2.1 Introduction

Now-a-days the supercapacitor plays versatile and pivotal role as a device for both energy and power storage in contemporary technology. One must be acquainted with the theoretical aspect behind the supercapacitive phenomenon and different techniques used for the optimization of the samples.

2.1.1 About supercapacitor

Electrochemical energy storage systems are highly desirable in today’s information rich modern society and technology. Supercapacitors have been used diversely in the field of power/energy storage of hybrid electrical vehicles and digital communications, military, missiles etc. The first supercapacitor was developed by General Electric Company in 1957 using a porous carbon electrode based on the assumption that carbon increases the surface area of an electrode, producing a higher degree of capacitance. The supercapacitor is an electric charge storage device that shows high power and energy density as compared to battery and normal capacitor. Electrical energy can be stored either electrostatically in conventional capacitors or electrochemically in cells/batteries (electrochemical power sources). Electrical energy can be stored fundamentally by two different ways:

1) **Faradaic**: through oxidation and reduction of the electrochemically active reagents and,

2) **Non-faradaic**: directly in an electrostatic way as negative and positive electric charges lies on the plates of a capacitor. The principle by which electrical energy can be stored in a charged capacitor has been known since 1745. The electrical energy stored in capacitors is given by:

\[
E = \frac{1}{2} CV^2
\]

(2.1)

Where, \( V \) is the electrical potential drop across the capacitor when electrical charge ‘\( Q \)’ resides on its plates. ‘\( C \)’ is the capacitance of the condenser defined as:

\[
C = \frac{Q}{V}
\]

(2.2)

The amount of charge as well as the capacitance ‘\( C \)’ is directly proportional to the surface area of the plates. For ideal capacitors, the \( C \) is a constant and the \( Q \) and the \( V \) are linearly related. During charge-discharge, electrical charges do not cross the capacitor but
move in and out through the external circuit. The battery stores and supplies electrical energy through a quite different mechanism. The electrical energy is stored as the chemical energy of reactants, which are then transformed at the interface of the two electrodes of an electrochemical cell.

The electrochemical capacitor stores an extremely high amount of energy and discharge that energy at rates demanded specifically by the application. In the preparation of the supercapacitor electrodes, a number of materials like transition metal oxides, conducting polymers, carbon and nano-composites, biomaterials were employed by using the chemical and physical techniques [1]. Supercapacitors are divided into a number of types depending on the nature of charge storage and combination of electrode materials.

![Diagram of Supercapacitor Types](image)

**Figure 2.1:** Types of supercapacitor.
2.1.1.1 Existing materials of the electrodes

The type of material used in the supercapacitor electrodes play an important role in its performance. There are three main categories of the materials used for the electrodes: transition metal oxides, carbons and conducting polymers.

a. Transition metal oxides

TMOs having multi oxidation states show an excellent electrochemical performance with good stability. At present, Lokhande et al. [2] reported a critical review on the transition metal oxide based electrodes for the supercapacitor application. The prepared electrode shows remarkable supercapacitor performance due to its nanocrystallinity and amorphous nature. The prepared samples show supporting morphologies such as nanoroads, nanowires, flowery, porous, 3D architecture. They also show high value of the SC, low internal resistance and large potential window with mixed capacitive behavior [3]. The metal oxide prepared electrode shows reversible as well as irreversible redox process it may be due to polarization effect. The TMOs prepared electrodes were highly adherent to the substrates. The TMOs based electrodes show excellent stability.

b. Conducting polymers

Recently the polymeric materials were used as the supercapacitor electrode materials. The conducting polymers have different polymorphous with excellent specific capacitance, conductivity and less stability. Snook et al. [4] reported a critical review on polymeric materials used for the supercapacitor application. The prepared polymeric materials have p and n type conductivities. The XRD shows amorphous and semi-crystalline nature with supporting morphologies. The prepared electrodes showed good values of SC with low stability. The electrodes showed quasi pseudocapacitive nature. The reported potential window of the CV curve is ±1.2 V (i.e. large potential window). The electroactive polymer materials have a problem of swelling and shrinking that may lead to degradation during cycling.
c. Carbons

The carbon electrodes show an excellent supercapacitive performance due to their different morphologies, good conductivity and porous nature. Zhang et al. [5] reported a critical review on the carbon materials for a supercapacitor electrode. The prepared carbon based electrode showed high power density, a large SC and a large potential window. The carbon electrodes show symmetric CV nature with good stability and low ESR. The carbons have different allotropes i.e. MWCNT, SWCNT, graphene, fluorine, activated charcoal etc.

d. Composites

The nano-composite based electrodes play an excellent role to increase the supercapacitive performance. The prepared electrode shows maximum SC, SE, SP with low internal resistance and excellent stability. Recently, researchers are diverted towards the preparation of nano-composite based electrode materials for supercapacitors. Wang et al. [6] reported different nano-composite electrodes for the supercapacitor application. The prepared electrodes show low ESR with increase in the SC. It may be due to the mixed capacitive behavior. The electrodes were found suitable for any type of organic and inorganic electrolytes. Ambare et al. [7] reported a critical review on composites of metal oxide nanostructured based electrode material for supercapacitor. Ambare reports that composite electrode help to enhance electrochemical stability and to diminish mechanical stress.

2.1.1.2 Electrolytes used for electrochemical characterizations

The electrolytes play a very important role as per their ionic conductivities. The electrolytes used in the supercapacitor must have maximum possible decomposition voltage and broad range of potentials of electrochemical stability. The resistance of the supercapacitor cell is strongly dependent on the resistivity of the electrolyte used and the size of the ions of the electrolyte that diffuse into and out of the pores of the microporous

a. Organic

The advantage of organic electrolyte is its higher potential window. The disadvantage of it is that it requires high voltage ~ 3 V. It has high ESR. Examples are \((\text{C}_2\text{H}_5)_4\text{N}\cdot\text{BF}_4\) (TEA+BF4−), (Tetra-ethyl-ammonium tetra-fluoro-borate), (poly-methyl methacrylate) etc. Furthermore, the acidic electrolytes have the problem of corrosion of electrode due to the acidic nature.

b. Inorganic

Inorganic electrolytes are less viscous, high ion mobility and low ESR having moderate potential window e.g. KOH, NaOH, Na2SO4, Na2SO3, etc. As compared to the organic electrolytes, the inorganic electrolytes have high conductivity and easy ion intercalation.

c. Ionic

The ILs are used to increase the energy and power density of the supercapacitor electrodes. These are the room temperature molten salts, which can be considered for further research [8]. These are moistly used in the energy storage because of their good chemical and physical properties, such as high thermal stability, high electrochemical stability over a wide potential window (> 3V), non-toxic, non-flammability, variety of combination choices of cations and anions, acceptable conductivity at elevated temperatures. The ILs are liquids at ambient or even lower temperature and are composed entirely of ions, making them attractive solvent free ‘green electrolytes’. These are typically high viscous liquids and have low ionic conductivity at room temperature. There are two principal factors involved in the conductivity of electrolyte 1) the ability of the salt dissociation to give out free charge that carries cations and anions 2) the mobility of the dissociated ions in the electrolyte system.
d. Solid state electrolyte

Although liquid electrolyte is able to provide high ion mobility and fast charge-discharge rate, electrolyte leakage may be a serious problem as far as the environmental concern is considered. Solid state electrolyte with ion conducting gel/polymer membrane can be a good alternative for this. Solid state supercapacitors do not require rigid packaging but they are thinner and elastic, hence strongly attractive for future applications in wearable electronics and energy storage systems. The disadvantage of the solid state electrolyte is that it provides less power density, however new materials have been and are being tried in order to improve the performance. Nowadays researchers are trying to develop the solid state electrolytes with high ion mobility.

2.2 Supercapacitors based on double layer

In the electrochemical capacitor, microscopic properties of the ionic solution at a molecular level determine the specific double layer capacitance. The double layer is formed at an electrode/electrolyte interface consisting of one electronically conducting plate and other virtual plate that is the inner interfacial limit of conducting electrolyte solution phase. The double layer distribution of charges is established across this interfacial region which is composed of a compact layer having dimensions of about 0.5 to 0.6 nm, corresponding to the diameter of the solvent molecules and ions that occupy it and wider region of thermally distributed ions over 1 to 100 nm, depending on ionic concentration. A practical double-layer capacitor device however be constituted from two such interfacial double layers, each exhibits its own capacitance behavior. The concept of a double layer corresponding to a model consisting of two layers of opposite charges, separated by a small distance having atomic dimensions and facing each other, as on the substrate. This model was adopted by von Helmholtz to describe his perception of the distribution of opposite charges, quasi-2-dimensionally, 1st at the interface of colloidal particles. Fig.2.2 (a) shows behavior of electrolyte ion (positive charge) in the pore of the electrode when being charged and being discharged [9].

Helmholtz double layer is a structure of charge accumulation and charge separation that always occurs at the interface when an electrode is immersed into an electrolyte
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solution. This layer is formed as the solvated ions are blocked and accumulated at the electrode/electrolyte interface. This would create a charge separation between the solvated ions and the electrode material that resembles the charge storage mechanism similar to conventional capacitor, where the ‘d’ is distance between the conducting plate and the insulating material. In general, positive and negative charges are arrayed at counter position with an extremely short distance, such as atomic distance (~ 10 Å), at the contact interface between two phases where, in this case, the two phases would be the solid carbon electrode and the electrolyte. This interfacial charge distribution layer is explained as the Helmholtz layer. Fig.2.2 b) shows compact structure and is referred to as the Helmholtz double layer model [10]. The excess charge on the electrode surface is compensated by an accumulation of excess ions of the opposite charge in the solution. This structure behaves essentially as a capacitor as it possesses the double layer. The amount of charge is a function of the electrode potential [11, 12].

Figure 2.2 (a): Behavior of the electrolyte ion (positive charge) in the pore at the time of charging and discharging.
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Fig. 2.2 (b): Helmholtz double layer.

There are two types of current flow.

**Faradaic:**

The charge storage is achieved by an electron transfer that produces chemical or oxidation state changes in the electroactive materials according to Faraday’s laws that are related to electrode potential. This is known as pseudocapacitance in the supercapacitors. The energy storage is indirect and is analogous to that in a battery \[13\]. The charge transferred across the electrified interface as a result of an electrochemical reaction. In this case, the charge accumulation is achieved electrochemically.

\[
Q = nFN, \quad \frac{dQ}{dt} = i - nF \frac{dN}{dt}
\]  \hspace{1cm} (2.3)

**Non-faradaic:**

The process is associated with the movement of electrolyte ions, re-orientation of solvent dipoles, adsorption/desorption etc. at the electrode-electrolyte interface. In this case, the charge accumulation is achieved electrostatically.

**Equivalent Circuit Representation of Double Layer Capacitor**

Equivalent circuit associated with double layer capacitor is achieved by using the nyquist plot between imaginary vs real (Z” vs Z’) as a function of frequency. The electrical
behavior of the electrode interface is conveniently represented in terms of an equivalent circuit, the behavior of which would impersonate that of the actual interface with respect to current or potential responses to modulation [14]. The simplest case to that of a double-layer capacitor is capacitance in series with the solution resistance $R_s$ [Fig.2.3.a) and 2.3.b)].

![Diagram of capacitor charged voltage distribution and equivalent circuit](image)

**Figure 2.3:** Capacitor charged voltage distribution and equivalent circuit [8].

There is no charge leakage pathway so that such an interface is referred to as an ‘ideally polarizable electrode’. In practice, faradaic leakage currents can arise depending on the electrode potential and solution composition, so the circuit (Fig.2.3.b) is modified by the inclusion of a faradaic resistance $R_F$, in parallel across $C$ (Fig.2.3.c). The $R_F$ is usually inversely related to the electrode potential. $W$ is ‘Warburg’ resistance which occurs at low frequency capacitive region in which capacitive behavior is dominant and it is also called general imperfection resistance measured in ohm ($\Omega$).
Electrochemical supercapacitors based on high surface area carbon electrode materials and a variety of electrolytes have been most studied and commercially developed. High porosity carbons, usually in the form of activated carbon or carbon black, are immersed in an aqueous or non-aqueous electrolytic solution that has a very high capacitance due to its large specific surface area. Tanahashi et al. [15] reported that double-layer charging process is taking place without complete charge-transfer to or from ionic species either in the solution or at the interface but the storage of electric charge and energy is electrostatic (non-faradaic). Regular double layer capacitance arises from the potential dependence of the surface density of charges stored electro-statically (i.e. non-faradaically) at the interfaces of capacitor electrodes. On the capacitor electrodes (metals or carbon surfaces), the accumulated charge is a combination of excess or a deficit of conduction band electrons or in the near surface region of the interface, together with
counterbalancing charge densities of accumulated cations or anions of the electrolyte on the solution side of the double layer at the electrode interfaces.

2.3 Supercapacitors based on pseudocapacitor

Electrochemical storage of the electrical energy, achieved by redox reactions on the surface of the electrode or by specifically adsorbed ions that results in a reversible faradaic charge-transfer on the electrode interface. The pseudocapacitor has electrochemical redox reaction \( \text{Ox} + z \text{e} \leftrightarrow \text{Red} \) similar to a battery. However, the distinction between a battery and an electrochemical double layer capacitor is not unambiguous. A battery relies on electrochemical reactions that involve active materials in the electrode, where the charges are not diffuse into the material and intercalate. On the other hand, in an "ideal" electrochemical capacitor that utilizes carbon or metal oxides, the electrodes play passive role. That is, the electrode surface only participates by serving as sites for charged species to accumulate and no electron transfer occurs across the solid/liquid interface. In a "practical" electrochemical capacitor there may occur some surface oxidation/reduction on the electrodes, that is, it operates partly as a capacitor and partly as a battery. This phenomenon depends on the material properties.

So in order to characterize a double layer capacitor, one has to investigate the double layer behavior. The metal oxide technology of the pseudocapacitor utilizes an electrochemical reaction similar to a battery technology for energy storage, thus improving potential energy density. Figure 2.4: a) represent schematic for charge separation in the pseudocapacitor and Fig.2.4:b) depicts ionic intercalation process in the pseudocapacitor. Since the pseudocapacitor uses a dense metal oxide as the electrode material, the load of the oxide is three times that of the EDLC for the same-coated area. With this advantage, pseudocapacitor cell needs to be only 60% in volume as compared to an EDLC of the same capacitance. Conversely, it also means that the pseudocapacitor holds 80% more energy than the equivalent-size EDLC. Finally, the pseudocapacitor uses the same manufacturing processes and facilities as EDLC production.
Figure 2.4 a): Schematic charge separation of the pseudocapacitor [8].

Figure 2.4 b): Ionic intercalation.
Equivalent circuit representation of pseudocapacitor

Similar representation of double layer charging behavior, an equivalent circuit representation can be given (Fig.2.5) for charging of pseudocapacitance ‘C’ through a faradaic resistance ‘RF’ and further faradaic resistance ‘RD’ for discharge (e.g. desorption of an adsorbed species). This combination involves a faradaic impedance (CR_F,ore R_D) in parallel with ‘CDL’[1].

Figure 2.5: Equivalent circuit of pseudocapacitor.

Depending upon the materials, either the electric double layer or the electrosorption of ions at the interface or both can contribute to the storage of a tremendous amount of charge when a high specific surface area electrode is used. High surface area electrochemical capacitors can store higher charge than conventional capacitors. While batteries have relatively large energy storage capability, their specific power output is relatively low. Thus, batteries are useful when sustained low power output is required. In contrast, conventional capacitors cannot store as much energy as batteries but can put out very high power levels for short times. This attribute makes electrochemical capacitors potential candidates for electric vehicles and other devices that can provide sufficient power to meet the short-term heavy power demands often encountered by electric devices. Electrochemical capacitors can also serve as back-up energy sources in integrated electronics. Therefore, it would be desirable to produce and use an inexpensive electrochemical capacitor having the desired capacitance and pseudo-capacitance.
properties to provide very high power output for short periods of time coupled with rapid and efficient recharge.

2.4 Supercapacitors based on hybrid capacitors

The combination of double layer capacitor fabricated with one electrode purely double layer (e.g., carbon based) nature and another electrode with pseudocapacitance (e.g., metal oxide/conducting polymer) nature called hybrid capacitor. The energy density of these devices is found to be significantly higher than that of pure EDLCs. Like the activated carbon cathode in EDLC, an activated carbon in the cathode of the hybrid capacitor absorbs anions at the electric double-layer and linearly polarizes to positive side in the charging process.

![Figure 2.6: Schematic diagram of composite electrode.](image)
The voltage is largely developed at anode but negligibly at cathode. Voltage developed in the electrolyte is due to a solution resistance called ohmic drop (IR drop). The voltages developed at each electrode are from resulting charge stored and electrode capacity. Because, the cathode capacity is much larger than that of anode, voltage development occurs mostly at anode when a cell is charged. Fig.2.6. depicts schematic of composite electrodes for hybrid supercapacitors.

2.5 Requirements for electrode materials of Supercapacitors

The preparation of supercapacitor electrode materials plays a fundamental role in determining the electrochemical properties of a supercapacitor. The requirements of ideal electrode materials are as follows-

1) High surface area in order to monitor the specific capacitance.
2) Assured porosity, which influences the rate capability and the specific capacitance.
3) High electrical conductivity, which is the fundamental requirement to control the rate, capability and the power density.
4) Adequate electroactive sites, which enable pseudocapacitance.
5) High chemical and thermal stability, which influences the cyclic stability.
6) Low costs and non toxic materials.

The EDLC supercapacitors utilize carbon-based active materials, which have higher surface area, lower cost and more established fabrication [16]. On the contrary the pseudocapacitors employ metal oxides and conducting polymers, which offer higher capacitance and energy densities than EDLCs as a consequence of faradaic processes [17].

2.6 Types of electrolytic devices

Environmental friendly devices like supercapacitors are considered as one of the promising candidates for energy storage due to its high power performance, long cycle life and rapid charge-discharge rate with minimum internal resistance.

a. Symmetric

In the preparation of symmetric device, the electrode used must be of similar type e.g. cobalt oxide: cobalt oxide. The symmetric supercapacitive device forms the viewpoint
of practical application. The supercapacitor needs not only good electrochemical performance but also high safety standards. The preparation of solid state symmetric device can also be possible using similar electrodes.

b. Asymmetric

In the preparation of asymmetric type supercapacitor, electrode used must be of dis-similar types. E.g. carbon: cobalt oxide/different conductivities (n or p type).

c. Solid state

This device solves the problems associated with electrolyte leakage and corrosion. solid electrolyte enhances the safety of the supercapacitor. Gel polymer electrolytes are capable of giving sufficient rigidity for enhancing device safety and provide much higher ionic conductivity than the polymeric solid electrolyte. For the preparation of solid-state symmetric as well as asymmetric devices, electrodes used are Co$_3$O$_4$, polymer gel: Co$_3$O$_4$, Co$_3$O$_4$: Polymer gel, Mn$_3$O$_4$ etc.
REFERENCES


