INTRODUCTION

Today’s world is much advanced as far as industrial innovations are considered. The industries include the producers of machines and components and also fabrications of say for example all means of transport including run our planes, trains, cars and buses, to drive our ships and submarines, to make the wheel move etc. And accordingly, to run the industries, there is great demand for the energy which is increasing day by day. It is well known since centuries back that, the coal and oil are the major sources of energy. But with the passage of time, coal and oil are bound to be used up, which will lead to big gap between demand and supply of the energy in all forms which is clear indication that the world is heading fast towards a major

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energy crisis. To meet the demand of energy by the growing population, industrialization, technology development the world today needs huge amount of energy production. At the same time storage of energy is also a very important issue in 21st century. This issue must be addressed well for the sustainability of human societies [1]. Because of global warming and at the same time the limited availability and storage of crude oil situation, there is an increasing need for an invention in the field of rechargeable batteries and supercapacitor science and technology. This invention shall also be able to satisfy the need for protection of environment and also sustainable economy [2–6].

To provide optimum energy requirement for the rapidly developing global economy, we are in need of the promising energy sources and at the same time those sources must be non-polluting and environmental friendly. At the same time care must be taken to discover sustainable and environmental friendly sources of energy. Simultaneously, this development will help to overcome the problem of the depletion of fossil fuels. If the clean sources of energy are invented and made use in practical sense on large scale, will definitely help to control the increasing environmental pollution. There are several technologies which are developed and used as devices for energy storage. One can list the prominent technologies which are dedicated to the energy conversion and storage called as electrochemical devices. For this purpose the use of the high energy storage devices such as the fuel cells and the batteries being used till last decade. In addition to this, because of the efforts of the large of the scientist and technologists across the world the new device called as supercapacitor is conquering the energy conversion science and also the storage technology.

The supercapacitors are having the special property as high power density and also the cycle life is more. The dielectric capacitors and batteries distance could be made less by the characterstics of the the supercapacitors, this way good effecting on the decrease the gap between [7,8].

1A.1.1 Thin Films

When the material of interest is to be deposited on support, mostly it is done forming a thin film. A deposited layer of material which ranges from few nanometers to several micrometers in thickness is usually referred as thin film. The deposition of the material on the support as thin films is the controlled synthesis. This is a very primary and fundamental step in many applications of these materials. In our day to day life there are numerous examples of
applications of thin films. For example, in the household mirror, typically the metal is thin coated on the sheet of glass at back side to form a reflective interface. Earlier the silver metal was used once commonly used to produce mirrors. But recently by the technique such as sputtering many other metals are being applied as thin layer which is deposited on glass.

The real growth of the thin film deposition advanced during the 20th century with the addition of more and more new thin film deposition techniques during. This advancement have led a wide range of technological breakthroughs in many areas such as electronic semiconductor devices, light emitting diodes, reflective and antireflective coatings usually called as optical coatings, hard coatings on cutting tools, magnetic recording media. The most important applications shown by the thin films are the production of the energy and also to store the energy. In the solid state solar cells developed from thin film deposition are now a days are recommended in energy generation. In case of energy storage, the thin films are being used as thin-film batteries. In life science also there are considerable applications thin films and thin film technology such as in pharmaceuticals. And this application is through the idea called as thin-film drug delivery.

1A.1.2 Thin Film Deposition

For the thin film deposition large number and type of methods are currently being used. The physical properties of thin films are dependent on the film deposition process on the solid material on which the film is being deposited that is the substrate. Such type of the surface modifications renders the expected properties of surface of

the films is expected after modification process for particular application. This happens because of the application of the very thin coating of desired material on the surface. This coating is very thin may be often just a few nanometers that is few millionths of a millimeter in thickness. Thus, so deposited thin films are often influences the properties of surfaces and in turn it is observed that the modification in the optical characteristics of a surface takes place. It is not the only effect that occurs because of the deposition of the thin film, but, in addition several other properties gets changed to useful applications such as its enhanced electrical conductivity, coating against
corrosion or leading to chemical inertness is because of the hardness or lubricity pertained by thin film on the surface.

In routine practical applications, the examples of applications of thin films include the reflective and anti-reflective coatings on compact discs, digital video discs and spectacles, thermally efficient double glazing respectively. Other application of the thin films include in micro-processor as tiny electrical pathways as decorative as well as passivater for food and drug rapping. For production of the thin films one needs to take care of the application of the materials to be deposited must be applied in a very controlled manner. In many case the atom-by-atom that is in the form of atomic monolayer. The conditions to be maintained while deposit the thin films are such as extremely clean environment in the working laboratory, care must be taken for particulate free conditions.

The techniques of depositing the thin film are in very large number. These techniques are mainly classified into two classes such as chemical vapour deposition and vapour deposition by physical path. The technique which is used on very large scale is the chemical vapour deposition. In this technique the precursors used are volatile in nature. These precursors are vaporized at elevated temperature. The substrate surface is exposed to the vapours generated from the precursors. Here, at this point of interaction of the precursor molecules and substrate, the deposition of the film starts to take place. It is always expected to produce the unwanted products of the reaction, which are usually removed by allowing the inert gas to pass over the reacting materials in the reaction set up. The so produced films are then heated to get well adhere film with remarkable morphology.

In physical vapour deposition, the mechanical and or thermodynamic methods are recommended to produce the thin films. One of the important mechanical method is a technique known as sputtering. In this the noble gas ions of high energy, most commonly Argon, is bombarded on the surface of a target made from the desired film material. This in turn releases a large number of material / ions from the target, this then which then embeds itself into the surface of the substrate. In thermal evaporation technique a solid material of the desired film composition is heated until it melts and then it is allowed to evaporate, or sometimes until it sublimes. The thin film growth is finally observed on the surface of substrate after the vapours condences in the vacuum condition.
Currently it is observed that the big scientific community is engaged in the deposition of the thin films of expected size and surface morphology. This technological achievement has become easy because of the innovative contribution of the researchers in the field of chemical solution methods. The chemical bath deposition by modification, the sol gel and the routine chemical bath deposition are being used largely. In the sol gel method firstly the precursor materials are brought down to molecular level in size and then these small molecules are then gets deposited on the surface of the substrate which eventually appears as the solid film. Mostly the metal oxides of the transition metal along with some metals from p-block of the periodic table of elements are deposited by the sol gel method of film deposition. The colloidal solution of the metal molecules is achieved which is called as sol. This sol in turn is applied as precursor for the formation of the gel. Gel may be composed of either discrete particles or network polymers.

1A.1.3 Metal Oxides

If the composition of a chemical compound is like at least one oxygen atom along with atoms of any metal is called as metal oxide. In the metal oxides there is typically presence of an anion of oxygen in the oxidation state of $-2$ i.e. $\text{O}^{2-}$. The materials which are considered to be pure elements often produces oxides which coats the surfaces called as oxide coating. This process of could be exemplified by formation of aluminium oxide, $\text{Al}_2\text{O}_3$, which typically develops on the aluminium foil. Such oxide films protects the metal from further corrosion. Similarly the transitions elements undergo oxidation with atmospheric oxygen or otherwise allowed to react with oxidizing agents to produce the metal oxides which are significantly of much importance almost in all field of science. Among the elements in periodic table, majority of them are metallic in nature such as cobalt, nickel, copper, iron, gold, silver, platinum, mercury, uranium etc. The substrate surface if gets covered by the deposition of the metal demands the variety of applications. For example the metals oxide such as cobalt oxide, nickel oxide, ferrites etc. are of utmost important in the applications supercapacitors [9].

1A.1.4 Electrolytes
The materials, which when dissolved in the solvents lead to the generation of the solution with property of electrical conduction is called as electrolyte. The solvent typically employed in such cases are the polar solvents. Water is the best example of such solvents. Thus produced solution now contains separated cations and anions. These cations and anions get uniformly dispersed throughout the solvent, and such solutions behave as electrically neutral. When these solutions containing ions are subjected to electrical potential, electrical conduction is shown by the solution. The mechanism is that, the cations of solution are drawn to the electrode with negative charge that is electron reach side. While the electron deficient side of the solution bath, called as cathode which is positive in nature, attracts the anions from solution anode. This movement of the positively charged ions and anions of minus charge in the solution gives the generation of the current. The electrolytes include soluble salts, acids, and bases. This property of the electrolytes makes it very useful in material science especially in the research area of supercapacitors.

In the performance of electrochemical supercapacitors (ESs), the electrolytes are being identified as the most influential components [10,11]. These supercapacitors include electrical double-layer capacitors, pseudocapacitors and hybrid supercapacitors. The electrolytes include many categories as aqueous [12, 13], organic, as well as ionic liquids as electrolytes, solid-state electrolytes, and redox-active electrolytes. The electrode materials greatly impacts on the performance of a supercapacitor [14]. But it is not the only component which influences the supercapacitor properties. The other component which has strongly affects the supercapacitor properties is none other than the employed electrolyte [15,16].

In addition to the aqueous electrolytes, there is emergence of non-aqueous electrolyte solutions which are employed in the commercial electrochemical double layer capacitors [17].

1A.1.5 Ionic liquid as electrolytes

Taking in consideration the environmental impacts of the chemicals used as electrolytes, a new category of the chemicals, ionic liquids, is being employed now a days as electrolytes in supercapacitors. The ionic liquids have some of the unique properties over the routine electrolytes, which led those to be in the category of environmentally friendly chemicals. These properties include high ionic conductivity, large liquid phase range, wide electrochemical
window. In addition those are non-volatility, non-flammability and also behave as and non-toxicity. These unique properties had projected these chemicals as an excellent electrolyte for electrochemical devices for storage of energy. Few examples of the ionic liquids being employed now a days in supercapacitor applications are imidazolium and pyrrolidinium. Some of these room temperature ionic liquids which is used commonly name of the ionic liquid could be illustrated as, methylimidazolium derivitised with the ethyl group at one position, 1-butyl-3-methylimidazolium [18].

1A.1.6 Supercapacitors

In the present situation, there is a tremendous progress in the technologies and that has led to the development in the fields from chargers of small devices to run big industries. To sustain this development, the human being is in need of the huge amount of energy and this need is increasing day by day. To meet this demand there is a tremendous need for the production of the energy in the form of electricity. And simultaneously, one needs to think of storage of the produced energy. The best option now a days for the storage of the energy is supercapacitors. There several types of electrical energy storage devices now a day’s available, among those one of the important is the supercapacitor. There several advantages of the supercapacitor such as they possess high power density, high efficiency, better charging and discharging time as well as speed. In addition to the advantages the supercapacitors are supposed to be environmental friendly. And thus, the supercapacitors has became an ideal option for high power applications. In case of the high power system devices such as hybrid power and energy regeneration, the supercapacitors are finding enormous applications [19,20]

Electrochemical capacitors have very high power density than lithium ion batteries may be equaling to thousand times. The electrochemical capacitors possesses remarkably larger energy density than conventional capacitors. By considering such special characteristics of the electrochemical capacitors can provide definite solution to meet the increasing power demands of energy storage systems [21].

The high power is required for running the portable systems and electric vehicles the growth of is tremendously increasing. This requirement of high power has led the scientists to increased interest in development of electrochemical capacitors also called as supercapacitors.
The conventional capacitors and supercapacitors have similar basic principles. The electrodes present in the supercapacitors possesses high surface areas (A). The supercapacitor mechanism needs the separation of the electrodes from each other. Thus to keep the electrodes away from each other at specified distance the insulating dielectric material is applied. Otherwise the gap in electrodes in solution would have been such that, the movement of the ions will not be efficient to reach the respective electrodes. This optimum distance between the electrodes is referred to as D. once the voltage is applied to the capacitor, as expected the movement of the positively charged ions and negatively charged ions start and they try to reach the electrodes of opposite charge. When the positively charged ions reaches the negatively charged electrode, it starts to accumulate on its surface. Similarly, the negatively charged ions called as anions will reach the positively charged electrode and start to deposit on its surface. As already the dielectric material is kept between the oppositely charged electrodes, the distance is maintained between the two electrodes, this distance leads to defined movement of the ions causing the production of the electric field. Thus produced electric field means the produced electricity is stored in the capacitor. This mechanism of the production of the electrical potential could be demonstrated with the help of the diagrammatic representation as shown in the Fig. 1.1. The equations used or the description of relation between capacitance and other quantities could be discussed as,

\[ C = \frac{Q}{V} \]  \hspace{1cm} \text{...(1A.1)}

The equation involves the terms for the capacitance as C, the term Q indicates the stored positive charge and V is the applied voltage. The value of C can be calculated by dividing the value of Q by value of V.

Whereas, if we take the consideration of the area of the capacitors, then in the conventional capacitor, the capacitance C becomes,

\[ C = \varepsilon \varepsilon_0 \frac{A}{D} \]  \hspace{1cm} \text{...(1A.2)}

In this equation, \( \varepsilon \) = dielectric constant
\( \varepsilon_0 = \) constant called as proportionality constant.
A = electrode surface area
D = distance between electrodes

This dielectric constant is also called as “permittivity” of free space. The other parameter is proportionality constant, \( \varepsilon_0 \). The insulating material has also a dielectric constant, which is denoted by symbol \( \varepsilon_r \). Under these circumstances the capacitance and surface area of each electrode are directly proportional to each. Whereas, there is inverse relation between the capacitance and the electrode distance from each other. The equation number 1A.1 and equation number 1A.2 are useful to explain the reasons for enhancement in capacitance. Similarly these relations also focuses on the reasons behind the energy enhancement.

The capacitors exhibits some typical properties. These properties are the compactness of the energy and density of power, which leads usefulness shown by the capacitor. The calculation of the density of capacitor is the value per unit mass. Also the density can also be calculated per unit volume of the electrode surface. A typical capacitor stores an energy \( E \). The capacitance and the stored energy are in direct proportion. We can make use of equation for demonstration of this relationship,

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

… (1A.3)

The advantages of the supercapacitor over the electrochemical batteries and fuel cells are numerous. The supercapacitors exhibits high power density, short discharge time, and can be used for large duration as those have better cycle life. It is also interesting to know that such supercapacitors have better self-life also [22, 23].
Fig. 1A.1 Outline of conventional capacitor with different components

The illustration of the physical features of the supercapacitors could be given as shown in Fig. 1A.1. and Fig. 1A.2.

Fig. 1A.2 Outline of the electrochemical capacitor of double layer type
In order to satisfy the requirements for large capacity as well as high power density, numerous attentions have been drawn in studies of hybrid asymmetric supercapacitors, which are composed of an electric double layer supercapacitor (EDLC) and a pseudocapacitor electrodes.

The electric double layer supercapacitor plays the main role in charge-storage mechanism which is build up between the interface of electrolyte and the electrode. The layers in the supercapacitor gets rearranged in the process of charging. Same is the observation for discharge mechanism, where also the rearrangement of the double layers in supercapacitor takes place. This mechanism provides that the EDLC has much larger specific surface area than conventional capacitor. In general, capacitance of EDLC or dielectric/ceramic capacitor is proportional to their surface area [24]. In electric double layer supercapacitor the Faradic process occurs wherein the redox reaction causes the pseudocapacitance. The electric double layer supercapacitor as well as pseudocapacitors have the broad electrochemical window and it ranges from 0.9V to 1.8V. This wide range of electrochemical window is because of the over potential in aqueous environment [25-27].

Fig. 1A.3 The densities of energy and that of the power of different devices for storage of energy
One can compare the capacities of the various storage devices on the basis of the power density and density of energy of different storage devices. The Fig. 1A.3 and Fig 1A.4 illustrates the comparison. The electrical energy storage technologies could be categorized based on their storage durations, functions and response times [28, 29]. In the energy storage where the mechanical mechanisms is used is called as hydroelectric storage, where use of water is done. In some other cases where air is used for storage of energy, could be called as compressed air, flywheels energy storage systems. It is well known that the there is use of the batteries, which are rechargeable, this type is another type of the electrochemical energy storage device. Recent years have observed that, there is great invention and modifications of the new kind of devices, which are much promising towards the electrical energy storage, are called capacitors and supercapacitors. There is also some scope for the magnetic superconductors in the field of energy storage.

Whereas, thermo-chemical that is solar fuels, chemical - hydrogen storage with fuel cells and thermal energy storage. Thus, the overall available energy systems could be classified as shown in Table 1A.1.
### Table 1A.1 Classification of electrical energy technology

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<td>➢ Pumped hydropower</td>
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<td>➢ Compressed air</td>
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### 1A.1.7 Electrochemical Supercapacitors

The very high capacitance shown by the supercapacitor differs those from a regular capacitor. The carbon allotrope as graphene is important. The lattice of two-dimensional hexagonal is the structural form exhibited by the graphene. It is present in a sheet of pure carbon and is only one atom thick. There are three types of capacitors as use electrostatic double-layer, electrochemical pseudocapacitance and the hybrid capacitors [31]. The most basic among those is the electrostatic capacitor. This electrostatic capacitor is equipped with a dry separator between the electrodes. But, unexpectedly, these devices show the capacitance towards the lower side. The common application of supercapacitor is to tune radio frequencies. English physicist Michael Faraday discovered the unit to measure capacitance, which is named him Farad. The range of the electrostatic capacitor varies from few pico-farads to microfarad. The capacitance provided by the electrostatic capacitor is very small whereas the electrolytic capacitor provides higher capacitance. The moist separators are present in the electrostatic capacitors. These separators acts as filter and also act as buffer. The same mechanism is being observed in the electrostatic capacitor, like that of battery. Another type of the storage devices are the
supercapacitor. The capacitance of the supercapacitors is much more than that of the electrolytic capacitor. In the supercapacitor charge-discharge mechanism is used for energy storage. This technology of the supercapacitor was commercialized the invention as “supercapacitor” for computer memory backup. Alter in 1990s the supercapacitor devices with improved performance and lower cost were developed due to advances in materials and manufacturing methods. In the supercapacitor there is use of special features as electrodes and electrolyte which has evolved crossed into battery technology. The electrostatic actions and electrodes are responsible for the electrochemical double layer capacitor (EDLC) and asymmetric electrochemical double layer capacitor (AEDLC) respectively. However the cycle life is short for both these cases.

The graphene electrodes are looked for the promising improvements to supercapacitors and batteries [32]. The carbonallotrope as graphene is important. The lattice of two-dimensional hexagonal is the structural form exhibited by the graphene. It is present in a sheet of pure carbon and is only one atom thick. Graphene has properties as flexibility, transparency, impermeable to moisture, and has good conductivity. These properties of the graphene are supposed to be useful for better supercapacitor. Large number and variety of electrodes are developed to be used for supercapacitor. In the common application, the electrodes are of carbon and the electrolyte is organic. It is very common that, all the capacitors have voltage limits. In comparison to capacitors the electrostatic capacitor can show higher voltage. The higher voltage is possible for supercapacitor, but such higher voltages reduces the life time of the supercapacitor. The arrangement as serial connection is hopeful to get higher voltage, for this several supercapacitors need to be connected in series. The series arrangement affects on the total capacitance and boosts the resistance. The specific energy for supercapacitor is less than the proven Lithium ion batteries, and is ranges between 1Wh/kg to 30Wh/kg. And also the discharge phenomenon is need to be also considered, which affects the performance of the supercapacitor, may be looked as one of the disadvantage. The charge and discharge phenomenon in the energy storage devices needs to be paid attention. In the supercapacitor while charging the voltage increases linearly. When the supercapacitor gets full, the normally the current decreases. Whereas, while discharging the voltage drops linearly. This mechanism of charge and discharge could be well demonstrated with the help of the charge-discharge plots / curves [33].
Thus, demonstration of the supercapacitor charge and discharge profile could be shown in the form of plots [34]. This is shown in Fig.1A.5 and Fig. 1A.6.

Fig. 1A.5 Profile of a supercapacitor while charging
The supercapacitor has a charge time in the wide range of 1–10 seconds. The charge characteristic and the charge current is in supercapacitor controlled by capacity of the charger. Up to certain amount, the charging of the supercapacitor takes place fast but in later stage that is at full charging stage, it will take extra time. One of the advantage of supercapacitor over the battery, is the supercapacitors are not overcharged. When the supercapacitor is fully charged the flow of current stops.

There is almost no wear and tear by cycling a supercapacitor thus, those could be maximum cycle life. Among the other advantages, the supercapacitor shows excellent performance may be up to many years also works well in hot and cold temperatures.
1A.1.8 Transition Metal Oxides in Supercapacitor Application

The transition metals are able to produce large number of variety of oxides. These oxides exhibit multidimensional properties and are also can be synthesized cost effectively [35]. Thus, the group of the wonderfull metals as the transition metal oxides are supposed to be the good and fascinating materials among inorganic solids. From one of the most important oxides of iron that is magnetite, Fe$_3$O$_4$, a group of spinel ferrites of the type MFe$_2$O$_4$ are produced in which M stands for Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$ etc.).

The spinel ferrites have the unique electrical and magnetic properties which has greatly attracted a wide range of applications. These applications include high-density data storage, heterogeneous catalysis, optical limiting, sensors, spintronics, magnetocaloric refrigeration. These applications are also extended in the medical sciences such as magnetic labeling in immunoassays, drug delivery, magnetic resonance imaging and hyperthermia of cancer cells. The nickel ferrite, NiFe$_2$O$_4$, particles of nanocrystalline nature, are reported to be synthesized by the coprecipitation technique. The characterization of which is carried out for their nonlinear optical properties. These NiFe$_2$O$_4$ nanocrystalline particles had shown optical limiting indicating its usefulness for device applications [36,37].

The synthesis technique such as solvothermally is being applied for the synthesis of ZnFe$_2$O$_4$ nanoparticles. In this by using the ethylene glycol as solvent, ZnFe$_2$O$_4$ colloidal nanocrystal clusters were obtained. These single crystalline phase ferrite nanoparticles were found to be ferromagnetic in nature [38-40]. The applicability of the spinel ferrites has been proved in electrochemistry such as lithium ion batteries, supercapacitors, electrochemical sensors, etc. From the applications of the spinel ferrites as supercapacitors, it could be forecasted that, the this could minimize the dependence on exhaustible natural resources and curbing. The metal oxides could be effectively used in the field of research for lithium ion batteries as the oxide anodes. The wide variety of compounds with various morphologies would be promising materials for their applications in energy storage devices [41].

The solvothermal synthesis of the ZnFe$_2$O$_4$ microspheres composing of nanocrystals is reported for the applications of supercapacitors. The investigation of the structure especially the morphology of the synthesized material is carried out by X-ray powder diffraction to confirm phase formation. The surface morphology of the material is understood by the TEM and FE-
SEM gives the idea of the size of the deposited film. The porosity of the film is checked by the Brunauer–Emmett–Teller technique using nitrogen gas adsorption. All this study revealed that the ZnFe$_2$O$_4$ is potential material for capacitance. The electrochemical performance of prepared material is reported to be checked by the charge–discharge galvanostatic techniques and voltammetry of cyclic type, which indicated the promising performance. It is confirmed that, the ZnFe$_2$O$_4$ has shown 131 F/g value of the specific capacitance with high percentage of capacitance retention after few hundred cycles[42].

There are reports that, in one attempt the direct electron transfer mechanism is studied in the living being, nanoparticles of the metal oxides, such as cobalt ferrite and also a linear polysaccharide like chitason films were employed. These nanoparticles were reported to be used to adsorb on hemoglobin molecules. This situation leads to the creation of the protein electrode. This facilitates to study the centers of reduction oxidation for electron transfer between the protein and the electrode. The cobalt ferrite nanoparticles produces a ordered layered structure after modification showed appreciable electrocatalytic activity and long-term stability [43,44].

There are several examples of the applications of the transition metals in the energy storage systems. Nickel and cobalt are the best known for their applications in the storage systems and also in catalysis. The electrolytic activity of the cobalt as well as nickel is demonstrated in literature. The cobalt and nickel catalysts could be used for energy conversion.

The oxides of the cobalt such as Co$_3$O$_4$ and CoO are reported to be used to show higher capacities. In such applications the cobalt oxides materials are acting as anodes. A typical application is in the batteries of lithium ion type. The oxides of the metals in such case exhibit various morphologies ranging in the size dimensions of at the nano level. Those may be sheets, wires and tubes of nano dimensions. To achieve these different shapes the method of synthesis plays very important role. Those methods may be chemical methods or physical methods including solution bath and microwave. The size and shape combination leads to better electrochemical performance[45,46]. One of the property of the transition metal oxides is they allow the reduction and oxidation reactions on their surface. This property facilitates the charge storage as well as show higher specific capacities values. One of the good candidate fulfilling this mechanism is nickel. Among the compounds of the nickel the hydroxide and oxide of nickel
shows higher theoretical values of the specific capacitance in the voltage window of the 0.5V. These type the materials are environmental friendly and at the same time are stable towards the chemical property and thermal property.

One can think of making use of the combination of the cobalt and nickel by using various proportions of both of those. Such combinations lead to produce desired morphologies useful for the energy storage applications [47]. These two metals as nickel and cobalt in the form of oxides as well as alloys find numerous applications. Especially the oxides are very important towards various reactions including the oxidation of carbon monoxide, water-gas shift reaction, and the most important is in supercapacitors for energy conversion and storage. These oxides act as semiconductors and thus possess an ability to produce the electron and hole pairs by absorption of the light. This lead to the transfer of the electron between the material that is oxide, which now acts as semiconductor and the surrounding solution. To study this mechanism an anode of the cobalt oxide and hydroxide is prepared and applied for the electrochemical oxidation of the water in presence of light [48].

The oxides of cobalt, nickel, manganese, iron, copper and zinc, which are typical transition metals, produces the spinel compounds. These widely being studied for batteries of lithium ion as one of the important applications as anodes. These oxides could, comparatively, be easily prepared and also possesses high capacity. The other metal oxides, than cobalt are preferred some times, owing to the toxic nature of cobalt. The other transition metal oxides of first transition series pose as eco-friendly alternative and also good performers of the electrochemical mechanism [49]. One can produce the mesoporous structure from the transition metal oxides. These structures are of nanomaterial type and are able to exhibit the ability of developing the electrode materials with better electrochemical performance. These mesoporous materials possesses big surface area approximately ranging from $m^2g^{-1}$ and thus have better supercapacitors properties and also show excellent performance. [50]. Other material mesoporous a-MnO$_2$ has been developed as an aqueous asymmetric supercapacitor. This MnO$_2$ nanostructured material retains its phase and even after 3000 charge–discharge cycles, which is supposed to be a good conductor [51]. Along with the metal oxides some other materials such as carbide derived carbons (CDCs) which are also called as active materials have seeded much of
the interest for supercapacitor applications. The pore size and as well as the distribution of the pore size distribution is supposed to be possibly controlled by these materials. This is achieved by selectively etching metal atoms from carbide powders, ceramics etc. [52-54]. The CDCs materials also deliver larger capacitance, which is in comparison with pseudocapacitive materials [55-57].

The supercapacitors can very effectively be used to fill the gap in the interval of time form seconds to minutes and these can be recharged quickly. In New York, to prevent voltage drop during acceleration of a train a 2MW supercapacitor bank is being recommended in case of failure of the flywheels. Such systems can have life span of years together provided the normal voltage gain of 10% and need not to maintain much as far as the device is considered. At the great demand time of electricity the power load could be well reduced by use of supercapacitor, and this mechanism is implemented in Japan in the places such as, in commercial buildings, this especially operates.

However, the supercapacitors are having certain advantages such as, they have excellent life cycle, may be one can observe these materials to be in use after cycling for thousands of thousand times. These can sustain high load of the current because of their good specific power. The resistance is also low for these devices. The supercapacitors draws electricity only when it’s needs to charge and also does not heats while charging as well as discharging. In spite of many advantages the supercapacitors have few drawbacks such as; they cannot hold large specific energy. The pattern of the energy while discharging is linear.
# 1B: CHARACTERIZATION TECHNIQUES

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## 1B.1 INTRODUCTION
In the deposition and fabrication of any material we choose the appropriate method and also optimize parameters. This, we suppose, will produce the material of our interest for a particular application. After the fabrication of the material, say for example a thin film, it becomes necessary to understand and to investigate the status of the material and success of the method. The evaluation of the characteristics of the deposited material is based on its nature. Due to progress in the characterization facilities, we have to our help large number of the techniques. These techniques gives us the correct prediction of the properties and also the structure of the synthesized material [1].

The group of techniques included both the qualitative and quantitative techniques. The properties such as the study of the surface profile of the material could be evaluated by qualitative techniques. Once we get the insight in the surface of the material, the next step is to understand the compositions of the materials with respect to atoms as well as molecules. Now a days technological innovations in the field of characterization techniques are helping the materials scientists The detailed imaging of the positions of the atoms placed in the structure may be understood by obtaining the images in various dimensions. The decent instrumentation facilities are giving us the images of solid materials in two as well as three dimensions. Because of the constant improvement in the sensitivity of quantitative techniques, it has now become possible to measure the lowest possible concentrations of the different entities in the bulk of the material including the impurities in the range of the parts per million as well as parts per trillion.Following are the section where some important techniques useful for the thin film characterization to know its structural aspects, and also for possible applications are discussed. In material science the characterization of materials synthesized is gives the through idea of the probable applications as well as the mechanisms. The characterization of the materials necessary to order to learn more about them. Today, there is large number of scientific techniques available to the materials scientist that enables this characterization.

The technologies meant for the thin-film deposition can be classified in several categories. The most important are based on the nature of the precursor used and the method used. The chemical processes are one type of process where we can again divide those in liquid-phase chemical film formation and gas phase chemical
processes. The other techniques are based on the evaporation and the discharge by electrical mechanism. The physical and chemical characteristics play role in the deposition process of the thin films and also materials for the specific needs. The films produced by any method could be assessed very well with respect to its physical and chemical aspects. This is possible due to the new discoveries and improvements in the characterization instrumentation. By these established techniques we can also focus on the nature of the surface and also the very small structural details of the films produced. The most commonly used characterization techniques in the study of thin films and their applications in supercapacitors are Cyclic Voltammetry (CV), X-Ray Diffraction (XRD), Galvanostatic Charge-Discharge (GCD), Scanning Electron Microscopy (SEM), Electrochemical Impedance Spectroscopy (EIS), and the Thermogravimetric Analysis (TGA).

1B.1.2 X-Ray Diffraction (XRD)

The powerful technique in material characterization is the X-ray crystallography by light bending type. This tool facilitates us with understanding the crystals with respect to the positions of the atoms as well as molecules. In atoms in the crystal leads to a diffraction of the beam of an incident X-rays. This diffraction takes place into many directions. The angles and the intensities of the diffracted beams are measured and by using the knowledge of the crystallography one can predict internal arrangement in the crystal with respect to the electron density and its presentation in picture of three-dimension. The picture of the density of the electrons gives us the idea of the mean position of the atoms in crystal under study. From this information, the bonding pattern in the molecule and as well as some other information could be revealed. The range of the materials such as metals, metal oxides, semiconductors, biological materials containing organic and inorganic atoms etc produces crystals. For study of all these type of materials the X-ray crystallography has been used as fundamental technique. By using the X-ray crystallography one can get knowledge about the size of atoms, the lengths and types of chemical bonds. In addition, with the development on the instrumentation of the X-ray crystallography, the structure and function of many biological molecules could be revealed. The information about the distances between the atoms in structure and also atomic arrangements in the crystal lattices could be understood from the X-ray.
crystallography, because of its peculiar property to cross any material and get diffracted by the atoms.

The diffraction of the X-rays is depending on the elements which are involved in the crystal lattice. This information leads to we can determine crystallographic nature of material. The energy of the incident radiation and the atomic structure both are responsible for the diffraction pattern of the X-ray. In the X-ray tube a measuring device is present which emits radiation towards the sample and then the sample diffracts some part of those radiations towards the detector. When the rays are interacting with the sample, this interaction follows some law called as the Bragg's Law.

The relation between the electromagnetic radiation wavelength and the angle of the diffraction in a crystalline sample is explained by the Bragg's Law. This, on satisfying the conditions of Bragg's Law leads to produces constructive interference. The Bragg's Law can be stated mathematically as in equation 1B.1

\[
n\lambda = 2d \sin \theta 
\]  
\[
... (1B.1)
\]

The terms in this equation are representing the
diffracting planes spacing is = \(d\),
the angle of incident is = \(\theta\)
the integer is = \(n\)
the beam wavelength is = \(\lambda\)

Thus, X-ray diffraction results from an electromagnetic wave that is in this case the X-ray. The impinging on a regular array of scatterers causes the X-ray diffraction(Fig. 1B.1, 1B.2, 1B.3).

The samples are scanned through a range of 2\(\theta\) angles. Because of the random orientation of the powdered material, it needs to address all possible diffraction directions of the lattice. Then the diffraction peaks are to be converted to \(d\)-spacings, which gives us idea of the identification of the material. The standard reference patterns are to be made use for the comparison with the \(d\)-spacings, which helps in the identification.

The instrument X-ray diffractometer consist of three basic components. These components are as, X-ray detector, a sample holder and an X-ray tube.
Fig. 1B.1. Diagram of the functioning of X-ray diffraction
The electrons produced by the X-ray, get accelerated by applying a voltage and reach at a target. Now, the target gets bombarded with these electrons. The electrons in the inner shell of the target leave the position because of the associated energy and this leads to the production of the characteristic X-ray spectra. The most common components of the X-ray spectra are $K_{\alpha}$ and $K_{\beta}$. The target such as copper, iron, molybdenum, and chromium produces the characteristicspecific wavelengths. For example Cu$K_{\alpha}$ radiation = 1.5418Å, which is the most common target material for single-crystal diffraction. It is observed that the sample as well as the detector undergoes rotation when these X-rays reach the sample. Simultaneously, the recording of the intensity of the reflected X-rays is achieved [2].

1B.1.3 Scanning Electron Microscopy (SEM)

In the scanning electron microscope (SEM) the sample are scanned with a focused beam of electrons which in turn produces the images. Different kinds of the signals are produced when there is the interaction of the sample atoms with the electrons. This is the principal of the
analysis by electron microscopy of scanning type. The bulk of the information is decoded by studying the signals which is the response from the material. The scanning electron microscopy study gives the detailed information about the status of the surface of material called, the chemical composition, the structural aspect such as crystallinity etc. In the scanning electron microscope the resolution as low as 1 nanometer or better could be achieved. In common application for detection of the secondary electrons emitted by atoms excited by the electron beam, SEM is being used in common application to detect the electrons emitted by the excited atoms because of the beam of the electrons. In most applications, samples specific area is selected and the electron beam is focused on it. This results in production of some signals. These signals are analyzed to obtain the data.

Then this data is used to create the two dimensional images. From the two dimensional images one can interpret the variations in the properties of the sample. In the SEM techniques the range of magnification for study purpose is from 20X to approximately 30,000X.

One can obtain the qualitative information of the materials chemical composition as well as this techniques become useful for the structure of the the crystalline type determination and the elemental composition of the material, provided it is supported with energy-dispersive X-ray spectroscopy. The electron backscatter diffraction gives an idea about the crystal orientations.

In the, the electrons are accelerated, which as a result carry significant amount of kinetic energy. Various signals are produced when the interaction between the electron-sample happens due to the transfer of the energy. The signals produced are referred as per the type of the electrons responsible. If the signals are produced due to the secondary electrons then it is called as secondary electron signal. The diffracted backscattered electrons lead to the different type of the signals and similarly the backscattered electrons as well as photons etc are also responsible for the production of the signals (Fig. 1B.4).

The imaging of the samples is possible especially because of the electrons of backscattered type and secondary electrons. Among those, the electrons secondary are responsible for study of the morphology and topography of the samples. The backscattered electrons are gives the information of the contrasts in composition in multiphase samples. In the scanning electron microscopy, there is no any loss in the sample volume there for it is called as non-destructive technique.
Fig. 1B.4 Interaction of the beam of the electron with the sample resulting in the production of the signals.

The tungsten filament cathode is used in a typical SEM as the support for the electron gun. From this cathode the beam of the electrons is thermi-ionically emitted. The tungsten has the melting point of 3420 °C. And the very important property of the tungsten metal is it has the lowest vapor pressure among all the metals. Thus we can electrically heat it for electron emission and thus it is used in thermionic electron guns. The other electron emitters installed in SEM
instrument are the lanthanum hexaboride (LaB$_6$) cathodes. The instrumentation of the scanning electron microscope has many components.

(1) Source of the electrons commonly called as gun

(2) Lenses for electrons

(3) Stage to mount the sample

(4) Signal detection system

(5) Output devices for data.

The detectors present in the SEM instruments have additional detectors with minimum secondary electron detector (Fig. 1B.5 and Fig. 1B.6).

Fig. 1B.5 The ray diagram of scanning electron microscope
1B.1.4 Cyclic Voltammetry (CV)

One of the widely used and dynamic electrochemical method for the study of the redox reactions is nothing but the cyclic voltammetry. The cyclic voltammetry technique could be well useful to study the surface of the electrode on which the deposition phenomenon of the precursor material takes place. This is the electrochemical behavior. There is always interface of the electrode surface with the surrounding ions, this is also monitored by the cyclic voltammetry.
The electrode has some properties due to the materials which could be observed by this technique[5].

The electrochemical cell is supplied with the voltage and then the current output from the cell is scanned in the cyclic voltammetry with respect to the potential. In the study of the materials, the cyclic voltammetry instrumentation typically consists of the three-electrode cell system. These electrodes are such as, reference electrode, counter electrode and working electrode(Fig. 1B.7).

In the cyclic voltammetry, the potential of the working electrode is controlled versus the reference electrode. In the cyclic voltammetry at the beginning due to the voltage there is not observation of the potential developed; this stage is scanned by the program. The phenomenon of the scanning continues till the switching potential. There is also need to maintain the expected linear scan rate. After words the scanning is reversed in the backward direction and reaches back to initial potential. There is wide range to choose the scan rate $1.0 \times 10^{-3}$ to $2.0 \times 10^2$ or more volts per seconds. During the cyclic potential scan the current flows in the cell and is nothing but the output of instrumentcyclic voltammetry [6].

Fig. 1B.7 Schematic of the cyclic voltammetry instrumentation
Where the potential developed between two electrodes is measured in electrochemical analyses is referred to as the potentiometry. Very low current is always very useful form the potentiometric studies. Here, the electrochemical potential of the reference electrode is fixed. This helps to measure cell potential with respect to the working electrode. At working electrode the equilibrium half-cell reaction takes place. In this the material of the interest is present. In the cyclic voltammetry triangular potential waveform is made applied to linearly scan the voltage of a working electrode of stationary type. The current resulting from the applied voltage is measured in the by the cyclic voltammetry instrument. A plot of the potential and current is drawn to represent the measured current. The shape of it is usually cyclic in nature, therefore referred to as a cyclic voltammogram commonly [7].

The time dependent function of the large number of physical and chemical parameters is the cyclic voltammogram. The material under study decides the utility of the cyclic voltammetry. The material under study must show oxidation and reduction reactions for study by cyclic voltammetry. The cyclic voltammetry study requires that, the material under study must be able to undergo reduction or oxidation in the forward scan and, also it must act reversibly that is oxidation or reduction in a return scan [8]. A typical cyclic voltametry wave function is shown in Fig. 1B.7.

![Cyclic Voltammetry Potential Waveform](image)

Fig. 1B.8 Cyclic voltammetry waveform

It is observed that the electrode potential linearly shows the sloping over the ups and shown in the plot (Fig 1B.8). This happens in cyclical phases. The plot is to be plotted against the
The experiment's scan rate (V/s) is the voltage rate change over time during each of these phases. The distance available between the working electrode and the reference electrode is applied for the application of the potential in cyclic voltammetry. The working electrode and the counter electrode are made use for the current measurement. The plot of the current versus applied voltage generates the data which is used for further processing. An increasingly reducing potential is applied at the time of the initial forward scan, thus the cathodic current will increase.

The concentration of reducible analyte almost finishes when the reduction potential of the analyte is reached at certain point and thus the cathodic current will decrease. The reduced analyte will start to re-oxidized in the reverse scan. This produces the current of reverse polarity (Fig. 1B.9).

![Cyclic voltammogram showing oxidation and reduction peaks](image)

**Fig. 1B.9** A typical cyclic voltammogram showing the oxidation and reduction peaks

**1B.1.5 Electrochemical Impedance Spectroscopy (EIS)**

By taking in consideration the function of frequency the dielectric properties of a material are measured in the electrochemical impedance spectroscopy (EIS). In this the
electrolyte when electrodes under study are dipped, then there is sample electric dipole moment and an external field interacts with each other. This is the basis the electrochemical impedance spectroscopy. The impedance spectroscopy facilitates the understanding of the distinction between the electric properties and the dielectric characteristics of components of the samples separately contribute to such study. It is one of the non-destructive techniques. This characteristics is useful to obtain the information of the ongoing electrochemical process.

A small amplitude ac signal is periodically applied and the system response is studied by EIS. At various ac frequencies the measurements are carried out. The potentiostats are normally being used for the measurement of the response of electrochemical systems. The frequency response of the system is generated when the direct current signal is supported with the extra voltage than required, in case of the EIS. The various ways of the measurement of the system impedance are indicated by various researchers. Those could be listed as phase sensitive detection, alternating current bridges, frequency response analysis, Lissajous curves and Fourier transform etc.

In an impedance experiment, the electrochemical cell consists of two, three, or four electrodes. The most basic form of the cell has two electrodes and three electrodes. The electrode under investigation is the working electrode and for the closing the electrical circuit the electrode used is the electrode of counter. The liquid electrolyte is applied to electrodes to be immersed in. A typical set up for the measurement of the impedance is shown in Fig. 1B. 10.
1B.1.6 Thermogravimetric Analysis (TGA)

In technique thermogravimetric analysis, sample under study is exposed to the particular system where the instrument is facilitated with the inert atmosphere and also the temperature is also controlled. Here, as the temperature of the system is increased the loss in weight of the substance starts to take place. This loss in weight is in proportion to increase in temperature as well as the time of heating (Fig. 1B.11). Basic principle of the thermogravimetric analysis, the sample of interest is heated at higher temperature. Because of the heating the volatile components leaves the sample leading to the loss in weight. At the same time oxidation of the some compounds in the sample takes place. This may lead to the increase or decrease in the weight of the sample. Most of the time the decrease in the weight of the sample is observed. In the thermogravimetric analysis the measurements of the weights of the sample at heating and cooling in monitored. For this a particular system of the controlled atmosphere is maintained.

A thermogravimetric analysis is facilitated with the setup including a unit for the sample holding usually called as the pan. As the main aim in a thermogravimetric analysis is the
measurement of the weight, the setup is provided with the precision balance. The pan of the sample is supported with the balance. This arrangement leads the pan to be in a furnace and facilitates the heating and cooling of the sample during the experiment (Fig. 1B.12). The inert gases are applied for purging of the sample gases. Throughout the experimentation a loss or gain in the weight of the sample is recorded online.

The measurements of the weight in loss in the thermogravimetric analysis are used primarily to determine the composition of materials and to predict their thermal stability at temperatures up to 1200°C. The loss in weight loss of the sample is due to decomposition, oxidation, or dehydration. The very important thing to be taken care in thermogravimetric analysis is the utmost care to record the weight and the corresponding temperature. The recording the minute changes on the mass corresponding to the change in temperature precision of high degree is maintained. For obtaining the high precision, in addition to a furnace with computerized program the precision balance is required in TGA as a basic arrangement.
1B.2 PROBLEM ON HAND

The population of the world is increasing enormously every day. All the countries in the world are trying to nourish this growing population with the jobs, food, amenities. This eventually created a pressure of the industries- manufacturing, agro-based, gadget producing etc. All these industries and in fact the entire population is in need of the large amount of the energy. Thus, production of the energy is one of the burning topics in today’s world. And thus scientists are developing good performing devices for the conversion of different forms of the energy in mostly the electrical energy. This is not enough to go for the supply of the electricity for various purposes. The other thing which more than important in the energy research is the how to store the energy. And to meet this demand of the energy sectors various devices are being produced including the batteries, fuel cells and supercapacitors. Bu still large amount of the innovation in this sector is needed.

And especially, the issues of the enhancement of the efficiency of the supercapacitors are at the forefront. The selection of the proper material for the purpose of the electrode is a big
challenge considering the efficiencies of the several materials to the lower side. Thus, in this
thesis it is focused on the development of the highly efficient material for the electrode using the
transition metal oxides. Amongst the transition metals oxides the best ne is the cobalt. This metal
in the form of its oxide is being focused well. The use of the specific material for the fabrication
of the electrode material. In addition to the electrode material the other very important factor is
the electrolyte to be used along with electrode. This is also an another challenge. This problem of
the selection of the better performing electrolytes as KOH and the green solvents as the ionic
liquids are studied. Though large number of the materials are available for this purpose, there are
limitation for those. May be sometime the material is good in its properties towards the energy
storage, but it may fail in long duration application. May be some time the electrolyte
decomposes after long cycles. There also observations that the supercapacitor may be goo in
cycle life, but undergoes heating that to excessive heating, which is never expected. By
considering all these limitations the focus is on the development of the good material which will
overcome all these limitations.

1B.3 RESEARCH OBJECTIVES

1. To select a proper method for the synthesis of the material useful for the fabrication of
   the electrode as the sol gel technique.
2. To select better substrate for the deposition of the films of the lower thickness including
   stainless steel.
3. To choose a good deposition technique for the thin films.
4. To focus on the transition metal oxide including the oxide of the cobalt as potential
   candidate for the electrode material.
5. To optimize the large number of the parameters for the good deposition of the
   synthesized material on the substrate.
6. The parameters to be optimized must include temperature, concentration of the
   precursors, pH, etc.
7. The various properties of the thin films using large number of the techniques for particular properties are to be studied. These techniques may be TGA, FTIR, XRD, SEM, EDAX, BET and XPS.

8. To select a better electrolyte for the study of the supercapacitance properties including the KOH and ionic liquids.

9. To heat the deposited film at high temperature for possible incorporation good properties because of the change in morphology.

10. To study application of the synthesized oxidethin films for supercapacitor.

1B.4 SCOPE OF THE RESEARCH WORK

In this thesis we were proposed to synthesize the electrodes for supercapacitors by sol-gel method. We were also proposed to take care of the environment and accordingly, we have focused on the application of the environmentally non-polluting solvents. Especially we have used the organic compounds as ionic liquids. These ionic liquids are used as electrolytes for the supercapacitors. In the demonstration of the full proof application of the supercapacitor, we have optimized various parameters, which in turn are related to device fabrication.