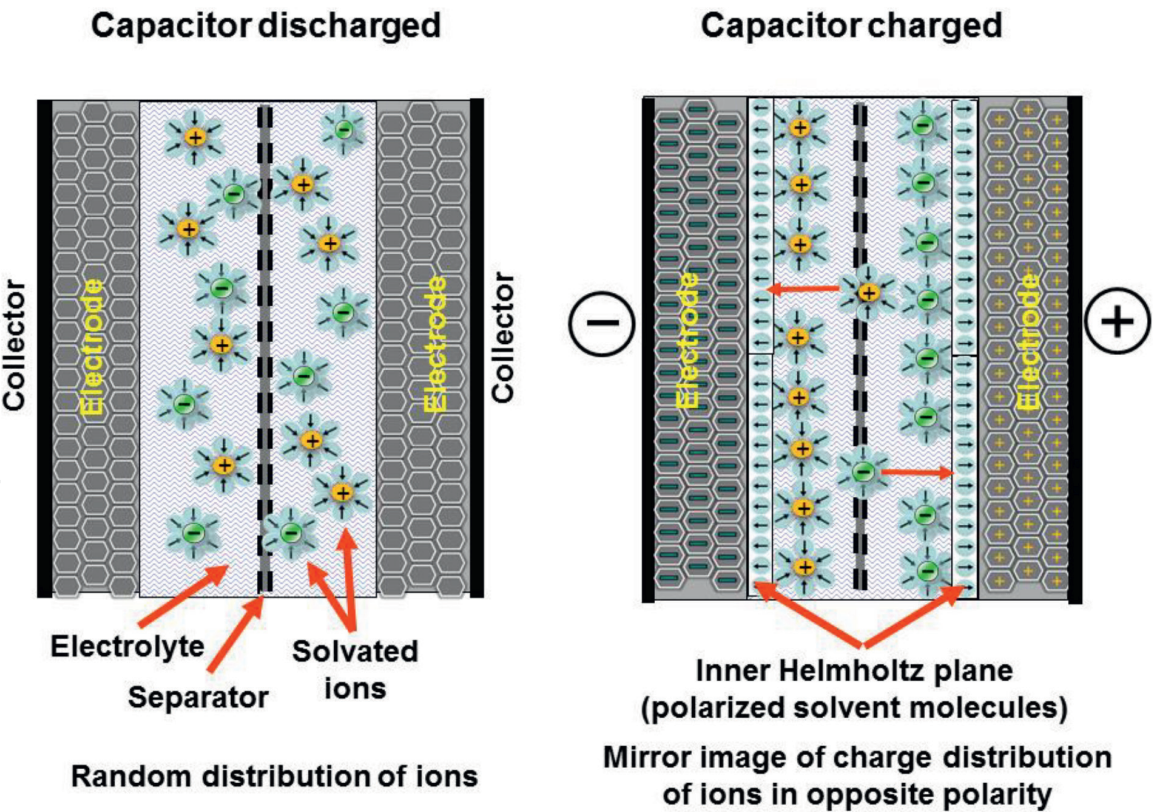


Figure 4.
Mechanism of charge storage in electrochemical double layer capacitor (EDLC).

Pseudocapacitance with specifically adsorbed ions

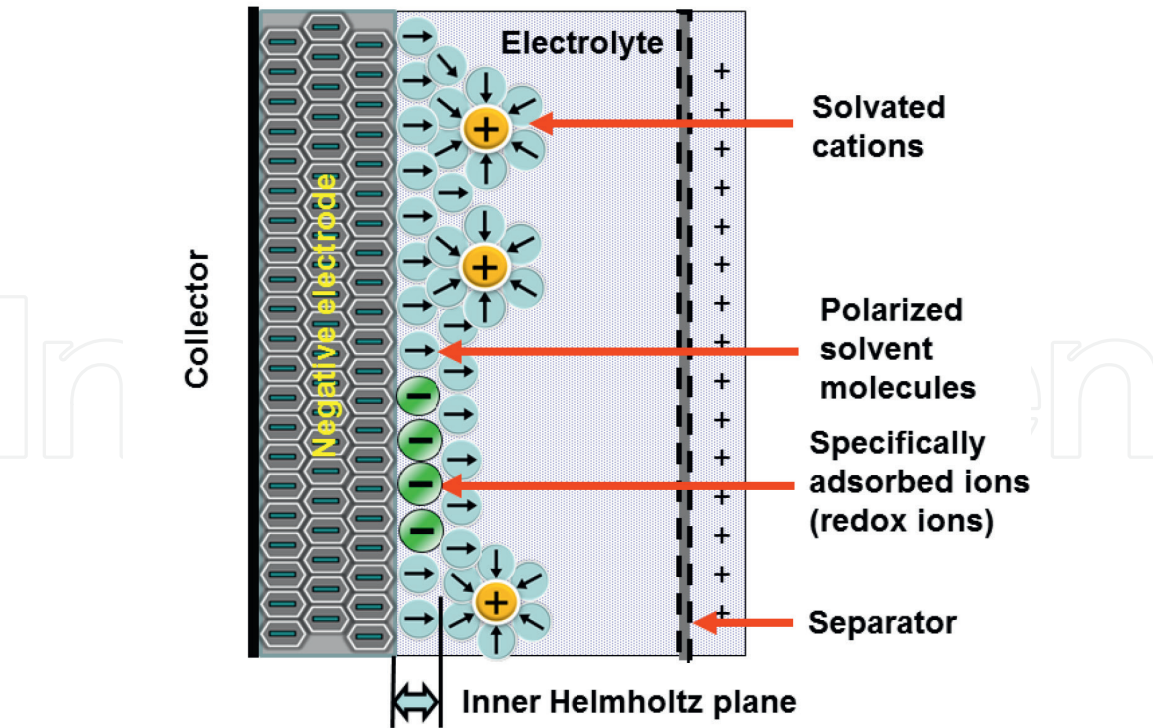


Figure 5.
Mechanism of charge storage in pseudocapacitors.

Materials with high surface areas are considered to enhance supercapacitor performance. In addition, pores in the electrode material not only increases the surface area of the material but also facilitates charge to be stored in these micro/meso pores. Electrodes in EDLCs have been designed using many types of carbonaceous

materials including activated carbons, carbon nanotubes (CNTs), carbon aerogel (CAGs), and carbon nanofibers (CNFs) and graphene. Activated carbon possesses very high surface area, relatively low cost and largely available and therefore a popular electrode material. It exhibits differently porous structures and classified based on their pore sizes like micro (<2 nm), meso (2–50 nm), macro (>50 nm) associated with high surface area. Ions get adsorbed and accumulated in the micropores to form double layer and ion diffusion to these micropores will be via mesopores which offers low resistive paths for electrolytic ions. These pores can be controlled to have uniform pore sizes with highly ordered nanochannels and large surface area in template carbons. Templated carbonization is superior than activated carbon in terms of degree of control over pore size distribution and interconnection of pores. Charge storage and rate capability can be seen enhancing in the case of interconnected pore structures. Alternatively, CNTs are also a common class of electrode materials as it is mechanically strong and highly conducting. These show higher accessibility to electrolytic ions due to mesopores of CNTs which are larger than micropores of activated carbons. One more class of carbonaceous materials, CAGs also being employed as electrode materials as they possess outstandingly high specific surface area and significant electrical conductivity. Mostly sol–gel method will be employed to design these CAGs, using resorcinol and formaldehyde aerogels. In recent past, graphene has become most popular materials for supercapacitor due its chemical stability, large surface area and high conductivity as a carbon based material, with restacking of sheets being a problem while fabricating the electrodes. CNFs which are derived from carbon based polymers are known for greater mechanical strength, surface area, flexibility and conductivity. The flexibility and freestanding capacity of CNFs dismisses the need for using binders during fabricating electrodes in turn enhancing the mass fraction of the active material in the device. Electrospinning is a simple and widely employed technique to synthesize nanofibers from a wide group of polymers. In general, the polymer blend technique is a promising route to design carbon materials with fine and controlled pores. This can be achieved by blending of two immiscible polymers allowing control over the blend texture to obtain desired pore sizes.

Supercapacitors have attracted a lot of attention recently as energy storage devices, due to their high power density, long cyclability, wide working potential window and broad temperature range. Though supercapacitors offer a higher energy density, they possess lower energy density compared to those of batteries. Therefore, there has been a lot of scope improving energy density of supercapacitors high power density. As mechanism of charge storage is different in different types of supercapacitors, routes to improvise energy density also varies. As EDLCs store the charges electrostatically, high surface area and porosity of the electrode material enhance the energy density. Additionally, type of the material, like CDC, graphene, CNF, etc. further influence the extent of charge storage in turn the energy. Among these, carbon nanofibers are one of the most promising candidates as they pose relatively good mechanical strength, high surface area, relatively higher conductivity, freestanding nature and flexibility.

One of the most popularly employed electrode material is activated carbon (AC) which may be attributed to large surface area, good electrical properties and moderately economical. AC can be prepared by either physical or chemical activation from various types of carbonaceous materials like wood, coal nutshell, etc. These can be physically activated at temperatures 700–1200°C in the presence of oxidizing gases like CO₂ and air. Chemical activation is carried out at a lower temperature 400–700°C employing sodium hydroxide, potassium hydroxide, zinc chloride and phosphoric acid. Activation process imparts AC to possess numerous physiochemical properties with well-developed surface areas of up to 3000 m²/g. Porous

structure of AC obtained after activation processes will have a broad pore size distribution consisting of micropores (50 nm). Research efforts have been made to see the effect of different electrolytes on the capacitance performance of AC. It was observed that the capacitance of AC is higher in aqueous electrolytes (ranging from 100 to 300 F/g) as compared to organic electrolytes [10–14].

With the discovery of carbon nanotube (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 overall resistance of the components. Seriously attention is been paid to CNT as supercapacitor material because of its unique pore structure, good mechanical and thermal stability with superior electrical properties. Catalytic decomposition is the most frequently adopted method to synthesize carbon nanotubes and further careful manipulation of different parameters, it becomes possible to obtain nano structures in various conformations and also control their crystalline structure. Carbon nanotube have interconnected mesopores which allow charge distribution that utilizes almost all accessible surface area. These have a lower ESR than those of activated carbon as the electrolyte ions can diffuse into the mesoporous network. CNT can be typically of two types; single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), both of which can be employed as supercapacitor electrode materials. While targeting high power electrode materials, CNT are considered due to their remarkable electrical conductivity and readily accessible surface area. In addition, they offer support for active materials due to their high mechanical strength and open tubular network structure [12–16].

Graphene has enjoyed significant attention from scientific community. Graphene a one atom thick layer 2D structure has evolved as a unique and special carbon material that has capacity to store energy because of its superior characteristics of high large surface area, electrical conductivity and chemical stability. Graphene has been recognized as superior supercapacitor electrode material as the charge storage is not dependent on pore distribution unlike in the case of other carbonaceous materials. Specific surface area of about 2500 m²/g could be obtained and if it is utilized completely, capacitance of 500–600 F/g could be achieved. Following methods can be employed to produce graphenes, like micromechanical exfoliation, chemical vapor deposition, unzipping of CNTs, epitaxial growth, arch discharge method, electrochemical and chemical methods and intercalation methods in graphite. Many strategies are being applied so as to refrain restacking of graphene sheets so that high specific surface area and intrinsic surface capacitance could be achieved. To list out major reports from literature, thermally exfoliated graphitic oxide offers specific capacitance of 117 F/g and energy density of 31.9 Wh/kg. Graphene from modified hummer's method and tip sonication, energy and power density obtained were 58.25 Wh/kg and 13.12 kW/kg at 7.5 A/g, which makes suitable for electric vehicle. Thermal reduction of graphite oxide at elevated temperature results in highly corrugated graphene exhibiting specific capacitance of 349 F/g [17–20].

3. Conclusion

Thus porosity of the material is very crucial and significant property in deciding performance in electrochemical energy storage. Different strategies are being practiced to obtain a porosity in turn a high surface area. The improved porosity and high surface area provides larger interfacial area between electrode and electrolyte which provides excess of interaction and charge storage.

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References

- [1] Conway BE. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications. New York: Kluwer Academic/Plenum Publishers; 1999
- [2] Arico AS, Bruce PG, Scrosati B, Tarascon JM, Schalkwijk WV. Nanostructured materials for advanced energy conversion and storage devices. *Nature Materials*. 2005;**4**:366-377
- [3] Simon P, Gogotsi Y. Materials for electrochemical capacitors. *Nature Materials*. 2008;**7**:845-854
- [4] Hall PJ, Mirzaeian M, Fletcher SI, Sillars FB, Rennie AJR, Shitta GOB, et al. Energy storage in electrochemical capacitors: Designing functional materials to improve performance. *Energy & Environmental Science*. 2010;**3**:1238-1251
- [5] Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical supercapacitors. *Chemical Society Reviews*. 2012;**41**:797-827
- [6] Hou J, Shao Y, Ellis WM, Obert B, Moore BY. Graphene based electrochemical energy conversion and storage: Fuel cells, supercapacitors and lithium ion batteries. *Physical Chemistry Chemical Physics*; **2012**(13):15384-15402
- [7] Patil S, Raut S, Gore R, Sankapal B. One dimensional cadmium hydroxide nanowires towards electrochemical supercapacitors. *New Journal of Chemistry*. 2015;**39**:9124-9131
- [8] Ma X, Zhang W, Kong L, Luo Y, Kang L. NiMoO₄-modified MnO₂ hybrid nanostructures on nickel foam: Electrochemical performance and supercapacitor applications. *New Journal of Chemistry*. 2015;**39**:6207-6215
- [9] Hu CC, Chang KH, Lin MC, Wu YT. Designing and tailoring of the nanotubular arrayed architecture of hydrous RuO₂ for next generation supercapacitor. *Nano Letters*. 2006;**6**:2690-2695
- [10] Brousse T, Belanger D, Long JW. To be or not to be pseudocapacitive? *Journal of the Electrochemical Society*. 2015;**162**(5):A5185-A5189
- [11] Zhao C, Zheng W. A review for aqueous electrochemical supercapacitors. *Frontiers in Energy Research*. 2015;**3**:23
- [12] Dubal DP, Ayyad O, Ruiz V, Gomez-Romero P. Hybrid energy storage: The merging of battery and supercapacitor chemistries. *Chemical Society Reviews*. 2015;**44**:1777-1790
- [13] Chen K, Xue D. Colloidal supercapacitor electrode materials. *Materials Research Bulletin*. 2016;**83**:201-206
- [14] Mohmood N, Zhang C, Yin H, Hou Y. Graphene based nanocomposites for energy storage and conversion in lithium batteries, supercapacitors and fuel cells. *Journal of Materials Chemistry A*. 2014;**2**:15-32
- [15] Boenstein A, Hanna O, Attias R, Luski S, Brousse T, Arbach D. Carbon based composite materials for supercapacitor electrodes: A review. *Journal of Materials Chemistry A*. 2017;**5**:12653-12672
- [16] Pumera M, Sofer Z, Ambrosi A. Layered transition metal dichalcogenides for electrochemical energy generation and storage. *Journal of Materials Chemistry A*. 2014;**2**:8981-8987
- [17] Li B, Zheng M, Xue H, Pang H. High performance electrochemical

capacitor materials focusing on nickel based materials. *Inorganic Chemistry Frontiers*. 2016;**3**:175-202

[18] Wang Y, Song Y, Xia Y. Electrochemical capacitors: Mechanism, materials, systems, characterization and applications. *Chemical Society Reviews*. 2016;**45**:5925-5950

[19] Feinle A, Elsaesser MS, Husing N. Sol-gel synthesis of monolithic materials with hierarchical porosity. *Chemical Society Reviews*. 2016;**45**:3377-3399

[20] Yang Q, Lu Z, Liu J, Lei X, Chang Z, Luo L, et al. Metal oxide and hydroxide nanoarrays: Hydrothermal synthesis and applications as supercapacitors and nanocatalysts. *Progress in Natural Science: Materials International*. 2013;**23**(4):351-366