3.1 INTRODUCTION

The entire planet is facing the crisis of the energy of all kind. This has also the concern of the environment, which need to be discussed at first. To meet the need and also to justify the protection of the nature, it is necessary to try to find the excellent energy storage equipment’s. These equipment’s may be called as devices, at the same time must be able to show good performance towards repeated use. The scientists across the globe who are working in the area of the synthesis of the better materials for energy conversion has come up with the some devices. These devices include, at the top priority the supercapacitors may be conveniently called as the electrochemical capacitors. This devise is having the ability to store charge at the efficient level, and thus are looked upon as good option. These supercapacitors are facilitated with some of the properties as capacity to show more energy density and also the better density of the power. These properties of the supercapacitors are leading the expectation from this technology to be the promising candidates to meet the high end and growing demand from the industries as
electronics, energy conversion received form solar rays and storage and also in the medicines field [1]. The supercapacitors have also received great interest for many potential applications such as electric vehicles, medical electronics, in addition [2]. The life cycle of the supercapacitors is longer along with the other important characteristics as efficiency to store are release the energy is high, and these devices could be repeatedly used for the purpose. In SCs, active materials are playing important role for electrochemical performance. Generally, transition metal oxides, conducting polymers and carbon materials are typically used as electrode materials in the supercapacitors [3]. Carbon based materials as well as the polymers materials have some of the characteristics related to the energy storage more favorable. These properties include more life of the cycle, good towards the electrical, and also the physical properties as mechanical. At the same time when we consider the metal oxide materials which have specific capacitance values towards the higher side and much better energy density than other two types of the electrodes. In SCs the energy storage mechanism is usually attributed to the efficiency at which the electrons are moved to cause an electrochemical reaction, and also the movement of the charge due to movement of the electrolyte ions at electrolyte and electrode interface [4]. The capacitance of the higher volume and superior energy density of the supercapacitor is due to the fast faradic reactions and also the reduction and oxidation reactions as compared with the EDL capacitors.

Comparatively better electrode materials for the supercapacitor are provided by the different metal oxides, especially the oxides of the transition metal as ruthenium oxide, nickel oxide, cobalt oxide and iron oxide. These metal oxides shows pseudocapacitance which is the basic requirement for the charge-storage. The high specific capacitance is shown by the ruthenium oxide and thus it is also called as the good electrode material. It is less attractive for application due to high cost [5]. One of the expectations from the electrode materials is that, it shall withstand the different surrounding conditions and also the corrosion mechanism while showing the performance at long-term stability with good efficiency. This description best matches to the cobalt oxides. It is also of low cost and has attractive properties and thus finds use for commercial application [6].

Co₃O₄ has been attracted considerable interest for SCs as an electrode due to its various oxidation states, less price and high specific capacitance. The cobalt oxide interacts with the
electrolyte ions throughout the bulk along with at the surface this is the reason why the cobalt oxide is performs well electrochemically in the pH range above seven [7]. There are various nanostructures with different morphologies of the cobalt oxide prepared by many researchers. These nanostructures includes nanoparticles, spheres solid and hollow, rods and plates of nanosize. There are also some examples of the cube shapes and wire shape of the nanosize. There are very large number of the methods are devised for the preparation of the cobalt oxide nanoparticles. By the technique of the sol-gel one can obtain the materials with the very high surface area of useful for the supercapacitance properties. The spinel type cobalt oxide is reported to be prepared by this technique. The carbonate of the cobalt was taken as precursor. It was then dissolved in the carboxylic acid with three carbon atoms. This mixture after heating produces the small particles, looking like the bid type material. The application of the nitrogen for cooling the produced material leads to obtain the spinel cobalt oxide. The cobalt oxide formed is stable in nature and able to show capacitance properties. Here comparatively low temperature is required to carry out the reaction [8].

The preparation of the materials with useful properties are synthesized by the chemical reactions carried out by the sonication process. Here the chemical reactions are done in the sonication baths at high frequency. This is one of the good technique for the deposition of the material of interest. In the sonication technique the high temperature in the range of few thousand degrees and high pressure is attained for the reaction to occur. Thereafter that very low temperature cooling of the material is allowed to of at rate. The mechanism involves the creation of the spaces and bombardment of the molecules at very high speed leads to the filling of these cavities. The films deposited will posses some of the extraordinary properties useful for many applications. The materials of various nature of crystallanity could be prepared by this method. The carbonyl compounds of the transition metals could be broken down choosing the solvents with lower chain of the alkanes. In some report the acetates of the transition metals are exposed to the allowed to undergo the chemical reactions in the sonication bath. Here the achievement of the transition metal oxides as iron oxide is accomplished in the presence of the aqueous solvent to dilute dimethyl formamide. This mechanism helps us to produce the transition metal oxides with the various surface morphologies and sizes [9].
The cobalt oxide was reported to be prepared by the chemical spray pyrolysis. After the synthesis of the cobalt oxide in bulk it is heated at the high temperature ranging from five hundred to eight hundred degree centigrade. This heating has converted the bulk of the cobalt oxide to nanosized material with the uniform distribution of the particles of small size. There is no observation of the aggregation of the particles. While the reaction is continued there is evidence of the application of the another additive chemical ethylene glycol. The use of this chemical enables cobalt oxide formation in the its nanosize dimensions. As per requirement and also to get the expected properties the annealing treatment is extended to this material in the chemical spray pyrolysis technique [10].

The nanocrystalline cobalt oxide particles were reported to prepared by the new technique of microwave. These nanocrystal of the cobalt oxide were then used for the film formation of thin type. The mechanism was started with the use of the precursor like the cobalt nitrate at the defined temperature. By maintaining the temperature of about 373°-413° the cobalt were immediately formed. For the stable cobalt oxide formation the stabilizer is being used. When the temperature is varied from low to high the shapes of the cobalt oxide particles changes. Such a materials with high surface area due to nano size is of importance in supercapacitance studies [11]. In one other technique of the formation of oxides from the transition metals is the combustion method. Here high molecular weight compounds of polymer type are being used as starting materials for this synthesis. In addition of the cobalt nitrate the alcohol containing the multiple vinyl groups was employed in the combustion method. The confirmation of the cobalt oxide nanoparticles was done by using the characterization techniques including XRD and TGA. As some organic entities are used in the synthesis, the removal of the volatile organics was achieved by heating the sample at comparatively high temperature to get the fine particles of the cobalt oxide of few tens of the nanometer in size [12].

The transition metal oxides show the very interesting chemical and physical and properties. These properties can be made use in the rechargeable devices used in energy conservation along with the gas sensing applications. The oxides and hydroxides of the cobalt are prepared in the nanomaterial size particles. Here the solution chemistry reaction mechanisms are used. The morphology of the cobalt oxides and hydroxides is in relation with the size of these
compounds. The methods employed for the synthesis of the cobalt oxide were working at the low temperature and involving oxidation reactions, which converted cobalt hydroxide to cobalt oxide material of nanosize. The commonly used characterization techniques were used in this case also for confirming the structural properties of the synthesized material. The techniques were including the XPS technique, SEM Technique, TGA-DTA Technique and Raman techniques. The XRD analysis was used investigate the phase formation and crystal formation information. The specific properties of the synthesized cobalt oxide indicated the probable application in capacitance studies [13]

The methods described for the synthesis of the transition metals oxides are mostly use the more than one precursor. Only few methods are concerned with the application of the only one chemical as precursor for the synthesis of these metal oxides. The use of the many source materials need the compromise between the properties of the compounds involved. As the different materials will have issues of reacting in combination with the other compound and also the properties dependent on the temperature are also different and thus their behavior needs to be taken care of. The stability of the sources towards the water molecules in the atmosphere and also the rate of the decomposition for the only one component in the source material could be controlled well. There is also the observation that the pure material of the interest could be easily produced from the single starting chemical. In a typical synthesis of cobalt compounds the source material including the nitrate of the cobalt was heated with ether solution of the oleic acid at the temperature of 673 °. After monitoring the effects of the various parameters of the reaction mechanism, the synthesized material was obtained in the one as to one proportion and also in the nanosize dimensions [14].

In one another technique instead of using the usual methods of material synthesis a different approach is handled. In this the lasers of different strength are used along with the condensation mechanism to produce the metallic or metal oxide nanoparticles useful for storage of energy and conversion of one form energy in another devices. The method in which the vaporization is happened due to the exposure to the laser, which is then allowed to condense the material on the supporting material is called as the laser vaporization controlled condensation. The conditions for the depositions are could be optimized at the very specific level which in turn helps to produce the materials of the expected composition and size, mostly nanosized. Here the
need of the precursor heating is not necessary and no chemical reaction takes place. The nanoparticles obtained in this way by using the laser treatment are usually of the uniform size and are round in shape. Here the gas nitrogen in ultrapure form is used for achieving the condensation of the cobalt and also has almost no impurities expected from involvement of the oxygen [15].

There are several approaches to synthesize the materials by chemical as well as physical methods. In addition to this several groups of scientists have worked on the possibility of the use of the biological materials for synthesis of the nanomaterials. There are some of the excellent capabilities of the biological materials such as the formation of the compounds with selectivity and ultimately with extra pure in nature. We can form the materials with various structures and also the different functionalities could be well addressed in these structures. In the formation of the material with specific shape as nanowires, we can optimize the conditions to get It done. The cobalt oxide nanowires are reported to be synthesized by using the amino acid containing phenylalanine. The natural material peptide is being used for this. The nanowires are having the capacity to attract the cobalt ions to produce the cobalt oxide nanoparticles. The phenylalanine functionalized amino acid are supposed to be support the self formation of the nanomaterials in the solid phase in the atmosphere of the basic aromatics compounds. The treatment of the taken first chemical and cobalt oxide films were prepared by the organic peptide derivative. By using ht sodium borohydride the reduction of the cobalt is achieved and the same is added to the earlier mixture to produce a expected material. Such a produced material is useful in the batteries lithium ion for the storage the energy purpose and in addition in the supercapacitors because of their charge and discharge tendency [16].

In the materials science one of the important issue is the morphology and structure control to achieve the expected properties as physical and chemical of the so produced material. The transition metal oxides with nanomaterial size are of importance to obtain the functionalized components for the supercapacitors as well as in batteries. In one of the study the scientist have developed the different morphologies of the cobalt oxide nanomaterials using the eco-friendly techniques of the solvothermal type. Here no surface binding material is used. The hydroxide of the cobalt carbonate was produced in this method which was then annealed at high temperature.
The control of the size and morphology is achieved by appropriate experimental conditions as concentrations of the chemicals and also the rate of the reaction. The materials deposited in this experiment are in the film form and is used as the negatively charged electrode in supercapacitance study and also in batteries. The metal cobalt can show variable oxidation state and thus the deposited materials can also show oxidation and reduction reactions useful for the supercapacitors[17].

The energy sources for small electronic devices is nothing but the lithium ion batteries. These batteries are rechargeable in nature and have the remarkable properties as appreciable life cycle and good density of the energy. The increasing demand for the energy has expressing the invitation to develop the improved devices with good performance towards the energy conversion and storage and capacity. In one report the method for the synthesis of the cobalt oxide material and its deposition involves the cobalt oxide deposition in the form of the nanomaterial on the silicon surface. The deposition by chemical vapour path is used for the evaporation of the cobalt oxide and ions are allowed to grow on the titanium. By this method the deposition achieved is excellent and there is no scope for the unwanted materials being produced in the side reactions. Though some of the other compounds are produced, those are get rid by varying the experimental conditions. The anode of this material is used in the lithium ion batteries that is the cobalt oxide, is. This formation helps to introduce the small sized lithium ion batteries with high efficiency. In the reaction system, the substrate temperature is varied controllably along with the pressure of the molecular oxygen.

These factors reflect son the nature of the morphology and also composition of the phase. The spectroscopy of the electrochemical impedance and charge and discharge measurements by galvanostat were done for the confirmation of the electrochemical properties of deposited nano cobalt oxide, indicting potential applications in the new generation lithium ion batteries [18]. The advanced technology of energy conversion and storage makes use of the transition metal oxides of the spinel type. The cobalt oxide and cobalt ferrite are among most attractive metal oxides for this application. This material leads to the evolution at its surface of the oxygen gas. The spinel phase of oxide of cobalt shows various properties in their nanosized an structured material. The different methods of the synthesis of the cobalt oxide at the nano level, produces the structure
with different crystallite size as well as available are external part of the film. The porous nature on the external face of the film te presence facilitates the interface between the solid surface of the electrode and the evolved gas in the electrochemical bath. The pore size and the surface dimensions was evaluated form the Emmett -Brunauer–Teller –technique by using the nitrogen gas. The XRD characterization was used for the confirmation of phase formation of the material [19].

The synthetic mesoporous structured material prepared of the transition metal oxide shows large surface area volume becomes better materials for the applications in supercapacitors. The usual methods of the aerogel synthesis are the processes like sole-gel. The precursor cobalt chloride was selected for the synthesis of the cobalt oxide aerogel by intramolecular displacement reaction in which the chloride form the cobalt salt is replaced by the epoxide ion and termination of the reaction in the production of the cobalt oxide. The properties of the cobalt oxide aerogle were showing the supercapacitive properties at par with the materials synthesized by other methods as stable cycle of charge and discharge, reversible reactions and excellent specific capacitances. The electrochemical studies indicated that the aerogel electrode shows ideal capacitive behavior with specific capacitance of range exceeding the six hundred faraday per gram [20]. The calculated value of the capacitance for the cobalt oxide is about thee thousand six hundred faraday per gram, which is supposed to be comparatively better among the metal oxides. This property along with the other useful properties of required for the supercapacitance, leads the recognition of the cobalt oxide as the superior oxide for this application. The large number of the methods are reported for the synthesis of the cobalt oxide in which the control of the size and dimension was at the top priority. But to have the controlled synthesis, more than one parameter needs to be optimized, and this situation does not assure the repeated production of the same morphology as well. To overcome this, the concept of the application of the materials containing the organic frameworks of the metal is becoming most popular. In the attempt to find better efficiencies of the supercapacitor materials, at the enhanced heating the metal organicframeworks could be converted to metals oxides of the nanoporous texture. It is well known that the nanoporous texture facilitates the large surface area required for the better supercapacitor properties. In one of the study the imidazolium based zeolite frameworks are
employed in as the metal organic frameworks. In the synthesis of the cobalt oxide of the nanoporous nature the above material acts as the precursor and also the carbon of the similar nature. Both these materials together are responsible for the better density of the energy [21].

Although the supercapacitors possess many positive characteristics related to the power and energy, those are having some limitation while we use those devices in the real applications as low density of the energy. One of the promising remedy to overcome this problem is to search for the advanced mechanism to produce supercapacitors. In this the reports are available where the focus is given on the development of the asymmetric supercapacitors. The combination of a capacitive electrode and the pseudocapacitive electrode in unique system gives us the formation of the asymmetric supercapacitor. This asymmetric supercapacitor set up can works at the wide voltage range and helps to increase the density of the device with respect to energy. Thus, so as to obtain better energy density by retaining the other important characteristics as it is, the electrode material shall be found out. The synthesis of the hydroxide of the nickel and cobalt of the very thin nature could be done by using the hydrothermal process. Here the reduced graphene oxide surface shows the growth of the two dimensional nickel-cobalt hydroxide nanolayer. The graphene was previously reduced with the well known reducing agent ascorbic acid of laevorotatory type. This acid also helps to control the morphology of the nickel-cobalt hydroxide. The deposited thin film material layer with optimum thickness in nano-scale has shown the increased stability of the cycle. The beauty of the material is that it works in the aqueous medium of the electrolyte. In the electrochemical studies the cobalt-nickel film deposited on the reduced graphene acts as the electrode of the positive charge. The negative electrode was made up from the carbon material. Overall this system of the asymmetric supercapacitor has shown better reversibility of the capacitance cycle in the potassium hydroxide of six molar concentrations along with the 56.1 Wh/ kg energy density of, eighty percent retention capacitance after cycles number of seventeen hundred charge-discharge [22].

The reactions and storage of charge on available electrode material area of the surface is the basis of the pseudocapacitors. Most wanted type of the devices as Co₃O₄ pseudocapacitors because of its high theoretical specific capacitance and conductivity. If we choose the substrate material such as the graphene, then we observe the conductivity of the cobalt oxide
pseudocapacitorto excellent increase. Because the graphene itself is the excellent conductor of the electricity. The hydroxides of the transition metals are preferred in the synthesis of their oxides, because of the their plentiful occurrence. These materials also provide major support for the efficient conduction cause of the electron giving and reduction reactions. The nickel hydroxide has the higher value of the specific capacitance if calculated theoretically, whereas the cobalt hydroxide shows specific capacitance than that of the cobalt hydroxide. But the cobalt hydroxide has the ability to deliver the excellent conductivity than its counterpart in this comparison. Thus if we think of mixing these two different hydroxides of the transition metals cobalt and nickel then it is observed that there is great enhancement in the capability of the rate as well as specific capacitance. This effect could also be referred to as the additional value of the specific capacitances shown by the two different transition metals. In the attempt to fuse together two metal cobalt and nickel, the special structure is designed in there dimensions. The growth of the special morphology as the nanobrush of the cobalt and nickel hydroxide on the surface of the graphene is achieved by the hydrothermal method followed by the electrodeposition technique. Here the ultrathin film of graphene was supported with the surface of the nanobrush morphology of cobalt oxide. This is composed of the large number of the ultrathin nanosheets and the cobalt and nickel hydroxide nanoflakes. These structures are immobilized uniformly and cobalt oxidenanobrush-graphene and were interconnected very compactly. This three dimensional architectural frames are of special importance to enhance the capacitance of the material. This fusion of the metal hydroxides and the graphene adds some features to the materials as fast transport of the electron and charge and discharge in reversible nature. This material has shown the high specific capacitance indicating high performance in terms of about two thousand five hundred fifty faraday per gram, better stability of the cycle of charge–discharge upto the five thousand cycles at eh good retention value of more than ninety percent. As usual the oxidation reduction reactions are shown by the metals involved in this study of electrode materials based asymmetric supercapacitor [23].

It has been found that in addition to the oxides the d block metal sulfides are investigated as the materials for the electrodes in supercapacitor study. There different kinds of the sulfides of these metals depending on the presence of the number of the metal atoms as binary sulfides and the ternary sulfides of mostly the potential metals as cobalt and nickel. These sulfides are found
to show improvement in the electrochemical performance. Hydrothermal method was employed to synthesise the hexagonal nanosheets of the cobalt sulfide showing the supercapacitance of around three hundred faraday per gram with the current density of sixty four units. Similarly the nickel sulfide electrochemical study in the three-electrode measurement system has shown 965.98 F g$^{-1}$ specific capacitance at a current density of lower value. The sulfides of individual metals has the capacity to show reduction and oxidation properties, but if we take more than one metal together to produce the film of the material then it is observed that he oxidation and reduction reactions takes place at fast rate. This fast mechanism of the oxidation and reduction is much needed for the much electrochemical energy storage better performance in the. The electrochemical deposition in one step strategy is used to deposit the cobalt and nickel sulfides binary type. This strategy leads the formation of the material in which the composition is controlled. Such a binary sulfide was employed as the electrode with cationic nature and it was showing the very good ability to store energy. At high current density, in the three-electrode system the capacitance obtained was also high [24].

It is the common observation that the different kind of the structural arrangements in the three dimensions of the materials always facilitates the larger surface area and in turn the availability of the more number of the sires for expected reactions. These properties are positive towards the application of such materials in the supercapacitors and also in the batteries. Instead of the depositing the metals as cobalt or nickel on the substrate by solution method or physical methods, the application of the foam like material of these metals leads to produce the threedimensional growth on the surface and thus enhancing the electrode materials electrochemical properties. Underlining the importance of this method of deposition of materials, it is found to be useful to obtain the expected structural properties such as easy transfer of the ions as well as the electrons and the large surface area. Such depositions allows better contact of the electrode and the substrate to lead for the enhanced ion transport, creating the particular paths for the cations and anions transfer. The ternary oxides of the transition metal oxides are now a day’s gaining the importance in supercapacitor applications. As an example we can see that the ternary composition of the manganese, cobalt and nickel could be the best candidate showing capacitance of twelve hundred units in the window of −0.1 to 0.4 V voltage. This combination of the metals to form the ternary composition
is achieved by the hydrothermal method to produce the material of the nano size. The supercapacitive behavior of the ternary oxides need to be enhanced.

The reduction is the cost of the synthesis of the electrode material by retaining the safety features of the electrodes could be expected from the ternary metal oxides. This could be achieved by using the three dimensional deposition methods of these materials. In comparison with the single metal oxides, there is great cumulative effect of all the three metals simultaneously on the oxidation and reduction reactions in the electrochemical studies. This effect is because of the some of the useful characteristics of the combining metals as high capacity leading to high conductivity, good electrical conductivity and capacitive performance. Because of the defects in the structures of the different metals there’s possibility of the enhanced stability and life cycle of the metal oxide electrode. The zinc nickel and cobalt mesoporous nanowire electrode could be developed by eco-friendly method. Such electrode is called as an asymmetricsupercapacitor, which acts as the cationic electrode and whereas the negative electrode is carbon material. The specific capacitance obtained for this material is of value 113.9 Fg \(^{-1}\). Along with this the cycle stability is also excellent [25].

The systems of modern electronics and high power needs the time-dependent and extremely high powers energy devices such as the supercapacitors. The pseudocapacitances as well as the electric double layer capacitances is shown by the supercapacitors based upon the metal oxide. It is evident that the noble metals are good candidates for the supercapacitors, but the cost of these metals is mostly not affordable. Thus the oxides of the transition metal as, cobalt oxide and nickel oxide, are given priority now days [26-29].

The electrode materials higher the specific surface area the more are the chances for the accommodation of the ions and charges cation and anions to produce the layers especially the double layers in large amount. This facilitates the reactions required for pseudocapacitance. If such high surface area is accompanied by the small sized pores, very less nanometers, then the reduction and oxidation reactions will be occurring due to the transfer of the mass of the electrolytes in the pores. These both the area of the sizes, the external face dimension of the pores are the characteristics related to the specific capacitance values of the electrode material [30-35].
For preparation of the excellent electrodes for the applications in supercapacitors one can choose the materials with large number of the mesopores including the oxides of the transition metal and aerogels. It is expected that the mesoporous materials must have the capability to be useful in the situation such as the applications in the thin film with low dielectric constant, glass with low index of refraction; these properties are absolutely dependent of the porosities and surface areas [36-41]. The routine methods for the synthesis of the aerogels are from the compounds with organic entity in the conjugated bases of the alcohols is attached to the oxygen and the methods preferred are the solution based sol-gel methods [42-44]. In the recent methods using the epoxide requires to make use of the metals with the higher oxidation state so that stable materials could be prepared. At defined pH and by epoxide route, the metal ions with two valences as cobalt, nickel, copper, manganese etc are recommended for aerogel preparation [45-51].

By taking the starting chemicals as cobalt chloride hexahydrate and the cobalt nitrate hexanitrate, the aerogels of the oxide of the cobalt was prepared with addition procedure of the epoxide drying by the supercritical CO$_2$. The nitrates of the cobalt are found to be the good candidate for the formation of the gel. The alcohol as methyl alcohol was taken and used for the dissolution of the cobalt nitrate hexanitrate. This mixture was then facilitated to get the transparent solution and for this it was added with cyclic compound the oxide of the propylene to the clear solution. The solution was cooled down at the room temperature after stirring for about ten minutes and this resulted in the formation of the gel in another twelve hours. It is evident that the some traces of the added chemicals and also the formed side reaction products are always remain with the expected product, and thus the washing of the gel with the ethyl alcohol was carried out. At the high pressure of the system such as the 83 bar and the temperature of 318 kelvin for almost two hours in the liquid CO$_2$. For obtaining the aerogel in dried form, as usual that of the routine procedure, the pressure and temperature was made brought to normal. By taking in consideration the aim to produce cobalt oxide the, aerogel of composition of the cobalt hydroxide was then heated to about 473 kelvin for about five hours. By using the mesoporous adsorbent the mesopores and micropores cobalt oxide was obtained. The procedure was involving the dispersion of the mesoporous adsorbent in ethanolic solution of the cobalt nitrate hexahydrate followed by stirring.
and drying at normal temperature. After the desired time period the excess ethyl alcohol was the evaporated by heating the whole solution. The heating was followed for another five hours to obtain the cobalt oxide of porous nature. This idea of the formation of the aerogel of the cobalt oxide as a material to be useful in supercapacitors is an ideal example. Here the material has shown the supercapacitance more than six hundred faradays per gram at reasonably high mass. The stability of cycle good as well as the reversibility was also remarkable [52].

At the electrode materials surface, the atoms are responsible for Faradaic reactions which is the cause of the specific capacitance like that of lithium ion batteries but rather much lower than the latter [53, 54].

If attempts are made to increase the number of the atoms on the surface of the electrode material, then there are chances to have more surface area for the supercapacitance properties. This increment in the atom number could be achieved by using the different morphologies in the dimension range of the nano level of the metal oxides. This application has evidenced in the increase in the capacitance [55, 56]. It is well know that the oxides themselves are the materials which show the conductivity of electricity to be very low [57, 58]. The good option is to make use of the sulfides of the metals to observe the comparatively good electrical conductivity [59-61]. The ultrathin nano sheet of the molybdenum sulphide material has shown to responsible for the observation of the high operation voltage and 95 percent Coulombic efficiency [62, 63]. If we change the composition from binary to multi-component, by doping of themetals with different metal sulphides of more metals, then the observation of the good electrochemical activity and electrical conductivity is common [64]. There are reports of the use of the binary sulfide nickel cobalt sulfide in the applications energy storage. This binary sulfide shows better electrochemical performance [65, 66]. This activity is comparatively better than if we take the oxides of the these metals. There are various reports on the different morphologies of the materials as nanoplates, nanotubes and spheres used in the electrochemical studies [67, 68].

Though there are few reports on the electrochemical activity of the nanosheets of the metal sulfides there is limitation for these materials for the better electrochemical activity and the related observations as ion transporting ability and the accumulation if the active sites is fairly good. In one of the literature survey it is reported that the ultrathin nickel cobalt sulfide is
efficiently used for the supercapacitance studies. The cobalt nitrate hexahydrate and the nickel nitrate hexahydrate were taken in the 2:1 proportion to this added the hexamethylenetetramine. This whole composition was then added to the mixture of the ethylene glycol, water and ethyl alcohol, resulting in clear solution. This then allowed to react the solution was for two hours at the temperature of 443 kelvin, this material was prior kept fortnightly as it is. Then the product was expected which was washed by de-ionised water thoroughly. The synthesized material is then mixed with stirring in the H$_2$O. For conversion of the prepared multi-metal oxide in the sulfide nanosheet form, the sodium sulfide solution was used. The entire solution was cooled after heating for the few hours of the time at the temperature of one hundred sixty degree celsius followed by alcohol washings the final desired material of the nanosheet form of the cobalt nickel sulfide was obtained in the very small thickness. Both the metal sulfides simultaneously contribute to the properties suitable for the supercapacitance by allowing the fast transfer of the ions accompanied by the fusion of the ions in the the material porous structure of. The specific capacitance of the value 1304.0 F/g was observed at a current compressibility of two point zero A/g and the capability rate was 86.0 % with twenty A/g. The retention after six thousand cycles is found to be 94.0 percent. The power density at high level and energy density of this material are indicators of the potential applications in the cars [69]. The reduction of oxygen and the applications of such materials in supercapacitors are facilitated by the spinel structures of the nano sized materials. In this case at the top priority are the oxides of cobalt. These oxides acts as the catalysts by electrolytic mechanism[70-73].

The method of the preparation as sol-gel provides the way to obtain the cobalt oxide materials to prepare with the dimensions of the high surface area favouring better electrochemical performance. This method also overcomes the difficulty of the competing performance with those of the routinely used materials. The possibility to obtain the uniform distribution of the ions in the materials prepared is also more in case of the sol-gel method, causing the high are of surface [6]. The gels produced by this method are further converted to aero-gel by the effective heat treatment. If the chemicals used involves the epoxide, then in such case we get the efficient formation of the oxides of the transition metals as zinc, copper, and cobalt [74-78]. In the sol gel methods involving the epoxides, the epoxides eat the hydrogen ions when mixed with the salt solutions of the metals. Here the gel is produced as a network
structure, which is controlled by the type of the slat, solvent and the hydroxide formation mechanism. These parameters also influence the material properties required for the electrochemical applications[79, 80].

The stock solutions of the cobalt oxide were prepared first from the starting chemical of Co(NO$_3$)$_2$·6H$_2$O. Then to the little volume of the stock solution of the Co(NO$_3$)$_2$·6H$_2$O, the epoxide was added in the room temperature. This combination on certain time interval has resulted in the formation of the gel. The gel so produced was allowed to remain as it is for few days and then the carbon dioxide was passed through it for drying. After the process of the heating at high temperature the aerogel was obtained as expected. This aerogel material was applied to study the electrochemical properties that is for supercapacitance studies by using the potassium hydroxide as the electrolyte. This gel allows the transfer of the charge for the effect of pseudocapacitance by the mechanism of the electric double layer [81].

The metal in cobalt oxide that is cobalt exhibits the different positive oxidation states of the two, three and four also. This behavior of the various oxidation states in the oxide leads to the easy accommodation of the electrolyte ions and the molecules of solvent on the surface of the material thereby facilitating the charge transfer and the reactions. This also shows less hindrance towards the transportations of the ions. The capacitance observed for the cobalt oxide aerogel is because of the specific porous morphology and fine structure and is more than the pure cobalt nitrate. The values 110 to 550 F/g were observed for the specific capacitances obtained from the aerogels of cobalt, as electrochemical performance. The particle size, surface areas and morphology of the cobalt oxide aerogel has played an important role in its application.

The supercapacitors of the type solid state are recently found to be more useful over the routine supercapacitors because of their characteristics such as eco-friendliness, good reliability, and are much handy for movement and thus have applications in the power sources and energy storage. By considering the limitations of the efficiency of the supercapacitors of the type solid state, the researchers have come with the solutions to modify these types of supercapacitors with the so called asymmetric structures. The nanostructured supercapacitors of the type solid state with asymmetric nature can combine the concepts of the pseudocapacitance and electric double layer capacitance and in turn shows for the same electrode material various voltage windows.
And this combination of the double layer capacitance and pseudocapacitance leads to the promising increase in density of the energy. In the energy storage devices of the advanced type, includes the category of the asymmetric solid state supercapacitors type with nanomaterials of the two dimensions. The performances of the energy storage at the level of atom is found to be enhanced, such atom level structures facilitates both the very thin films, and allows the diffusion of the ions, and because of the maximum exposure of the surface area the sites responsible for the electrochemical reactions will be in large number, this allows the formation of the supercapacitor of the desired properties [82].

There are reports of the nanosheet synthesis of the sulfide of the nickel and cobalt, which exhibits as micelle, has shown the specific capacitance 1304.0 F/g with the 41.0 Wh/kg energy density. Similarly the manganese phosphate trihydrate nanostructures synthesised by sonication method in dimethylformamide solution and has shown the high capacitance of specific type of value 2086.0 Fg⁻¹. The cobalt hydroxide with atomic layer of fraction of the nanometer size led to the formation of the asymmetric solid state supercapacitor material with 99.0 Wh k/g energy density and also the performance of cycle is also very good. In the synthesis of the nickel cobalt hydroxide with carbonate ion layers, the precursors as nickel nitrate hexahydrate and the cobalt nitrate hexahydrate were taken in the ion free water and mixed well to dissolve. This was followed by the sonication in presence of the ascorbic acid. The base potassiumhydroxide in water was separately taken and added to the former mixture with stirring at 453 kelvins. The various samples with different time factor were reported with different morphology. After washing and drying in the cold condition, the samples were characterized by various techniques. The so prepared material was then subjected to the formation of the gel by addition of the alcohol and potassium hydroxide in ion free water and stirring at 360 kelvin temperature. The gel electrolyte was applied for supercapacitance study of the solid state supercapacitor of nickel cobalt carbonate hydroxide. The electrode material behaves as the cationic electrode carbon with porous nature is the anionic electrode to show the supercapacitance of the 2270 F/g. with cycle stability of the nineteen thousand cycles at power density 8.70 kW k/g and 50 Wh /g energy density[83].
For instant storage and also for fast dissipation energy the devices of the electrochemical energy storage called as the supercapacitors are being recommended and also used on priority. The electrochemical pseudocapacitors and the double-layer electrochemical capacitors are the categories of the supercapacitors based on the mechanisms of energy storage. Especially the mechanism of the oxidation and reductions by the faradic reversible way is the backbone of the in the case of the electrochemical pseudocapacitors, where as in the case of the electrochemical double-layer capacitors the storage mechanism follows the involvement of the interface space between the solution carrying ions and electrode for the separation of the cations and anions. In case of the electrode materials in these mechanisms the oxides of the transition metals are playing the very important role. The ability of the transition metals to exhibit the variable oxidation states leads the characteristics of these materials to show the high specific capacitance. The transition metals oxide of the priority are the manganese dioxide, cobalt oxide, vanadium oxide and iron oxide. Among the variety of the oxides the one of the oxide that is the cobalt oxide is important and have preference in the supercapacitance studies especially in the electrochemical pseudocapacitors. The cobalt oxide has the very less adverse effect on the environment and also it shows the good characteristics towards the capacitance. The value of around the three thousand five hundred $\text{F} \text{g}^{-1}$ of cobalt oxide shown as the specific capacitance when theoretically calculated. In the applications of the cobalt oxide in the capacitance studies, the important role is played by the surface. The oxidation and reductions by the faradic reversible path takes place because of the involvement of the surface and allowing the process of the instant and reversible reactions. However, the applications of the transition metal oxides may lead to poor performance. Thus, several attempts are made to enhance the performance of the capacitance system. In this task the modifications in the electrode material with respect to the shapes and sizes could important role play an. The fast transportation of the ions between the in the electrolyte and electrode interface of the and the inside components of the electrode need to addressed. In this, the attempts are made to synthesize the electrode materials with large active surface, small pathway for ion diffusion and high capacities for charge. These all requirements are satisfied by the structures of nanoporous type. The electrochemical supercapacitors performance can be improved by allowing the above mechanism of fast diffusion etc. which are predominantly satisfied by the cobalt oxide material of the
mesoporous nature. The substrates are also important entities in the supercapacitance studies. In the electrodeposition of cobalt oxide the substrates usually more preferred are with thermal stability and high surface area, especially the nanotubes shaped titanium oxide materials. The titanium oxide also adds the capacitance of electric double-layer type but to the very small amount and thus could be neglected. Whereas the specific shape such as nanotubes, with the large area surface the substrate facilitates to increased capacitance by allowing the dispersion of ions of the positive charge as well as the negative charge. Overall the fabrication of the materials with porous surface is important in the supercapacitance studies. Thus, while progressing to synthesize the cobalt oxide of the porous nature several attempts are reported in the literature. There are several techniques, including the spray techniques, which could be implemented for the formation of the cobalt oxide. However some of the techniques are sophisticated. To avoid the complication and requirement of the sophisticated techniques the solution methods are reported in the literature. In one of the report, the titanium metals was selected and after ultra-cleaning was used for the growth of the nanotubes of the. Here the titanium dioxide material acts as the anodic cell and the counter electrode was the foil of the platinum. Here the precursors used were the zinc chloride and cobalt chloride hexahydrate and traces of the boric acid. After the conversion of the titanium to the anodic material, the whole material was heated at the higher temperature of the 450 °C. This plate was then allowed to take part in the electrodeposition of the cobalt and zinc by electrodeposition path, with prior treatment with the sodium hydroxide. The application of the sodium hydroxide also helps to remove the some part of thee zinc and leaving behind the cobalt oxide with the porous nature. This facilitates the formation of the cobalt hydroxide, which on annealing for few hundred degrees gets converted to the cobalt oxide deposited on the titanium oxide. Thus the so produced electrodes are responsible for the observation at the current density of one A/g as 430 F/g specific capacitance. The retention of about 80 percent for the specific capacitance was noted.

The growing demand of the energy for various purposes could be managed and for this the scientists are making a tremendous progress in the development of the batteries as well as electrochemical supercapacitor. But, if one thinks of the using these two technologies fused together; there is alarming enhancement in the energy storage and conversion mechanisms. If it
is looked in the progress of the electrochemical supercapacitors, there is much improvement, but still the electrochemical supercapacitors suffers from the low energy density ability. In this concern, the electrochemical science hints the modifications in the electrode materials, which plays an important role with respect to the self-discharge, cycle life and the energy density in the electrochemical supercapacitors performance study. Large amount of the work has been carried out for the improvements and also in developing newer types in the variety of the electrode materials. Transition metal oxides and also the hydroxides, polymers of the conductive nature and the carbon materials are vastly studied as the promising materials for the electrode applications. In such cases the very important themes which are at the fore front are the materials must be environmental friendly and at the same time must be abundant in nature or as resource including cheap availability. It is true that the single transition metal oxides are well fitted for the supercapacitor applications but there are some limitations to observe the highest performance. Thus, now days the researchers are considering the taking the more than one metal oxide together called as synthesis of the composite materials. Fortunately this way of the applications of the transition metals oxides has led the observation of the great enhancement in the electrochemical supercapacitance enhancement. Here, the enhancement in the supercapacitance simultaneously positive effect of as a result of the both the materials towards the expected characteristics of enhancement in the supercapacitance is observed by overcoming the limitations of the individual materials. The composite formation process facilitates the enhancement in the active surface area, appreciable conductivities of both the positive and negative ions and the excellent porous nature of the material. These properties are directly responsible for the greater pseudocapacitance with the material showing wide potential window, and retaining the material as it is for long life cycle [84].

As an example the conducting polymer based carbon nanotubes especially multiwalled, the specific capacitance observed is the 170 F/g. This material can be doped with the transition metal oxide such as the ruthenium dioxide leading the appreciable increase in the capacitance. The retention power of the 95 % capacity and good stability is accompanied by excellent supercapacitance of the value 1000 F/g using the large surface area and porous nanostructures when the carbon based polyaniline electrode of composite type is applied. In one another
composite formation the ten weight percent of the tri-cobalt oxide based on the aerogel of carbon is preferred, the supercapacitance was observed to be increased from the value of the 350 F/g to one thousand seven hundred faraday per gram. The composite formation provides the good background for the free movement of the electrolyte cations as well as the anions and high utility of the tri-cobalt oxide in the electrochemical mechanism. If the cobalt oxide is added with the multi-walled carbon nanotubes, it shows the boost in the size of the pore and also their distribution reflecting in the better surface area and the good conduction of the electricity. In this case, in presence of the electrolyte potassium hydroxide and at the density current of the 0.625 A/g the supercapacitance observed is of the value 410 F/g. In addition to the oxide composites, the examples of the hydroxides are cited in the literature. Specifically the high porosity and high specific surface materials as the hydroxides of the aluminum and nickel shows the supercapacitance of the value 475 F/g with good cycle stability and better density of the current. In this case the transport of the electrolyte molecules as well as the discharge and charge mechanism is better because of large surface area. The trend now a days is to search alternatives for the solid state supercapacitors and the solution is flexible supercapacitors. In such cases the hydroxide of the cobalt is loaded on the fibers of the cotton to experience the large surface area and the long life cycle for the supercapacitor mechanism. Here the distribution of the cobalt hydroxide is good and also the fibers also facilitate the good conduction because of the availability of the active sites in large quantity of the especially electroactive nature. The other metals from d-block of the elements table such as the manganese dioxide, nickel oxide and the cobalt together can be taken and the composite of the nanostructure type can be obtained showing the performance of at around 620 F/g and 500 F/g. But if we compare the supercapacitance values of the individual metal as manganese, it is much higher and the cycle life is also long [85].

In the storage of electricity and for the reactions involving the catalytic activities initiated by the solar rays in generation of the hydrogen by splitting the water and to prepare devices with the good materials like supercapacitors is a technological important challenge to prepare those from the metal oxides of conductive nature and of the nanostructured type. The oxides as the titanium dioxide, tricobalt tetraoxide, ferrous oxide and ruthenium dioxide are the important semiconductor materials in the applications of the current priority as energy storage as
Supercapacitors are greatly studied. Among the many transition metals oxides the most studied and also applied in many applications is the tricobalt tetraoxide for gas sensors and most importantly for supercapacitors. In the synthesis of the tricobalt tetraoxide materasil utmost interest is shown in the area of the surface of the material which eventually becomes the key point in the enhancement in the supercapacitance by the mechanism of the transport of the charges and thus the preparation of the smaller structures as nanostructures is at the priority. There are few methods which are used very commonly of the synthesis of the tricobalt tetraoxide are including the sputter method and deposition using the electrochemical bath. The other forms of the tricobalt tetraoxide are reported to be obtained by the synthetic routs as the hydrothermal and solvothermal paths, these leads to the formation of the forms in colloidal nature. These physical methods generates the shapes for the tricobalt tetraoxide as the spheres and crystals of nano dimensions. The reports are also available for the preparation of the porous materials of the tricobalt tetraoxide and also the structures with nano size by the precipitation by sol gel mechanism. The sol gel mechanism also effects in the production of the tricobalt tetraoxide materials in the one dimension, which is also possible by the spinning by electrical way method, reduction method, hydrothermal method. Here one needs to look in the very small wire preparation of the cobalt oxide, which is very challenging. These type of the morphologies may be obtained by the seeding materials as the as the reagents as nanoparticles. The nanoparticles may be the molecular colloids obtained by the entirely new ways are reported. In this concern the inorganic chemistry of the platinum group metals and also the gold has important role played an as the chemistry of the ligands as that in the coordination chemistry, to produce the nanoparticles form the Fe$_3$O$_4$and the gold. These materials in the solution behaves as of the polar type especially two polar. In one report the very attractive and demanding way for the application of the particles of the nanosize to synthesis the semiconductors of the materials with the cavity inside the structure is demonstrated.

There is a demand to produce the semiconductorsmaterials with the cavities inside and accordingly the oxide of the cobalt can be efficiently converted to the desired form by using the sulphurisation and also by the oxidation of the nanoparticles of the cobalt. The another p-block element from the chemical elements is the selenium which is being used for the wires of the nano size formation form the cobalt precursors. In such preparations the magnetic properties of the
materials also plays some role in presence of the surface active molecules. The nanowires of the Co$_3$O$_4$ were reported to be obtained from the starting materials as the dipolar nanoparticles of ferromagnetic in nature. As in such cases the combination of the few metal atoms takes place as the polymer formation in the colloidal condition, the nanowires cobalt oxide of the internal spaces are obtained in the same way. In such cases the polymers like the styrene molecules in the polymer form are being applied as the support materials. Here the mechanism leads to the creation of the situation wherein the polymer structures are eventually converts to the monomers. The styrene monomer which are combined to produce the polymer are reported to be used as the support for the growth of the nanoparticles of the cobalt via oxidation to produce the uni-dimensional structure. The uni-dimensional cobalt oxide nanoparticles in the later stage grow to the polymer formation by coming together the many nanoparticles cobalt oxide through the colloidal phase, this overall leads to the big molecule formations. The beauty of this mechanism is the formation of the nanowires of tricobalt tetraoxide with the layers which are showing the stability in the presence of even the solvents of the organic nature. In a synthesis of the nanowires of tricobalt tetraoxide the starting materials taken were chloro derivative of the benzene and the seeding material as the polymer supported nanoparticles of the cobalt in presence of the oxygen molecules at elevated temperature of approximately 450 Kelvins. The polymer supported nanoparticles were of the ferromagnetic in nature and of the colloids with even size. These materials are indicated as the promising for supercapacitor applications [86].

The nanomaterials show the specific and very important chemical properties as well as the physical leading to their importance among the other materials of the same composition but larger sizes. Thus, the synthesis of the nanomaterials is now a hot topic which is made easy by the unimaginable progress in the field of the nanotechnology. The tool developed by the nanotechnology helps us to produce the nanoparticles with great care and especially the controlled size. It is observed since last few decades that the applications of the nanomaterials and subsequently the performance of the systems where these nanomaterials are being applied is wholly dependent on the shape and size of the nanomaterials, which is taken care during the formation and the fabrication stage only. By considering the utility of the nanomaterials large number of the research groups and also the industries are looking for the approaches for the
synthesis of the nanomaterials which will be cheaper and same time also at the be the friendly environmental. Among the many precursors the oxide as the tricobalt tetraoxide is at the center point form the point of view of the special characteristics and accordingly numerous uses in various s forms and in the large number of devices as per sensitivity and also the performance. The conversion and storage of electrical energy the tricobalt tetraoxide material has find the importance. In search of the somehow good method for the manufacture of the tricobalt tetraoxide of the particles of the nanosize needs the proper methods which are wisely designed. The deposition by chemical vapor of the precursors, solution methods including the chemical bath depositions, hydrothermal etc are reported to of the importance to produce the very small sized tricobalt tetraoxide formation as well as the shapes are also of expected nature as the nanobelts,nanoboxes,nanotubes,and nanosheets. The tricobalt tetraoxide possess the exceptional characteristics as acting as the excellent oxidizing agent by the way of the catalyst to convert the carbon monoxide to the relevant oxide and that to at the ambient temperature. It is true that the texture of the material is also of the importance if we select thetricobalt tetraoxide material in the form of the nanostructure of one dimension then it is observed that the devices in which it is applied shows the enhanced performance with respect to capacitance that is the supercapacitance may be around one hundred faradays per gram. It is usual to get the transition metals oxides in the spinel form, which is not much of the useful things, thus the scientists have attempted for the various mechanisms as the use of the templates of soft type as well as some times the concept of the magnetism is also considered. The hydrothermal route and also the electrochemical route is the choice for the formation of the shapes as nanowires and nanotubes of the tricobalt tetraoxide material. One can think of the path in which there is the scope for the transformation of the one morphology to other or also to retain the morphology in such cases the starting materials play role good to the system. In the high temperature decomposition of the substance path the wisely selected and prepared precursors conversion to the very well formation of the cobalt oxide of the nanostructural size is evident, on which the control is by the precursor materials status. The precursors with the cobalt metal combined with the OH groups, CO$_3^-$ groups, HCOO$^-$ groups are of the prime importance in the synthesis of thetricobalt tetraoxide material of nanosize. If the alkyl oxide of the cobalt is heated at very high temperature then the
formation of the cavity containing spheres of the $\text{Co}_3\text{O}_4$ takes place if solvothermal route is used and supported with the polymer. The oxalate of the cobalt metal also is useful for the synthesis of the tricobalt tetraoxide in nanoporous form and this mechanism is comparatively leads to the better stability of the material structure, affordable path and also applicable at lower temperature. These mechanism can make use of the solution method making use of the microwave in the the organic solvent presence of produces the nanorods. The emulsion phase of the precursors is also useful for the formation of the nanowires and nanrods of the $\text{Co}_3\text{O}_4$. The applications of the stringent conditions including the choice of the chemicals as the liquid phase ions, the surface active materials, and also the methods containing the high temperature mechanism with the solution phases are the entities to be taken in consideration for the nanostructured materials synthesis. The methods and the chemicals used of these synthesis must abide to the conditions such as the low cost mechanisms, and must confirm the most wide applications. Some of the new strategies instead of the the usual methods of the synthesis involving the high temperature methods and the involvement of the very small droplets of the dispersion must be thought in the preparation of the desired shaped and with the nano sized tricobalt tetraoxide. There are some reports on the applications of the precursors as the oxalates of the cobalt and the ions of the cobalt element when allowed to mix together then there is observation of the fast and uncontrolled growth of the cobalt oxide material because of the exchange of the ion mechanisms among the two materials. Such reactions are tried in the applications of the organic solutions especially with the ability to favour conduction of the ions. The other problem with the oxalates of the cobalt and the ions of the cobalt materials in the organic solutions is that the size of the molecules leading to the severe effect on the ion formation ability in the liquids taken for study. Instead, some to the researchers have discussed the idea of the making use of the cobalt dichloride in the solvents of the nature of the polar type. This idea seems to be better, but has limitations of the dissociations because of the nature of the electrolyte to be weak. The best way out for the successful formation of the oxalate of the cobalt is to make use of the $\text{H}_2\text{O}$ medium which allows the reaction of the oxalic acid to it to produce the ions in the aqueous medium as the $\text{HCOO}^-$ and $\text{H}^+$ ions. These ions in further course of the reaction will lead to the reactions between the cobalt ions to produce the expected $\text{CoC}_2\text{O}_4$. In this mechanism the$\text{H}_2\text{O}$ plays its role to binding on line of its capacity as ligand, which exerts it active role and also
forces, the mechanism to proceed. In this mechanism the reactions product formed may be back converted to the original reactants as well as the again to the products. It is interesting to see that the control of the size of the cobalt oxide nanomaterials is possible by the systematic protocol for the selection of the solvent and the addition of the materials.

The literature indicates the use of the method involving the precipitate governed by the water of the formation of the one dimensional nanostructured CoC_2O_4. Here it is reported that the formation of the CoC_2O_4 is appreciable by the path called as the precursor in solution form and H_2O method. The reports shows that the precursors as the cobalt chloride and the oxalic acid were need to be made in solution form and for the formation of the precipitate H_2O was used. The organic chemicals of the category of the methyl derivatives of the sulphoxide and the CH_3CONH_2 were also allowed to take part in the reaction. In efforts to synthesis the different morphologies nanowires and the nanorods, firstly under the maintaining of

the stirring condition the methyl derivative of the nitrogen containing acetamide was applied to make uniform solution of the oxalic acid. This solution was then used for the accommodation of the hexahydrate of the cobalt chloride and also some amount of the ion free H_2O was added at last, which also helps to produce the precipitate of pink appearance which is nothing but the cobalt oxalate. Similarly in another simultaneous procedure the sulfoxide form of the methyl derivative was also found to be useful for making the solution of the oxalic acid followed by the addition of the hexahydrate cobalt chloride to produce the cobalt oxalate. The cobalt oxalates produced in both the above methods is then heated a about 675 Kelvins for stipulated time leading to the production of the nanostructured cobalt oxide of the porous nature in which the pore size was typically ranging up to the 50 nanometer. But the utmost care is taken while increasing the temperature may be very slowly. This facilitates the production of the material with interesting properties than the expected in the bulk materials of the same composition and also when observed through the different angle. The way or the protocol of the use of the various solvent in the fashion of the addition of them in different steps has produced the various morphologies of the cobalt oxalate. The typical morphologies observed for the cobalt oxide are of the growth of the crystal structures anisotropic type. In the formation of the cobalt oxide the water molecules are playing the important role of the bonding between the different planes of the molecules. This results in the synthesis of the nanorods of the cobalt oxalate in the
uni-dimensions and the structures of the column type. The nanorod cobalt oxalate synthesis is influenced by the solvent which are playing role in the formation of the crystals. Various shapes of the nanostructures are reported to have the effects of particle stability, solution type, the mechanism of the reaction with respect to the rate of the reaction. If this is taken in consideration the different products could be achieved by having some modifications in the solvent systems to get the variations in the growth and the seeding of the materials. The seeds of the cobalt oxalate are produced in different way by the effects such as the ways of bonding and also the solution formation abilities. The solution of the dimethyl amine when added to the prepared solution this results in elongation of as well as the increased dimensions of the nanorod materials. The nanostructures of the different morphology are observed if the solvent tis changed to the dimethyl sulphoxide to produce the flower type morphologies. Here it is demonstrated that the steps by which the different chemicals are added to the synthesis system causes to get products of the various shapes. May be one can try for the use of the water. The cobalt oxalate precipitate formation is observed when one makes use of the synthesis at the ambient temperature in presence of the water. For the observation of the formation of the bonds between the ions of the cobalt and the water then there is completion in between the solvent used and the H₂O. And the complex of the cobalt and water becomes useful for maintaining the cobalt concentration at the level of high so that the enough cobalt ions in the form of the complex will be available. The molecular formula to the cobalt oxalate indicates the presence of the water molecules of the crystallization, which are supposed to be supplied by the use of the water as solvent in the synthesis system. Here the addition preference of the solutions and the H₂O is that instead of pouring water in to the solution of precursor, reverse mechanism of addition helps better to get cobalt oxalate formation. Thus, these observations were sharply indicating the effects of the solvents for the observation of the particular morphology. This specific morphology of the cobalt oxalate have reported to show better supercapacitance properties as the two hundred faradays per gram in potassium hydroxide electrolyte and with the considerable window of potential. This material has also sustained for long cycle life [87].

The electrolyte and the material of active nature interface and allow the reactions of faradaic and reversible type. This phenomenon creates the mechanism of the supercapacitors and
pseudocapacitors, and this fact is now at the center of the energy storage devices. The RuO$_2$ hydrate as an electrode material is an excellent for the properties as the good conduction carrier. The reason behind this is that it is capable of showing the specific capacitance of high order because it is a transition metal exhibiting the more than oxidation states. It is to be taken on consideration that the process involving the second row and the third row transition metals and the metals lying nearby the platinum and gold proved to be very expensive, and the reason for this is that they are not cheap as that of the other transition metals. In addition the other aspects for not preferring this hydrate of the RuO$_2$ is that raw sources of it are very less in the nature and also another characteristics of this is the poisonous nature. While thinking of these numerous drawbacks of this one can make the use of some other metals in the transition metals series including the hydroxides and the oxides of the manganese, nickel, cobalt, iron and copper. Not only the metal oxides or hydroxides but the other forms of these metals as combination of the different metals is also taken as the good source of the electrode material for pseudocapacitors involving the mechanism of the reduction and oxidation. The properties as the very cheap in nature, the required reversible reactivity, the well conversant with the electron giving and reduction processes are the eye catching in the application of the oxides and the hydroxides of the cobalt metal.

As it well know that the better characteristics as the morphology, structure of the crystal, in the materials size of the particles, dimensions of the surface which are observed for the nanostructured materials are well preferred for the good electrodeperformance properties of the electrochemical mechanism. The dimensions of the material surface can be changed to desired high level and that to with the enough activeness by many methods which are developed by the dedicated researchers across the world. These surface dimensions may be of the type particles with the cavities to accommodate the maximum space available, tubes of nano dimensions, the sheets of the nanosize and the wires can be collectively called as the nanstructures which could be produced by many techniques with the close monitoring. The electrode materials supercapacitor behavior of related to electrochemical nature could be enhanced by the structures nanosized with high activities. The enough concern shall be given to the stability related to the electrochemical behavior whole the cycle of the discharge and discharge, while finding the
materials which will match with our requirements say the capacitance. Higher great stabilities, capability of rate to be the good, di—usion of ions be the better and the transport of electrons to be better these thing should be expected from the nanostructures and microstructures of the type having the tri dimensions. The material which will be having the advanced properties should be targeted and must be of the micro structured nature, this overall requires the very perfect approach and it also must be the able to further convert to the fabrication of the device. Such materials will be called as the very good for the electrochemical performance in the form of the electrodes and ultimately will be explored as the alternatives for the production and conversation of the energy.

The sol—gel method as well as the hydrothermal method are the good choices for the preparation of the oxides of the transition metal with the decomposition of the precursor of the metal by applying the high temperature. In one of important report the carbonate of the cobalt and also the hydroxide of the cobalt is reported to be used by applying this mechanism is well suitable for the and also used efficiently for the preparation of the oxide of the cobalt. The preparation by this method helps to get the desired product at the very easy level and also the product is also the stable though the temperature is comparatively elevated during the process. Along with the required electrode material of interest the supporting material for the electrode that is the carbon precursor could be obtained from the carbon containing compounds as the glucose, dimine carbonyl compound and also the carbonate of the sodium. Utmost care needs to be taken while using the supporting material as carbon compounds, because these materials may lead to add some problems in the synthesis of the electrode material with the required size and shape. The cobalt nitrate in the is reported to be used for the preparation of the cobalt oxide in a systematic manner which then led to the generation of the cobalt oxide. This laboratory level study is indicated to be useful for further production in large scale. The bell shapes of the micro size are obtained by the used preparation technique of the cobalt oxide in three dimensions. The carbonate compound of the hydroxide of cobalt after heating at high temperature and by hydrothermal method produced the very small structure of the desired oxide. It is very common practice that, if one adds the seeds of the certain precursor material of the defined shape then there are more chances to get the formation of the product of the material in the different type of morphology most of the time of the desired shape.
Accordingly, in the formation of the bell type morphology of the cobalt oxide if we add the cubes of the nano size of the oxide of the cobalt in the system containing the desired composition to lead to the nanostructure formation the result is very positive.

The better form of the shape of the bell shaped cobalt oxide formation was made possible by the use of the ethenyl pyrrolidon polymer of homo type. It was also reported to see the formation of the shapes of the brush for the product increasing its surface are very useful for the capacitance properties. The solutions of the potassium hydroxide is reported to be applied for the supercapacitance properties study of the of the cobalt oxide. Result is as a the observation and confirmation of the output was the value of the four hundred and three hundred faradays per gram of the capacitance in the presence of the potassium hydroxide aqueous media. This so obtained material is supposed to be show optimum performance for at least two thousand cycles by retaining the almost ninety six percent of the retainance. In a typical procedure, the use of the trisodiumhexanitrocobalt was reported to be applied with the $\text{H}_2\text{O}$ and ethyl alcohol in the presence of the ethylene tetra fluoride polymer in the reactor at about the four hundred twenty three kelvin temperatures for overnight. This resulted in the formation of the oxide of the cobalt in three dimensions. Because of the specific shape of the material produced the surface dimensions seems to be the better equivalent to seventy square meter per gram with good performance of the material.

If we compare the devices of useful for the energy storage with the battery devices, which are in use since decades together, then it is observed that the among the other large number of devices the devices which can give the observations as the stability of cycle of the reaction as the good enough long, the power of the accumulation of the power that is the density, and also the ability to store the power are nothing but the supercapacitors. There are the large number of the sectors in the industries and also in other areas where the supercapacitor devices are applied including the vehicles and techniques involving the lasers. The reactions as the reduction reactions and the oxidation reactions if they are of the nature of the conversion to each other are at the most demand in the supercapacitor performance with high side. At the same time the maximum surface must be made available by the material of our interest, this will facilitate the entry of the ions of the positive charge as well as the negative charge to the inner level below the surface or one can say it as the deep inside. This situation of the entry and the presence of the
ions in the materials structure definitely will have very positive effect on the overall supercapacitance which obviously will be very high. The knowledge of the support of the surface dimensions indicates that the materials choosed shall have the very good structure with the pores inside. This situation of the pores presence leads the researchers to predict that the, these spaces will be made available by the materials to accommodate the ions from the electrolyte and also form the system composed of the various ions. This situation of the presence of the porous nature is mostly available in the compounds of the d-block elements. But this porous nature is created in the d-block elements because of the special characteristics which are possessed by these elements as the which commands the usefulness of those in the supercapacitor application of the electrode materials prepared form these metals [88].

The manganese dioxide is found to be a good electrode material because it has ability to show capacitance of pseudocapacitive type and also specific when compared with the other oxides of the metals in the periodic table d block metals, the very reason of this is that this material it can be prepared at the cheap economy. Like few of the elements in the periodic table, the manganese is of that kind which shows the semiconductor property and obviously very small conduction. This small conductivity is could be correlated with the effect of the ability of the manganese dioxide showing the specific capacitance to be very small than expected. The composition of various forms in which the manganese is added such as the manganese dioxide with sulphate of zinc, manganese oxide with the allotrope of carbon and also the polymer has shown to be with the enhanced output with respect to the supercapacitance. The very small increase in the supercapacitance is possible if we change the manganese oxide weight to small extent in the above described method. Therefore there seems to be many limitations in the fabrication of the manganese oxide with the good voltage of the pseudocapacitance. The real problems in the less capacitance properties in case of the manganese oxide is the hindrance in the transfer of the charge and thus affecting the capacities of the material to show the specific capacitance. To overcome this some of the research groups have developed the new ideas of use of the other transition metals along with the manganese dioxide. There are large number of reports which indicate the possible applications of the precious metals platinum, silver and gold in the synthesis of the manganese dioxide material. There are reports of the observation of the more than seven hundred faradays per gram capacitance if the attempt of
addition of the Ag with only five percent is tried to produce the composition of the two metals in oxide form. In then materials chemistry of the transition metals there are many fantastic reports on the high performance properties when we control the morphology to the defined shape such as the nanowire of the manganese oxide containing little amount of the gold. Surprisingly the value of the supercapacitance observed was one thousand one hundred faradays per gram at the optimum voltage of the fifty millivolts per second. A per the economy of the any synthetic route or the fabrication method depends on the ingredients used for the same. In the periodic table there are many potential metals for the energy applications but at the same time these need to be checked for the cost effectiveness. Among those are the noble metals recently explained. The stability of the rate of the supercapacitor cycle of the and thereby to prepare an electrode for the supercapacitor of the mixed type showing both the pseudocapacitive behavior as well as the redox reactions, which are supposed to promote the conductivity of the manganese dioxide material and also the overall expenses for the system must be at the lowest possible. The work indicated in one of the report informs the details of the bead type Co nanoparticles covered by the C shows some magnetic behavior of ferro type could be synthesized by the heat treatment in flame technique. This coating of the carbon on the cobalt is giving the good structure by retaining the performance of the material. The evenly distributed cobalt and carbon nanoblocks in the all dimensions could be synthesized by using the plate type nanoparticles of the manganese gives the high performance.

In the synthesis of the nanoparticles of the manganese oxide covered with the cobalt in the carbon the precursors selected were salts of the manganese and cobalt and for carbon graphene. In a procedure for the synthesis of the material the sonicator was used for the ultrasonicate the liquid containing the cobalt over carbon particles in the solution as a hanging particles. In such type of the synthesis the oxidizing chemicals are needed, in this synthesis the chemical potassium permanganate was applied. The microwave equipment was used for the heating of the entire composition of the reaction mixture for about the ten minutes and at one hundred forty degree celsius temperature. This treatment was resulted in the formation of the very small sized particles of the material. The so obtained solid particles by the above mechanism after heating for one hundred degree celcius overnight to remove the excess water molecules. The product at this stage was then fine crushed to the small particles and kept for few
amount of the time in $\text{H}_2\text{O}$ on the top of the magnetic stirrer. The strong oxidizing agent potassium permanganate along with the monohydrate manganese sulphate was all together was allowed to mix with the fine powder od the earlier particles synthesized prior. The catalyst like sulphuric acid was added to the whole mixture which helps to converts the reaction chemicals to the products that is the reaction between the potassium permanganate and manganese sulphate to produce the coloured material. After agitation for about the sixty degree celcius and keeping for next quarter to one hour the coloured samples of the material was obtained and the final product that is the manganese dioxide nanoparticles over the carbon and cobalt was received at the end.

There is option for the synthesis of the manganese oxide nanoparticles and one of the option used is the making use of the various amount of the cobalt on carbon nanobeads ranging from five to thirty percent as compared to the manganese dioxide nanoparticles. The effective amount employed is found to be nineteen percent by weight unit. Overall the maximum use of the manganese dioxide nanoparticles with the respect to the performance is reported by the mechanisms of the enhancement in the capacities as reduction and oxidation mechanism by transfer of the ions and also by allowing the ions to go inside the material structure by the addition of the cobalt over carbon nanobeads. It is know that about the thirteen hundred is the highest possible value for the specific capacitance for the manganese dioxide and if we compared with the materials synthesized as discussed above the efficiency shown was about the twelve hundred faradays per gram, which is very interesting indicating the utility of the prepared material. In further study it is observed that the use of the prepared material as electrode and testing for over ten thousand cycles in presence of the sodium sulphate in water medium as well as the salt of the lithium also are capable to show the good performance with the respect to the energy density. Form the study in use of the manganese dioxide embedded with the cobalt over carbon has proved to be good alternative in the selection of the transition metals of the lower cost as compared with the high performance showing but very costly platinum metals [89].

The batteries of the traditional type energy storage systems are now overcome by the alternate systems capable of showing the good enough cycle numbers stable, good density of the power and the capacity of conversion and storage of the energy which are called as the supercapacitors. The active materials undergo reactions in the way of the reactions of reversible
type and allow the entry of the ions in the material of the electrode, this helps in the enhancement in the supercapacitors capacity. If the electrode materials targeted to be more efficient then they need to be supported with the properties which are very useful for the better supercapacitance as the structure with the pores on the surface to facilitate the easy transport of the ions. This properties and also some other properties required for the capacitance to be observed in quantitative performance, the materials such as the most perfect materials supposed to be most active, and the oxides of the d-block elements with variable oxidation state are found to be the better supercapacitor materials. In the selection of the supercapacitor material the thing to be considered are as the ability of the material to be made available for the purpose of the supercapacitance. This is not the only criteria but at the same time one needs to check the effectiveness with respect to the expenses for the entire system and feasibility on this ground. In this thinking the preferred materials are those which are containing the transition element as the manganese, The manganese dioxide exhibits the specific capacitance values pseudocapacitance as high enough. The beauty of this material is that it is available in the comparatively lower amount in terms of the economy and also surface area is more.

The manganese oxide has exhibited the small value of the specific capacitance compared to that expected usually. This observation is related to some characteristics of the manganese dioxide material as the, manganese oxide material has able to show the lower conductivity of the electricity as is well known that and is proved also that the manganese dioxide has semiconductor properties. One of the drawback of the manganese dioxide material is its property to show little conduction thus deviating from the expectation of the ability to show higher conductivity. Then also there are hopes in the application of the manganese dioxide material to be useful in the supercapacitance studies if we could develop the materials of the manganese dioxide with the improved properties, as the increased number of the cycles of the charge and discharge and also the dissipation of energy properties, the, by using the processes as in which we could add some other transition metals in the manganese dioxide such as the polymers materials which are able to show conduction, the another transition metal as copper. The mixture of zinc over the oxide of tin and allotrope of carbon is also found to be very useful materials in
the improvement of the supercapacitance properties of the manganese dioxide material in the case of its application as the material for better electrode.

The as expected by the world of scientific community the higher potential from the manganese dioxide of the pseudocapacitive type is not yet become possible achieve because of the limitations of the materials such as the dioxide of the manganese as those are possessing the lower capacity to hold the quantity by the weight as compared with those of the other materials which shows the better pseudocapacitance. The pseudocapacitance could be increased by taking care to decrease the obstacles in the free and fat movement of the charges and ions as well in the device. This could be to obtained from the material oxide of the manganese if one adds to it the very interesting metal ions from the specific type of elements from the periodic table containing the rare and valuable metals which usually does not undergo the reactions at ordinary reaction conditions, These type of the materials include the compositions of the platinum, silver and gold with that of the dioxide of the manganese. These practices of the addition of the very small quantities of the other metals as described above definitely result in the enhancement in the observed capacitance to many folds.

There are several reports inn which the application of the silver is at priority to get the capacitance in the range above the six to seven hundred faradays per gram. In addition the another reports also adds to the knowledge of the ideas behind to get the better performance are use of the gold nanomaterial’s over the addition to produce the composite with the manganese dioxide to reach upto the capacitance over the value of the thousand plus faradays per gram at the tens of five millivolts per second voltage. If the survey is made for the possible incorporation of the other metal ions to the manganese dioxide to produce the electrode material, it is observed that the option of the addition of the little amounts of the gold, platinum and also silver are not feasible economically and the very important concern in this is the prices of these metal salts in the global market in spite of the very god capacitance properties exhibited by these metals. Because of this reason the scientists across the globe are in search of the comparatively cheap materials but at the same time providing the good performance towards the electrical conduction of the manganese dioxide material at large number of the cycles. In this search the reports are evident on the effective use of the twenty seventh element in the periodic table that is the Co,
which on the combination with the coverage on the surface made up of the carbon in the nanosize. This exercise leads to the effective coating of the manganese dioxide along with the Co-C material composite on the substrate of nanolayer and at the same time the so deposited film was with the properties as the stable towards the heat. The preparation of the nanosized materials from the manganese dioxide where the typical addition of the carbon on cobalt composition is done the formation of the plate like structures takes place that to in the shape more remarkable than the usual dimensions. The so produced films are tested to be well capable of the conduct of the electricity at par with that obtained by the applications of the costly sources of the metals to be added along with the manganese dioxide. One of the best composition that led to the formation of the effective composition to get the better pseudocapacitive performance is thus the carbon coated cobalt in combination with the manganese dioxide. The process of obtaining the nanobeads of the manganese dioxide with the carbon on cobalt coat nanoparticles involves the addition of the carbon coated cobalt in the liquid as $\text{H}_2\text{O}$ in the vibrations mechanism along with vigorous stirring specifically by sonication. After the process of drying and heating at the some elevated temperature around the 413 kelvin produces the fine particles. These particles of the carbon coated cobalt were then allowed to react with the manganese sulphate monohydrate and potassium permanganate. The sulphuric acid treatment for the above mixture led the formation of the expected composition of the carbon coated cobalt in the manganese dioxide. The performance shown by the prepared composition deposited on the substrate has found to be the twelve hundred forty faradays per gram and also at the considerably larger cycle performance in the range above ten thousand.

The nanosized structures made from the carbon as one example is the nanotube are of the importance in the various fields of the study in the many branches of the science. The typical characteristics of this shape of the carbon nanomaterial includes the properties to be mentioned of the prime importance are mechanical and electronic and the applications of these leading to the very good performances shown by the devices in which these structures are used. And thus these shapes of the carbon materials are the topic of the discussion at the top among the many materials which are able to show the improvements in supercapacitor performances. In addition the many researchers have again tried to get the improvements in the performances, in addition to the responses shown by the carbon nanostructures. These efforts include the making use of the
metals in the periodic table of the chemical elements in between the transition series as well as the lanthanides. In these attempts it has been recognized that the mere application of the metals ions may not be useful in the improved properties of the electrode materials. Thus one has to think of the different compounds originating from the metals may be of the use. In this it is found that the oxides of the metals if used to add to the produce the composites of the carbon by adding the carbon nanotubes to and the oxides of the metal results in the better activities towards the electrochemical performances. There are several reports in which not a single metal is employed but more than one metal are being employed many times. This type of the application and study indicated that there shall be many applications of such composite materials. In all such efforts the oxide of the cobalt is at the priority. The metal oxides are being considered to be useful for the carbon nanotubes improvements in the surface of the. These improvements could be only achieved by the application of the many typical mechanisms involving the checking of the possibilities rather making available many opportunities for the better associations and or the reactions between the metal ions and the carbon nanostructures being used as the nanotubes. In many papers as literature survey is made in this angle it is found that the reactions such as involving the coating or additions of the nanotubes structures of the carbon with the metal oxide typically of the cobalt. These reaction paths includes the applications in the formation of carbon nanotubes in composition with the cobalt oxide, batteries of the category lithium ion, the sulphur containing compounds, the applications of the synthesis gas produced compounds hydrogen, the carbohydrates, the formation of the tricobalt tetroxide nanstructures of sheet type. There are several methods which are reported to be available for the synthesis of the carbon nanotubes cobalt oxide with, these methods include the applications of the Nanotubes of carbon in the addition of the oxide of the cobalt in the specific shape as the small beads in case of the some equipments used in the circuits for the electronics purpose. The application as the required for the decomposition of the ammonia in the form of the catalyst and also in the synthesis of the composites of the nanosize. The use of the starting material containing the cobalt in the oxidation state of two could be the good option for the synthesis of the nanotubes with the many walls instead of the single wall, of the cobalt oxide. The solvent as the neutral solvent xylene could be used for the preparation of the solution of the complex of the bis acetylacetone of the cobaltate and then by applying the heat treatment process may be called as the pyrolysis
by spray technique. The catalytic activity of the oxide of the cobalt in the synthesis of the carbon Nanotubes is observed. In such reaction mechanisms the other role played by the cobalt oxide is the involvement in the reactions by the complex of the cobalt metal. The reported mechanism of the preparation of the carbon Nanotubes in the literature is from the acetyl acetone complex of the cobalt where in the usual experience in making use of the acetylacetone and probable drawbacks are tried to minimize by the application of the transition metal ion like cobalt. The typical mechanisms indicates that the there is the observation of the adherence of the nanoparticles of the cobalt to the outer surface with the carbon nanotubes. By maintaining the one atmospheric pressure, the acetyacetone complex of the cobalt was made to be inside the chamber of the reactor by reaching the temperature of about one thousand degree celcius in presence of the inert gas atmosphere. In this system the solvent like neutral solvent xylene was employed for the preparation of the initial precursor solution of the acetyacetone complex of the cobalt, where the reaction was undergone to completion by the way of the sonicator use. This resulted on the getting the totalSly decomposed material as is called now as the product after decreasing the temperature to the normal temperature of the working lab and or place. Thereafter the confirmations of the various properties of the prepared materials was done by employing the techniques useful for the morphology assessment, size determination, phase formation, crystallite size determination etc. By having the options and making use of those for the synthesis of the nanotubes with the functional groups of interest for the purpose of the application. In this case the trials are done by having the different amount of the starting materials and also the metal salt used was the oxygenated materials of the cobalt. The beauty of the developed mechanism is the, we can have the full scope to lead the formation of the product as we decide and accordingly use the various quantities of the starting material. It is evident that the higher quantities of the cobalt in the solution has led to the accumulation of the oxide of the cobalt over the carbon nanotubes of the multiwall type and deeply present in the allotrope of the carbon graphenes. The tools reported to be explored for the characterization of the synthesized material and to indicatge the probable role in the materials are performance of the the spherical capacitor analyzer, spectroscopy X-ray photoelectron, X-ray diffraction,high-resolution transmission and the transmission electron microscopyelectron microscopyetc [90].
In the capacitors of the conventional type the common observation and experience is that those show very low densities of the power and thus it becomes customary to go for the development of the new devices with the mechanisms to overcome the problem of the common capacitors. And in this search the excellent option is the select a system with the mechanism of the supercapacitance. In this search the attention is paid to the metals from the transition series including those of the platinum group metals. To the forefront is the forty fourth element in the periodic table. The member of the noble metals is the ruthenium. But if one looks at the many characteristics of the ruthenium metal then it is found to be not much suitable for common applications due to its cost is much higher and supposed to be environmental non friendly. Though there are many excellent responses such as the good values of the when used as the material for the electrode synthesis specific capacitance. Thus to go for the better materials for the synthesis if the electrodes, the category of the hydroxides and the oxides is at the top priority as far as these compositions are made

from the transition metals. The reasons to be noted for such preferences are the properties shown by these special category of the metals as the cycle life of high enough length, good capability of the rate, specific capacitance of high order etc. The semiconductor nature of the oxides of the some metals is one of the very important properties for their applications to be considered in the supercapacitors for as the materials for the electrodes. But if we compare the oxides with the hydroxides then the situation differs means that the, hydroxides of the metals possesses the property to show the density of the current to the lower value and his is because of the inherent property of these materials to be showing the very small conduction. Though there are the observations that the nickel oxide has very less reversibility and at the same time less conductivity. The metal oxide from the transition metal series is the nickel oxide mostly preferred as the material for electrode synthesis. There are several reasons for the preference such as the nickel metal is available in the nature at very good amounts, and thus is obtainable at the economical prices. The nickel oxide material is among those materials which show the good performance.

If one chooses the synthesis of the nickel oxide as the porous form with three-dimensional structure and at the same time achieving the lower particle size then there are chances to get the scope of this material to overcome the encountered drawbacks, to be made
available for applications in the supercapacitors. There are reports that the some transition metals other than the nickel could also be applied for the formation of the material for the electrode along with the nickel. The other metals for the d-block are used along with the basic material made up of the carbon. The mechanisms implied are the in addition to the original protocol for the formation of the nickel oxide electrode material. One reports indicates the application of the cobalt oxide in the form of the tricobalt tetraoxide to be added to the formation of the composition with the nickel metal in the form of the oxide to produce the nickel cobaltate in the result of the formation of the supercapacitor IT is noteworthy that this composition of the electrode material has shown the at the five milliamperes per centimeter square of the density of the current to obtain the excellent capacitance of about the one thousand seven hundred and seventy one. There is the successful possibility that one can make a composition of the manganese dioxide with the nickel oxide to produce the better devices for the storage of the charge in which the metal oxides are produced in the form of the structure on the stainless steel in the form of the flakes of the nanosize

which were arranged in the form of the tube like display. The so produced material has capacity to show the observation of the long life of the cycle and also the comparatively high performance.

The metals of the transition series group of the elements are known for the properties to give supercapacitance of the high order, density of the energy to be high and the ability to show the variable oxidation states. All these characteristics are leads the metal oxides transition to be the attractive materials for the specific applications to get the electrochemical performance of the enhanced nature. The other metals of the transition series may be mixed with the metals of interest say for example the nickel or cobalt. In such cases the added metal oxides behaves as the materials of the better towards the activeness of the electrical conduction. There are several reports which have indicated that the individual metal materials can exhibit the supercapacitor performance and also shows the reasonable stability with respect to the cycle number. But there are few reports in which the possibility of the enhancement in the supercapacitor performance and also the stability of the with respect to the cycle number to test the total performance could be well enhanced if one takes the help of the more than one metal that is the bimetallic systems
or multimetallic systems over the those properties obtained by the application of the single metal compounds may be oxides of hydroxides etc.

The main reasons for the reduction and oxidation reduction reactions causing the faradaic processes is because of the availability of the maximum active surface and also the involvement of the active components on the surface. This overall leads to the supercapacitor with the materials of the electrodes which in turn becomes responsible for the density of the energy is the main component of the supercapacitor. It is observed that the materials useful with the porous nature and the structural modifications in three dimensions are preferable for the applications in the supercapacitor. There are several combinations reported of the different metals in the form of their oxides that is the oxides of the transition metals. Amongst the many metals form the transition series the metals as the cobalt and the nickel are of the prime importance for the supercapacitor applications. If more than one metal is used in the supercapacitor then the different metals shows their effects simultaneously to add up for the result of the better supercapacitance [92].

Comparatively good properties as the supercapacitance of the materials of the some transition metals are attracting the attention of the material scientists for their efficient applications. In addition the structures of these materials are also promising for the applications in the energy research. The transition metal series element the cobalt in the form of its oxides poses to meet the above two requirements and thus looked as the useful material for supercapacitor applications. The transition metal oxides if taken in the more than different elements that is the bimetallic compositions again are shown to be the more applicable to get higher capacitance properties. In this consideration the combination of the little amounts of the cobalt oxide in the nickel oxide, it adds the sizable improvement in the observation of the capacitance. Here the important thing is that the care is to be taken to maintain the relative concentrations in the molar form at the optimum level. There are many options to synthesis the oxide of the nickel and the cobalt together for the pseudo capacitive applications. There are several reports wherein it is observed that the composition of the cobalt and nickel together could be well synthesized by the protocols in reported elsewhere such as simultaneous precipitation, by hydrothermal way, the electrodeposition and also by the sol–gel technique.
Some methods show amazing features which definitely favours the synthesis of the materials at the lower temperature. These types of the methods also help us to synthesis the electrode materials with the expected properties as structure, morphology, shapes and crystal size. These methods include the one which is called as the hydrothermal method. It is very interesting to know that the chemical compounds involving the complex forming agents from the category of the coordination chemistry gives the very important contribution to for the materials of interest, when once thinks to make use of the method of synthesis of the by hydrothermal mechanism. It is true that the there are certain disadvantages of the applications of the complex forming reagents in the synthesis mechanism of the materials for the electrodes, that because of the strong bonding ability of these reagent sit is very difficult to get rid of the traces of these chemicals form the product mixture. There are also reports that these chemicals may be removed but special efforts need to be taken and various strategies need to be developed and also the processes are much long if we consider one of the physical parameter as the time needed for complete separation of the material of our interest and the impurities therein. There are few reports where in the applications of the liquids are made which helps to reduce the tensions on the surface which may in turn have effects in the formation of the size and shapes of the materials. For the supercapacitor applications, the materials showing specific capacitance of higher order, are reported to be synthesized from the binary type metal combinations originated from the transition metals as the cobalt and the nickel. These metals are first converted to the compounds such as the respective oxides. Here specialty the mechanism is developed wherein the formation of the product is taking place in the second step of the reaction. This has led to the excellent surface properties of that of the flowers. The intensity and the control of the shapes of the particles of the surface of the material are well controlled by the few chemicals which specially does not involve the chemicals which are responsible for the reduction of the tensions on the surface. So usual to obtain the desired nature of the synthesized texture of the material the process of the heating the material at the higher temperature is carried out for the material of the nickel and cobalt. In such type to the synthesis the way of the formation is mostly because of the various amounts of the starting material taken, this in turn is proved that the performance of the capacitance performance is much affected by the proportion of the amounts taken of the starting materials and the ratio of the components in the final synthesized material. Therefore it seems
very necessary to think of to take the review of the ratio of the components in the synthesized material time to time and impose some control over it. The nickel and cobalt oxides were taken in the various ratios of the amounts in the organic compound of the heterocyclic in nature having the chemical formula $(\text{CH}_2)_6\text{N}_4$. The various molar concentrations were implied. The chemical forms especially the nitrates of the cobalt and nickel were made to mix homogeneously with the $(\text{CH}_2)_6\text{N}_4$. As is the routine process in the hydrothermal mechanism the all the material is then taken in the reactor made up of the polytetrafluoroethylene compound covered on the inner surface of the stainless-steel and kept for the constant heating at about the four hundred Kelvin for the calculated time. The product in the form of the precipitate showing the green colour and the chemical form as the hydroxide of the cobalt and nickel in the various proportions were obtained after the through washing followed by heating to boiling point of the water temperature below the to confirm the removal of the impurities including that of the water. The expected the material composition of is achieved by heating the entire material at the annealing temperature of the six hundred kelvins. The heating at his high temperature helped the material to be converted to the oxide form. The so produced oxides of the bimetallic material are then confirmed by the various techniques of the characterizations including the BET for the evaluation of the pore size using the adsorbing gas as the nitrogen. The composition of the nickel and cobalt by the X-ray fluorescence equipment. The composition of the elements by the X-ray photoelectron spectroscopy, the TGA is also reported to be applied to study the weight loss and lastly the X-ray diffactometer was applied to confirm the formation of phase.

In the application of the metal oxide as the supercapacitor material, the current collector employed was made up of the foam of nickel. This nickel foam was impregnated over the surface by the layer prepared in the solvent of methyl derivative of pyrolidine. The impregnating material was containing the fluoride complex of the vinyl compound along with the acetylene and the oxide of the metal. Where in the metal oxide was acting as the working electrode. The working electrode was fabricated by the use of the optimum quantity of the oxide material in terms of few milligrams and the electrode was of the shape of the flexible foil which was previously heated to some temperature below one hundred degrees. It is learnt in this application that the porous form of the nickel is being used for the purpose of the acting as the important materials for the conduction along with the Pt metal in the same texture having the assignment of
Interestingly the electrolyte being used is the potassium hydroxide of the optimum molarity in presence of the silver and silver chloride electrode system as the reference. Here typically the combination of the oxides of the cobalt and nickel in an exact proportion that required for the supercapacitor applications is reported to be efficient for the energy storage [93].

The colloidal stable suspensions are the result of the anisotropy in the structural properties of the extreme end as nothing but the physicochemical properties. Such properties are specifically shown by the materials nanostructured and two dimensional in nature. There are If one uses the technique of the removal of the layer of the materials synthesized or deposited over the substrate accompanied by the liberation of the hydrogen gas through the different layers of the materials, the result will be the separation of the various sheets of the nano size and also of the two dimensional in the nature. Some of the typical examples of the formation of the two dimensional and nano sized solid materials in the inorganic composition are reported such as the phosphates type composition of the metals, chalcogenides metal type, metal hydroxides and oxides, minerals of the clay type etc. The prominent properties obtained by the way of the layer by layer removal method are the highly charged surface and thus very useful for the multilayered films developed by the hierarchically way and specifically of the nanohybrids of heterostructures and are acting as the basic structures of the formation of the desired structures. There is scope to get the many desired properties form the nanosheet type materials if one changes the compositions in the terms of the chemical form and these properties range from the non-conducting type materials to the conducting materials as that of the metals. The lithium ion materials used in the energy storage cells if accompanied by the metal compounds with some specific properties as manganese, nickel and cobalt and their oxides are able to show the better energy density and thus are much preferred. Almost all the transition metals are having many properties which are very wisely made use by the scientists across the world in the case of the supercapacitance applications, and that to the most widely studied and used metal is the cobalt in the form of the oxide. The dioxide of the cobalt when made in the compound formation with the lithium leads to the wonderful properties for the energy storage. It is true that the issue of the cost of the cobalt oxide and also the environmental effects are the serious hurdles in the application of the cobalt oxide in the recommendation of it in the applications to produce materials useful for the batteries. And thus, the researchers across the
world are trying to replace the cobalt with some other metal. There are several reports in which it is proved that one can have the options of the application of the manganese and nickel along with the less amount of the cobalt. These all metals in their oxide forms are made in to the composite with the lithium to produce the cathode material of the reasonably price and also contributing well to the capacitance properties. This multi-metal composition is thus the recent wanted materials for experiencing the better performance, because of the higher thermal stability and larger capacity. These types of the compositions are made to form layers and thus allows the movement of the ions of the lithium. These layers are made to the porous form by applying the specific techniques. These porous nature allows the lithium ions to move freely through the spacing between the two layers of the material of the electrode. The application of the materials as nanoclusters of the inorganic composition, graphene and nanotubes of carbon to produce the hybrid structures while synthesizing the nanosheets of the oxides of the nickel and cobalt and also some times the manganese in presence of the lithium leads to the supportive for the better activity towards the electrochemical reactions to show better conduction as an indicator of efficiency.

The application of the (CH₃)₄N⁺ion for the filling of the spaces in the structure of the oxide of the metal containing the hydrogen ion with it formation of leads to the the layers of the electrode materials of the composition having the equal percentage of the oxides of the nickel, manganese and cobalt in the very porous form useful for the better movement of the lithium ions among the each layer. Here care must be taken to maintain the appropriate proportion of the organic quaternary cation. The proper proportion say one portion of the organic ligand to the one hundred parts of the hydrogen ions, and this situation will help us to go for the obtaining the expected particles in the form of the nanometer size dimensions nanosheets of the oxides of the nickel and the cobalt. The morphology of the atoms of the metal oxides in this sheet is of the form six straight sides and six angles type geometry. The transitions of the electrons in form lower d orbitals to the higher d orbitals is indicated in the study at the expected wavelengths.

The application of polymeric agent as the citric acid was made in of the process defined as the sol gel method which was adopted for the preparation of the fresh material of the composition including the oxides of the cobalt, manganese and nickel and accompanied by the lithium was reported. In this material all the transition metals contribute to the on third portion
each and two oxygen atoms are present whereas only one atom of the lithium was present. In
details mechanism of the synthesis of the material involves the heating of the so produced
solution from the one as to one with respect to all the three transition metals after dissolution in
the citric acid which was previously made in solution by the addition of the water. The solution
was kept at the slightly acidic condition at six pH. The starting material including the three
transition metals was resulted in the formation of the product of the powdered texture, which was
given the heat treatment at some four hundred degree centigrade temperature. This whole
material is then added to the carbonate of the lithium at the high temperature around nine
hundred, to get the final product, lithium manganses cobalt nickel oxide. After the preparation of
the desired material, it was subjected to the transfer of the hydrogen cation in presence of the
hydrochloric acid by maintain the ambient condition of the temperature. The fresh oxide of the
metal was obtained

by the reaction between the\text{N}(\text{CH}_3)_4\text{OH} in the water solution and the so prepared material of the
transition metal oxides and lithium. Here the optimization of the amount of the \text{N}(\text{CH}_3)_4\text{OH}
required was carried out. Thus, so produced material was then used in the deposition of the thin
films. Especially the layer by layer deposition technique was used in this particular work. The
ultra-cleaned substrate glass of the quartz, which was made cationic using the (\text{C}_2\text{H}_5\text{N})_n, a
polymer, was allowed to be available for the growth of the film in the sheets of the nanosize.
The step by step mechanism was adopted to grow the different layers of the materials one over
the other leading to the hybrid structure.

In urge to get the energy, the supercapacitors are developing a long way, because those
devices are of the properties to show cycle life of long duration, density of power to be at higher
side, and also the discharge and charge at the fast rate. The types as pseudocapacitors of faradaic
type and the double-layer electric capacitors are storage mechanism as per the energy in
supercapacitor. The electric double-layer capacitors are attracting more and there are several
reasons with exception of one that these types of materials are capable to show only low specific
energy. But the other positive properties as good conduction and power capacity as high. These
all parameters are best meet by the carbon materials including nanotubes, graphene etc.
In contrast to the EDLCs, in addition to the surface layer the inner part of the material is being
used in the other type of the supercapacitors incorporates the oxidation and reduction reaction
involving the d block elements in the periodic table. These types of the materials are poor in the density of power but showing the density of the energy to be very high. This behavior could be connected to the limited movement of ions inside the material structure of the electrode. While considering all these things one can develop the electrode materials by the combination of the ideas of the oxidation and reduction showing materials and the materials produced form the carbon. Amongst the large number of the options for the electrode materials the materials with the basic properties as the structures with the channels with well order, size of the pore to be same throughout, showing the electricity and above this the large surface areagood conductivity of. These all things are well meet by the carbon contacting and the oxide of the transition metals as the materials for the electrode fabrication. For the better supercapacitance the very important thing is that is the availability of the maximum surface area and also the maximum use of that area for the purpose of the capacitance properties. This is well achieved by the addition of the nanoparticles to the existing electrode material. In such cases typically the carbon based materials are of the structures of the nano type and the particles of the oxides of the metal are also the small in size. This overall helps to electrode materials increase the ability of the to show better capacitance. In this search for the better incorporation of the particles of the metals the scientist have made use of the various techniques including the sonochemical method, reduction and oxidation along with diffusion, exchange method for the ions, all these methods are supposed to be helpful for the insertion of the metal oxide particles in the carbonaceous material.

The comparatively no friendly methods for the synthesis of the electrode materials are not usually preferred in such cases of the fabrication for the materials for the supercapacitors. There are reports of the applications of the polymers as the $\text{H}(-\text{OCH}_2\text{CH}_2-)_{x}[-\text{OCH(CH}_3\text{)}\text{CH}_2-]_{y}(-\text{OCH}_2\text{CH}_2-)_{2}\text{OH}$ along with the$\text{Fe(NO}_3)_3$ and methylol phenol as the carbon precursor. Here the growth of the electrode material takes place on the polymer substrate. The so produced material however was showing the properties such as the smaller sized pores. One another attempt to overcome the size problem and to achieve the better performance abilities could be the use of the ferric oxide of the nanoparticles size. These materials are supposed to exhibit the surface of the pore to be complimentary because of the irregular shape leading to the overall surface area, and also has the capacity to tolerate the high amounts of the ions. Because of the channels present in
it created by the carbon. This situation becomes friendly for the transfer of the ions from one place to other through the surface available and also this is particularly not making use of the much of the surface with respect to the active utilization. In another attempt the material with the lower nature of the pores and also the order less structures were reported to be synthesized from the aerogel type carbon and the oxides of the transition metals.

The selection of the metal hydroxide is beneficial, because these materials are with the large number of the layers and these layers are facilitated with the enough spacing in between them. This spacing is very useful for the fast movement of the cations and the anions leading to the excellent electrochemical activity. Thus, these hydroxide based metal materials are supposed to be preferred electrode materials. Here as an example, the cobalt hydroxide, synthesized from the saturated solution, of the various shapes including the flakes of the nanosize has shown the supercapacitance of 750 F/g in the potassium hydroxide electrolyte. The various shaped hydroxides of the nickel as the plates or the honeycomb are also promising in the supercapacitor studies and also shown the capacitance of the value more than 1500 F/g with good density of current. The high performance is shown by the composites synthesized from the many metal hydroxides of the transition metals and used as the electrode material, including that of the cobalt hydroxide. The supercapacitance of the amount 850 F/g was observed for the electrodeposited cobalt hydroxide with good retention. The shapes and the textures of the cobalt hydroxide materials are the governing factors for the observation of the high values of the supercapacitance as 3000 F/g for zeolite structures and the 1000 F/g for the flakes of the nano size. There are several ways for the modifications of the cobalt hydroxides especially by the addition of the other materials in very small quantity called as the doping, for example aluminum doping helps to capacitance and also the specific energy. The discharge and the charge nature of such doped system is good indicator of the properties tending towards the good supercapacitive behavior [94].

Storageenergy as well as conversion in addition to the uses as the sensors, photonic device and electronic are considered to be the important, which are caused because of the special characteristics of the structures of the very small dimensions including the tubes, rods and the wires of the nano level. The crucial importance is due to the sulphur containing compounds, nitrogen derivatives, oxygen contacting compounds, pure metals and also the polymeric
structures which are used as support to the formation of the composite materials from the tubes of the nanocarbon with uni-dimensional type. The solar cells of sensitized dye, the supercapacitors and Li-ion batteries are being the devices which are extremely dependent on the sulphur containing compounds of the cobalt in which the percent of the sulphur is used in the varying quantities. At the same time some of the compounds are with the variable number of the sulphur atoms. It is observed that the bigger molecules of the compounds of the sulphur containing cobalt may be lacking in the some required properties to be used as the materials for the applications in the capacitors. Therefore the attention of the large number of the researchers is diverted to the preparation of the sulphur containing cobalt compounds in the form of the very small size called as the nanosize. This sized compounds could be obtained in the various shapes including the nanosheets, flower, worm, hollow spheres, nanowires etc. The value of the supercapacitance shown by the so called sulphur containing wires electrodes of the cobalt are shown to record the two to twenty mill ampere per centimeter square of the density of the current and five hundred farad per gram and the three hundred fifty farad per gram [95].

The capacitance of the three hundred forty farad per gram was shown by the different morphology of the sulphide compound of the cobalt that is the sphere of the hollow type. This efficiency is compared to more than the half the theoretical value. The supercapacitance of the amount one thousand farad per gram and the seven hundred fifty farad per gram at the different values of the angstroms per gram density are reported by the researchers Wu and coworkers in the chemical communications paper. However there are observations that when the density of the current is maintained at the ten angstroms per gram the value of the capacitance is observed to be at the lower side. Although the several advantages are there the experiences that the there is dis-connectivity of the current because of the no response from the interconnection of the collectors of the current material and the material of the electrode. This reflects in the process of the discharge and the charge causing the decrease in the performance observation and the capacity decrease. This is the one of the drawback needs to be addressed. The other material showing the good performance that is remarkable one is reported to be prepared of the sulphide of the cobalt of the dots of nano size type and also the nature of the amorphous. The reported capacitance is three hundred farad per gram at the three amperes per gram of the density of power. In the basic solution for the deposition is not more preferred or
the study of the solar cells of the dye sensitized wherein the application of the sulphur containing
the urea and the chloride of the cobalt for the deposition of the expected layer on the substrate as
the electrode in the galvonostatic method for the record of the response. There is need to develop
the material for the used to be the easily applicable on the polymer material at low temperature.
However in one of the report the method used was indicating the application of the solution at
comparatively elevated temperature using the cobalt sulphide as successive step.

The comparatively more stable material is achievable, if one goes for the application of
the neither basic nor acidic solution the formation of the sheets of the nano size of the sulphide of
the cobalt is possible which is better achieved by the deposition by the electro type. The
deposition by the electro way is demonstrated by

the various ways in which the mixture of the carbon nanotubes along with the sulphide of the
cobalt is recommended for achieving the good performance in the concern of the capacitance.
The supercapacitor and the dye sensitized devices for the solar cells predominantly are useful for
the additional good performance provided those are made up of the tubes of the nano carbon and
also the nano sized sulphur cobalt. The performance is found to be about seven percent. The
formation of the tubes of the nano carbon are synthesized by the heat process using the water
molecules in a step only single. Here the use of the one point zero ninety seven part of the
sulphur was added to the cobalt to form a complex. The acidic carbon nanotubes were prepared
first by taking the sulphuric acid and nitric acid for the treatment of the multiwalled carbon
nanotubes for about two hours and at the one hundred twenty degree temperature. The cobalt
chloride hexa hydrate was allowed to mix with the already prepared composition of the C₆H₁₂O₆
along with the sulphurous cobalt containing the carbon nanotubes.

The whole composition was then heated for two hundred forty degree to the period of
twelve hours of the material composition which was supposed to contain now the already
prepared solution and the thiourea for the stirring of the five minutes.
This was practically taken in the heated container for reaction to carry out made up of the
stainless steel and kept in the oven for four hours about one hundred ten degree temperature. The
product was dried at the temperature of the eighty degree centigrade for overnight before which
it was ethyl alcohol washed after the filtration by using the suction pump. This was done after the
cooling at temperature of the room level of the product removed from the oven. While avoiding
the use of the chemicals glucose and the carbon nanotubes, the preparation of the cobalt sulphide in then proportion of the one point zero nine seven was achieved and that to with the carbon nanotubes also. The use of the printing on screen for the preparation of the film of the titanium oxide was adopted in which the temperature of the one hundred fifty degree Celsius was recommended for the time period of the ten minutes and subsequently with the decrease in time of the period of five minutes three hundred twenty five was arranged. The air was allowed to flow throughout the experiment. Of course the surface of the substrate was added with the F ions.

The solution heated process in combination with the sol gel method was adopted for the preparation of the small rounded particles of the titanium oxide with the specific porosity. These so produced titanium small particles with almost round shape were then applied on the surface of the substrate as the layer by the method called as the screen printing.

The cooling of the deposited material to the temperature of the eighty degree centigrade followed by deeping in the aqueous alcohol which was earlier mixed with the light absorbing colour. The earlier process done was the heating of the material for thigh temperature for the duration of half an hour. Herein the material of the titanium oxide was supposed to acting as the negative electrode. This titanium oxide material was then allowed to remain with the colour absorbing solution for more than a day’s time, this facilitates the anode material to be covered with the sensitized dye.

The properties as physical and chemical of the materials are mainly responsible for the special characteristic shapes of the nanoribbons, nanotubes and nanostructures are of the dimensions of the unique-dimension. In supercapacitors material which are used as the electrodes are of the many metals oxides of the size mostly tertraoxide of the tricobalt cobalt nanoporous posseces the enhanced supercapacitance. For the evaluation of the structural details the large number of the tools are being employed including the testing for the electrochemical properties, spectroscopy of the kind visible and ultraviolet and the electron microscopy of transmission type. Raman is also very useful and also being used for this purpose and also the magnetic properties are being investigated. These investigations will give the details of the properties of the cobalt oxide including the information about the supercapacitance, magnetic, optical and crystal
structure properties. Obviously, in this case the cobalt oxide material was prepared by the method hydrothermal. When the temperature is maintained at the lower side the magnetization change resistance is observed as compared to the situation in the normal state. This happen because of the change some property of observation of the material when viewed thorough the different angle of the material called as the nanowires of the cobalt oxide. For the batteries of the lithium ion type one requires the good capacity for the rate of the charging and discharging, life cycle be of the increased fold and also the capacity of the reasonable high enough. Capacity of the storage of the lithium battery could be obtained to be high when synthesized with the starting materials of the cobalt oxide and the cobalt oxide with the gold doping wires of the size of the nano. The nature of the material is the many crystals closely packed together. One can synthesize by the use of the solution methods for the wires of the cobalt oxide in the form of the texture of the mesoporous type. The many applications as the magnetic properties, for absorption of the energy form the solar light, for observation and development of the colours by using the electrochemical phenomenon, as sensors in the many application devices, and the as the catalysts, these applications are shown by the spinel type cobalt oxide specially of the nanowires shape [96].

The synthesis of the nanorods of tricobalt tetraoxide in the colour of the black is obtained by the heating of the product at some three hundred degree centigrade. This product was developed form the starting materials as the chloride of the cobalt in the amount of the slightly more than a gram and combining of the same with the basic compound urea. The distilled water was used for the dissolution of the starting chemicals separately. By procedure the addition of the solution of the urea to the solution of the chloride of the cobalt was carried out. The care must be taken seal the reactor that the container of the reaction materials. This was followed by the heating at the temperature of the one hundred and five. This heating is allowed to continue for six hours to complete the reaction. After the enough time to allow the whole reactor to cool down to the room temperature, the ethyl alcohol and water was implied for the washing of the product which was made free form the solution by the effective use of the centrifuge.

The investigation by using the spectroscopy called as the ultraviolet and visible was made for getting the knowledge of the nonorod type cobalt oxide material band gap. Raman
spectroscopy was employed for the spectral characteristics to infer the optical properties which are supposed to be the important for applications. The technique called as the surface area analyzer using the different gases specially the carbon dioxide and the nitrogen being employed for the surface area which is the specific parameter for the supercapacitor applications in case of the materials as the cobalt oxide. And the commonly used instrumentation for as the transmission electron microscope and the x-ray diffractometer were in picture for the structure of the crystal and the phase formation.

In addition to the useful characteristics of the cobalt oxide so prepared material towards the supercapacitance, the other important part is the properties related to the magnetism. The loops of the hysteresis are observed to be at the various fields as the five, one hundred and the two hundred units of the K, which is studied up to the seven t value. In this study fifty octave per second was the rate of the sweep. The stability of the moment of the magnet at the cooled field and field of zero has shown no much change in the temperature though the change in sweep rate was made to the value of the one point five per minute which better accounts for observation made above. For the measurements in the field cooled the lower temperature plays important role that is may be requirement of the five Kelvin or so in the range of the one t value. The measurements related to the magnetic properties of the synthesized materials one needs to study or investigate the mechanism in the presence of the cooled atmosphere both for the zero as well as the only field condition. It is usually very less the temperature required in the earth’s condition and may be slightly more in the actual study. After the synthesis of the materials and somehow investigation of the parameters required to get knowledge about the applicability of the materials so prepared is utilized to observe the supercapacitance properties. It is observed that the values were obtained by implementation of the proper rate of the scanning that is about one hundred millivolts per second for about the one thousand cycles. The whole system was contained in vessel to accommodate the binder along with the electrodes of the different types as the black carbon, reference and the nanorods of the cobalt oxide. The mixture of the all these ingredient materials was thoroughly mixed together to produce a paste in the presence of the pyrrolidinone containing the methyl group and which is attached through the nitrogen. The condition maintained was free of the air and to be kept for twelve hour long period. The reference electrode calomel saturated in the potassium hydroxide
solution and in presence of the substrate employed in this case for the application of the paste was the platinum was used [97].

The morphology as such the nanorods of the cobalt oxide was investigated by the use of the sophisticated instrumentation called as the high resolution transmission electron microscope and transmission electron microscope. The formation of the pure material is confirmed by the techniques as the diffraction pattern observed in the x-ray studies. The actual structure is identical to the ten raise to the power of the three. The dimensions of the range of the four hundred in the units of the nanometer were observed from the studies carried out using the equipment called as the tem, which indicates the exact dimensions of the rods of the cobalt oxide and was found to be touching the few hundred nanometers. The magnification normally employed in such case is the lower in scale. In the synthesis of the nanorods of the cobalt oxide, the initial chemicals used were containing the compounds of the cobalt including the chlorides of the cobalt and the process passes through the formation of the compound which is termed as the middle compound. This compound has the composition of the cobalt metals in the oxidation sate of the plus two and the other elements such as the oxygen and the hydrogen united together in the form of the functional group of the hydroxide. It is also evident that the water of the crystallization is also present in this compound. This overall mechanism discussed is confined to the initial stage in the overall synthesis of the cobalt oxide nanorods useful for the applications as the electrodes in the supercapacitor applications. Eventually, the successive steps progresses with the continuation in the next step for further reactions to produce the final product or the material of the desired nature. Here, the process of the high temperature heating in oxygen and air of the starting materials leads to the formation of the desired nanorods of the cobalt oxide. The chemistry behind this can be discussed as the there is point of attraction between the hydroxide ion and the cobalt in the middle formed compound carbonyl cobalt hydroxide having the water of the crystallization. As it is true that the composition of the mixture at this stage contains the water molecules, the process of the removal of the water molecules is carried out by using the heating technique at high temperature. This leads to breaking of the bond between the hydroxide ion and the cobalt metal to produce the cobalt oxide in the form of the layers and simultaneously the carbon dioxide and the hydrochloride in the form of the gas are released in the process. The
removal of the different molecules in the form of the gas leads to the formation of the vacant positions in the entire material surface and also inside the layer, which eventually acts as the pores of the very small size called as the nano sized. It is observed that the nanorods of the cobalt oxide are obtained and were confirmed by the technique as the saed the cobalt oxide structure which is cubic in nature was revealed by the saed study. The size of the nano cobalt oxide is found to be the twenty to thirty nanometer which was confirmed by the transmission electron microscope. The transmission electron with high resolution microscope become useful for the investigation of the existing distance between the different planes and the distance recorded was the zero point two hundred eighty five nanometer. This distance is in close relation with the two hundred twenty type of the plane of the crystal of the material. One of the parameter which becomes very useful for the supercapacitor study is the area of the surface of the material. This parameter is investigated by using the equipment which gives the details of the surface dimensions is surface area analyser. This observation leads to the obtainance of value of the two hundred thirty two meter square per gram of the material. One can compare the observed values of the surface area obtained for the nanorod cobalt oxide to the cobalt oxide of the crystal nature but with the small size upto few microns. The spectroscopies as the ultra violet and the raman become useful tool for the investigation of the related to the responces as the optical. The active raman modes observed for the cobalt oxide of the nano size as three f-2 g, one eg and the a a one g which are because of the observed peaks at the six hundred thirteen, five hundred sixteen, four hundred seventy five and the one hundred seventy four. The arrangement of the atoms in the three dimensions with respect to the cube shape is investigated by the peaks form raman study and are because of the plus three oxidation state cobalt and the plus two oxidation state of the cobalt ions. These ions are located at the specific locations if the crystal structure at the corners of the hedral of the octa and the tetra type. The various parameters as the area with respect to dimensions, shape and size are required to be considered while the study is to be conducted for cobalt oxide while using the spectroscopy technique as the ultra violet. These properties which are mentioned are responsible for the gap of the band required for the optical properties of the nanorods of the cobalt oxide. The transition of the type indirect and the direct tails us the value to be used for the calculations of the gap of the band in the synthesized material structure, which is
responsible for the energy of the photon and also the coefficient of the absorption. Two hundred eighty one farad per gram was the supercapacitance observed from the nanorod cobalt oxide and the reason was the structure with the pores of the nano size and the area of the surface which was reasonably high. The nanorod cobalt oxide has shown the coupling of the magnetic type resulting in the observation of the bias of the exchange type. The minus five hundred thirty oe at the five k value, indicates the shifting of the loops of the hysteresis of the nanorods of he cobalt oxide having the nanoporous in nature.

The efforts are made in the history to make use of the natural materials including the agricultural materials for the sensing property observations. It is also well known that such natural materials called as the organic matter is being used for the purpose of the good performing storage equipments for the energy which ultimately behaves as the materials friendly for the environment. The main content investigated in the natural materials useful for the various purposes as described as above contains the material of the carbon. The typical property of the material that is the porous nature very useful for the supercapacitor is exhibited by these materials. In the daily life for the large group of the human beings who are suffering from the illness as the bigger levels normally more than the expected in the healthy person leads to the disorders in the body as far as the functioning of the various organs is considered. So for the reason to make it easy that is to facilitate the needy peoples there must be development of the technology for the instant investigation of the sugar levels in the body. For this scientists have come up with the tools that is the useful techniques for the determination of the sweetning component in the sugar glucose. For this purpose the tool called as the sensors of the glucose. If such sensors are being prepared form the bio materials then that sensor is prominently called as the biosensors. The working of the sensor is especially based on the biological mechanism including the enzyme useful for the oxidation of the glucose. But there are some issues related with the activity of the electrode to give response towards the glucose concentration. The reasons for the issue are due to the parameters such as the stability which is very limited extent, as these systems are studied in the presence of the natural environment the issue of the water molecules in the atmosphere are also playing the important role to make the electrode less sensitive. In addition to this as one works in the natural body fluid system the acidity as well as the alkalinity is also to be considered while studying
exact concentration of the glucose in the given sample by using the nanorods of the cobalt oxide electrodes as such. The hotness of the reaction condition while investigating the concentration of the analyte is to be measured and it poses some problem while working with the system to detect the concentration. While going thorough above discussed limitations of the detectors for investigation for the glucose concentration some new techniques are developed as the sensing equipments. The reported detection tools usually are related with somehow the macromolecules catalyzing the reactions in the natural system and thus having some limitations. Thus the new techniques developed takes the help of the other ways such as the use of the other chemicals which will not have the route of the catalytic macromolecules. The usability as the storage of the energy in case of the supercapacitors is also exhibited by the materials which are supposed to act as the sensors at the same time they show very good sensitivity. These materials includes the dihydroxide cobalt, tetraoxide tricobalt, oxide of the zinc, oxide of the copper, oxide of the nickel and also the hydroxide of the nickel. These are typically from the class of the type of the oxides of the metals of the transition series. There are few options to select the proper materials as sensor for the glucose. One among those is the allotrope of the carbon graphite. But it is very clear that, while going through the procedures of the synthesis of this allotrope of the carbon mostly are very tedious and cause some accidents. Thus the other materials to be checked are the oxides of the metals in the group of the elements. The criteria to eb applied while selecting the metal are usually the stability in the various chemical environments and must have the catalytic and the electric properties to be better [98].

By considering the probable obstacles in the synthesis of the graphene form the graphite, one has to search for the alternative sources of the materials. But things to be always remembered are the availability of the some of the points. The functional groups containing the oxygen atom at the surface is one of the important requirements. The stability in chemical environments, comparatively less hazardous, and eventually such materials must have the size of the pore must be large, and the area of the surface to be large enough. All these conditions tend the materials to be not causing any harmful effects on the environment and at the same time must become available at the lower prices. There is a good demand for the materials obtained from the natural resources including the medicinally valued plants as the family of the pea etc. The cover of the seeds of this family tree fruits are found to applied for the large number of the
applications. It is interesting that if one prepares the carbon called as the activated from the cover of the seeds. The oil producing seeds and there covers are reported to be used to kill the unwanted bacteria’s. Here one can add the information that such materials can be found in large number and quantity in most of the part of the world.

The activated carbon prepared from pongam can be used as the base materials for the preparation of the composite materials of nano size. It seems to be very wise that the if we add the oxide of the metal then there are many expectations from these composition to show the useful properties towards the capacitance. In addition as per the literature survey, one can think to make use of the more applicable knowledge by using the transition metal oxides for the addition with the carbon of the activated from the natural resources. These wise solution of the getting the composition of the expected type leads to the good properties in fact demanding characteristics for the observation to read the efficiency in the better ways. Especially the tetra oxide of the tricobalt in the form of the material of the very small grain size is found to show the excellent properties useful for the energy storage mechanisms. It is also noted that the materials prepare from the pongam has been successfully shown good response towards the estimation of the sugar contents in the body fluid in the form the glucose. The electrodes prepared from these materials are being shown the properties as the stability of the long duration, capacitance of the specific and excellent, good sensitivity, could be used for the investigation of the smaller concentration of the analyte present in the samples of any type particularly of the fluids of blood form the human body for its glucose content.

The activated carbon of the seed of the pongam shows the required morphology containing the indications of the porous nature of typical shape of the type prismatic and hexagonal appearance. This whole things could be well confirmed by using the sophisticated technique such as the electron microscope of the scanning type. In the interest of the better performance expectation form the material, especially in this case the natural material is supported with the compound tetraoxide of the tricobalt. This oxide on successful addition to the activated carbon material leads to the formation of the round shape textures and are also accompanied by the layers of the element C. The nature of the carbon as the graphitic and amorphous is clearly seen in the study done of on the sophisticated instrument such as the xrd.
Wherein the study is carried out using the theta angle of two and the observations are made at the clear peaks of twenty three degree and the forty three degree peaks. Interestingly these are showing the resemblance with the reflection plane of (zero zero two) and the (one zero one). The zero point eight zero one eight nanometer is found to be the constant of the lattice and the twelve nanometer as the size of the crystallite which is obviously the average one. These observations are of the materials of interest the cobalt oxide of the spinel type with the activated carbon prepared form the pongam seeds. And the typical phase is the cubic with face center. All these are possible to be confirmed form the xrd data readings and the analysis of the same. The formation of the pure form of the material is also justified by the observation of the peaks in XRD of the nanocomposite of the seed activated carbon on the cobalt oxide.

The g band of the s p two of the carbon in the form of the graphite is indicated by the observation of the marks in the raman study at the one thousand three hundred forty and one thousand five hundred ninety per centimeter. The observations of the peaks at these values are related to the d band and the e two g type. The route by the friendliness with the environment if adopted will be effective for the formation of the energy by the constant production mode and this is being identified by the current scientists working in this field of the energy. Which in thus is the need of the world to produce the by the alternative methods for which it will become as the energy source called as the sustainable source. The electrical double layer capacitors which are acting as the priority sources of the storage of the energy amongst the supercapacitors. One of the good things that is available in the thoughts of the supercapacitors is the combination of the energy storage required properties which are typically exhibited in the capacitors and the batteries. The additional features of the materials supposed to be used in the manufacture of the supercapacitors can be mentioned as the properties of supercapacitorsas highcyclic stability and the fast charging rate. If we visit the literature pages it is observed that there are main two types of the supercapacitors as one is as described above. Here the above described type of the supercapacitor is of the electrical double layer. The reduction and oxidation reactions, which are the part of the mechanism of the capacitance in the EDLCs are taken into account and accordingly the selected metals are to be employed to create such situation of the reactions. These reactions are possible for the compounds such as the conducting polymers, transition metal hydroxides and the oxides. In the electrical double layer type capacitors the storage of the energy is caused because of the interface of the electrolyte and the electrode. Which is again
governed mainly by and also made efficient because of the presence of the electrode materials of the porous carbonaceous nature are recently utilized for high performance electrode fabrication. The materials such as the tetra oxide of the cobalt with traces of the molybdenum, manganese ferrite, nickel cobaltate are some examples of the category oxides of ternary metal composition. In addition to this the other materials which are found to be very efficient are the pyrophosphates, carbonates, hydroxides, nickel hydroxide, nickel oxide, ferrite, cobalt hydroxide, cobalt oxide, manganese oxide etc. These again are very useful in the actions of the energy storage devices with the device type containing the pseudocapacitive electrode materials. The other materials than that of the transition metal compounds includes the graphene, carbon nanotubes, activated carbon etc. The features in the morphological and the methods of the preparation of the oxides of the vanadium along with the transition metals are responsible for the properties electrochemical type of these metals materials. The other type of the energy storage devices with the extensive applications are the lithium-ion battery with the recharging capacities. These batteries could be well established by taking the help of the materials electrode obtained from the oxides of the vanadium which in turn is part of the transition metals. The investigation of the high performing materials of the type lithium-ion storage from the starting materials such as the ocatoxide of the di vanadium along with the tricolbalt nanosheets has proved to be the good options for energy storage. The cyclic stability of the good efficiency is demonstrated by the materials showing the specific capacitance of high value by using the nanplates prepared from the ocatoxide of the di vanadium along with the tricolbalt having very high values along with. The cyclic stability and capacitance of the expected high value is shown by the material prepared from the hybrid nanorods composed of the cobalt oxide and cobalt vanadium oxide composite. The cycle stability of the reasonably high value could be obtained from the nanohybrid of the nickel oxide and nickel vanadium oxide. The rate capability shown by these materials is also very high [99].

The electrode materials for the pseudocapacitive observation is obtained from the nickel vanadium oxide and the cobalt vanadium oxide. If the geometries of the materials are obtained as the platelets of the very small size that is of the micron size along with the arrangements of the hexagonal type of the material cobalt vanadium oxide shows the remarkable reproducibility of the storage mechanism.
The capability of the charge storage is made easy by the several mechanisms as the transportation ion method which has become the most comfortable by the electrolyte ions diffusion in the nanostructures of the layer type. Here the important factor that plays role in such a favorably mechanism is the contact space of the electrolyte and the electrode. This is depending on the movement of the ions by the way of the arrangement involving the layers. The electrochemical properties are in turn in good observation. The applications of the supercapacitor electrode material prepared from the single materials made up of the vanadates of the cobalt made in the form of the nanostructured layers are not much studied. The energy density of the intermediate level is shown alongside the high power density by the nanohybrid structures. The drawbacks such as the accommodation of the more spaces in the structure while showing the performance when we use the vanadium oxide as the electrode material is because of the presence of the layers in the structures while one prepares the material. There is also the possibility that the conditions when is study is going on about the capacitance the cycles are being checked out there the layers alternate to each other makes the problem for the accommodation of the proper arrangement. This also leads to the deformation of the original structure of the vanadium material due to the electrolysis. These unexpected things can be avoided by using the use of the addition of the other transition metals alongside the vanadium oxide. This will enhance the chances to change the morphologies of the materials which will become more useful towards the applications in the supercapacitors. The conductivity at the improved efficiency alongside the electrochemical properties are obtainable for the good materials for electrode used in pseudocapacitive studies. Which are typically obtained from the transition metals as the iron in three oxidation state and the iron in the two oxidation state. These are typically used in the form of the oxygen compounds. The simultaneous reactions between the two types of the starting materials in the energy studies as the materials which is basically used and the oxide of the transition metal. If such combinations are being used then it is observed that the crystal structure and morphology is decided by the properties of the combining metals and their composites [100].

The material of electroactive nature and with providing the high efficiency towards its applicability is because of the preparation of the materials from the transition metal oxides with
the size which is about the nano size. If we take an example of the 26th element in the table of the elements as the iron and if we choose for the formation of the oxide of the same with the very small size then there observes the expected properties. It is also possible to have the coatings of the oxides of the iron after careful deposition over the other materials leads to the development of the material with the excellent properties including the stable nature of the material. In general it is observed that the iron metal is also available in the large quantities in the earth crust and ultimately will serve as the cheap source of the expected material for the energy storage applications. In addition it is also of that kind that, it does not cause any harm to the environment. The materials for the advancement in the electrode fabrication could be obtained from the use of the deposition technique and in such cases the deposition of the iron containing compounds especially the oxides are mostly preferred. In the case under reports in the literature the addition of the other metal oxides as the manganese dioxide in the structure of the ferric oxide with particles shape in the nanosize level and also spread all over in the surface and inside with the uniform way proved to be very efficient combination. The electrodes of the trioxide di iron in the form of the morphology as the sheets of the nanosize if applied along with the electrolyte solution in the applications such as the supercapacitor, then it is observed the output as desired for the good device matches with the output obtained from these materials combination. If the base material is applied with the conducting path surrounding the electrode materials then there are many chances to enhance the power density and at the same time there will be minimization in the resistance of the internal system. The reaction kinetics with the electrolytic support will help to decrease down the movement of the ions in the interfaces between the electrolyte – electrode. This is possible because of the conduction which indirectly helps to keep high degree of the minimize the conducting channels interconnected to mesopores. This helps to decrease the polarization effect on the conductivity phenomenon.

In the process of the supercapacitance there is the involvement of the repeated cycles. This process of the cycling at the regular action leads to the creation of the pressure on the system and this pressure is of the chemical type. To get the relief from the such type of the stresses in the phenomenon we need to see that the material to be used for the electrode formation to show the properties or arrangements in such a way that the resultant material at the
end will have the remarkable closeness of the entities of the composition and also will show the exceptional stability due to the fixed arrangements of the components in the space. The other materials which could be selected for the pseudocapacitor studies possesses the good density of the energy and needs to be provided with the surrounding of the electrolytic phenomenon and also includes the polymers. These are also work in the voltage window of the large gap. The nanocomposites of the hybrid and mesoporous type are possible to be prepared from these polymers are usually added to the oxides of the metal. The conductivity of the increased value could be obtained from the electrode material of the low in weight materials obtained from the thiophene compound of the poly dioxy ethylene thiophene with the poly nature and the aniline derivatives and polypyrrole. These polymers of the conducting type are acting as the coatings to the nanomaterials of the oxides of the transition metals [101].

Some of the promising properties of the pyridine phenyl lead to its applications alongside to the transition metals. The pyridine phenyl has the strong points with respect to the characteristics such as the stability in the atmosphere at about two hundred and fifty degree celsius temperature reasonable discharging and charging rates, high density and the good range of the conductance between the ten to hundred siemens per centimeter. Interestingly the pyridine phenyl could be well prepared by the addition of the some transition metal in it at the time of the preparation itself. The important facilitation for the good performance of the device is the presence of the diffusion of the ions through the internal spaces in the nanostructures. This facilitation could be achieved by the nanocomposite formation of the carbon nanotubes having the many walls in its structure which are also having the final composition with the content of the metals of transition series. The existence of the more properties towards the conductivities and the capacitance are shown by the material of the above described preparation.

In the presence of the solution supposed to be the electrolyte with expected properties the requirement from the prepared material is the material to remain in the condition, of the application in the processes discharge-charge, which shall not undergo the swelling and shall not compress down to small size. The application of the hard electrolyte the ions form the material shall not mix up with it thereby deviating from the original properties, this will help in this case to produce the phenyl pyridine material formation on the oxide of the iron. The formation of the
hydrate of the vanadium with cobalt in the form of the cane like structures having the nanosize. These materials have the high density and being reported to be prepared by the process of the heating in the reactors with the presence of the water molecules. The addition of the FeO and the phenyl pyridine along with the so produced nano sized material from the combination of the different transition metals of the first series. This ultimately leads to the excellent properties towards the observation of the expected efficiency as per the electrochemical requirements. The above material is showing the porous that to meso type nature. The applicability towards the conductance shown by the material prepared from the vanadium oxide and the cobalt oxide leads to the increased capacitance. This observation helps to think of application of the oxide of the vanadium and cobalt to be useful for the materials called as the capacitive in nature. Though there are some reports that indicated the less applicability of the oxide of these two transition metals to be less useful towards the energy storage devices, the improvement in it can be brought by using the iron oxide and its doping in the oxide of the cobalt and vanadium to produce the nanocomposite. This composite is being resulted by the careful processes in which the Py is allowed to undergo the polymerization along with the oxidation phenomenon. The main strategy used herein is the hydrothermal path. The oxide of the cobalt and vanadium in the form of the nanosized morphology if is supported with the environment of the polypyrrole network. This network formation is result of the interaction of the iron in the plus three oxidation state which helps in the polymerization reaction. The conditions mentioned for the reaction to be carried out for the conversion of the monomer in the polymer is maximum of the five degrees temperature and also the pH of the medium is to be towards the higher side. The increase in the conductivity and the electrochemical efficiencies in case of the materials as such the oxide of the cobalt and the vanadium and it’s another important component is the covering of the same with the polypyrrole material. The role is also played by the presence of the iron oxide in which the iron is in the oxidation state of the plus three. The overall dimensions of this material is nano sized, leading to the good materials for the supercapacitors. The stability of the cycle and the good specific capacitance is because of the composite materials prepared as the hybrid. The size of the less than hundred nanometers along with the shielding by the polypyrrole and the main amtersasil as the iron oxide over the cvo.
The attempt has been made to synthesis the material for probable application in the case of the estimation of the glucose. Wherein the use of the enzymes is avoided. And the concept of the electrochemistry is being used. This material also shows good efficiency towards the supercapacitor activity. The material was composed of the composites of the wires of the nano size made from the tri cobalt tetraoxide on graphene support. The batteries made up of the lithium ions and typically of the reusable along with the other devices such as the sensors making use of the electrochemistry, catalysts of the hetero type and supercapacitors are being observed to show better efficiency with the application of the nanocomposites of the tetraoxide of cobalt. The properties such as the electrocatalytic and the electrochemical and in addition the optical are being demonstrated with the use of the metal oxide prepared form the transition element and typically the trioxide of the cobalt, in which three atoms of the cobalt are being composed to the oxide formation. Electrodes of the composite and monolithic type and defect free are demonstrated by the use of the three dimensional structures with great porosity leads to the conducting nature. Among the various methods for synthesis of the graphene based materials prepared by using the deposition by vapours of chemicals leads to get the rid or overtakes all the other problems in the observation of the efficiency towards the conductivity, wherein the problems such as the resistance of the contact because of the sheets between he themselves. The graphenes specific area of the surface is controlled because of the pi pi interaction in the graphene structure which ultimately leads to the packing of the entities in the shuffled way and also in the cluster type containing the composite nature. The process of the chemical useful for the removal of the upper layers of the materials the starting materials use were of the oxide of the graphene which is pre- reduced by application of the chemicals instead of the pure graphene. This application is an example of the biosensors and supercapacitors in the form of the nanocomposites. The interesting properties of the graphene lead to the formation of the nanomaterials and also the large number of the opportunities for their potential uses. The research areas as the sensors, conductors, conversion and the storage of the energy are the possible applications of the graphene. If someone thinks to apply for the material as the carbon containing graphene it becomes advantageous because of the overall properties of these materials. The transmission electron microscope and scanning electron microscope images of the material produced form the tetra oxide of the tri cobalt grown on the graphene substrate in the
form of the porous type gives the important information about the structural and the surface properties [102].

The surface of the graphene as well as the inner part of it are well filed with the nano material generated from the cobalt oxide. This filling of the oxide is practically spread over the entire graphene with the oxide mixture. The dimensions of the carbon allotrope material is observed to be around one hundred micrometer. Incidentally the overall structure behaves as the three dimensional and with many whole to accommodate and make free available space. The transmission electron microscope reveals the plane spacing between the two layers being the three one-one type arrangement and the crystalline nature of the cobalt oxide. The area of the surface of the material being produced is big enough which is made up of the oxide of the cobalt along with the graphene and the main reason for the big surface area is the nano sized material and the foam type texture typically in the three dimensions. The presence of the large number of the entities of the oxide of the cobalt in the very small size having around the dimensions of about the two hundred to three hundred nanometers. This property is being verified by the study on the scanning electron microscope. The overall structure of the cobalt oxide along with the graphene leads to the formation of the ten micrometer thick. If one takes the separate materials prepared from the cobalt oxide and the graphene then there would have been no good results as observed for the composites. Because of the addition to the foam of the cobalt oxide wires in the nanosize there is observation of the increase in the surface area. The rates of the scan were reported to be measured at the fifty millivolts per second at the voltage of the zero to point five for the material of the electrode composing of the cobalt oxide and the graphene. Which ultimately shows the plots in the cv measurements well illustrated in the figure. Thought such materials are low in weight, considering to their properties as such the strength towards the mechanical applications they act as the electrode of the free nature. The cobalt oxide and the graphene combination led to the better performance of the towards the supercapacitor usability for electrochemical nature. The fast oxidation reaction occurring at the cobalt oxide electrode is clearly seen in the voltametric study of the cyclic type. This also shows some of the intense peaks of confirmation of these reactions. This is observed when the scan rate of the system is increased. The foam type material from the graphene structure does not lead to the observation as that of the capacitance of double-
layer but in contrast it is leading to the pseudocapacitance. The structures responsible for these observations are the wires of the nano size obtained from the electrochemical reactions activity. Here the high specific capacitance is also indicated by the system studied for the purpose[103].

In the present investigation one-step, simple and inexpensive method sol-gel reflux is used for the synthesis of Co$_3$O$_4$ electrode. The films were characterized by XRD, SEM. Electrochemical performance in supercapacitor properties study carried out by CV, GCD, and EIS techniques.

3.2 EXPERIMENTAL DETAILS

In the preparation of the solution containing the ion available for deposition first of all study was done for appropriate selection of the starting chemicals. The ultrapure chemicals such as the hexahydrate of the cobalt nitrate was taken. This chemical was of the analytical reagent grade with 98% purity. In this starting chemical the cobalt which is a transition metal was with the oxidation state +2. This nitrate of the cobalt was then converted to the hydroxide. Here, utmost care was taken to take the pure water. And hence the water applied in this case was prepared in the glass distilled water plant called as the doubly distilled water. It was optimized by repeating the experiment for several times that the concentration of the cobalt nitrate was to be maintained as the 0.04 molar. In the formation of the film of the cobalt oxide it was expected to have some additional chemical in the process called as the complexing agent. Here it was also studied very well to the select which of the chemical form the available range for the good complexation. At the end it was optimized that the chemical to be used must be the ammonia. Thus the complexing agent ammonia was purchased from the Runa Chemical Pvt. Ltd. This ammonia was in the composition of 28%.

Then in the next step, it was to be decided to choose the substrate. It is true that large number of the solid materials are available which are in common use for the film deposition. These materials include stainless steel, indium tin oxide glass, fluorine doped tin oxide glass, paper etc. Thus for the efficient deposition of the film it thoroughly studied for the selection of the substrate. Then it was optimized that the stainless still will be effective substrate.

Once the precursor solution for the film deposition was prepared and also the material on which the film is to be deposited that is the stainless steel is fixed, then the next step is to choose
a proper method for the deposition of the film. Now a day’s large number of the methods of the deposition are available in the scientific world. Amongst those the method selected for the deposition in this case is the solution based method called as the sol-gel method. Here, especially though the original method used was sol-gel, in this typical synthesis it was opted to make use of the concept of the reflux along with the sol-gel. Therefore here typically it is called the reflux sol-gel method. By considering the need of the special feature of the material to be produced that is the maximum surface area it was planned to produce the nanomaterial of the cobalt oxide. Especially in this case it was proved that the overall mechanism led to obtain the nanotubes-like morphology for the Co$_3$O$_4$ thin film. While the reaction was going on it was observed that the basic condition is necessary. Thus, proper care was to taken to maintain the higher pH of the solution. By optimizing such conditions at the end the proper deposition took place. To prepare a film of the good stability it was decided to heat the prepared film at higher temperature that is called as the annealing.

In a typical synthesis, nanotube-like Co$_3$O$_4$ thin film were obtained by deposition of the ions from precursor on the substrate usually in this case steel, The method employed is modified sol-gel method commonly called in our case as reflux method. The 0.04M cobalt (II) nitrate hexahydrate (A R. 98%) precursor was prepared in doubly distilled water. Complexing agent ammonia (28%) (Runa Chemicals Pvt. Ltd) was added to adjust pH~12. The time required for the complete Co$_3$O$_4$ film formation was about 2 hour. Pure Co$_3$O$_4$ formation was obtained after air annealing at 773K. Fig.3.1 shows the schematic representation of Co$_3$O$_4$ nanotube.
Fig. 3.1 The schematic representation of formation of Co$_3$O$_4$

The figure shows that in a clean container cobalt (II) nitrate hexahydrate was taken first. Then to the same contained which was already containing the precursor, doubly distilled water was added to produce the cobalt hydroxide. Then in the next step it is evident that, because of the addition of ammonia in the reaction mechanism and maintain the pH at basic condition the deposition of the cobalt oxide on the still took place. Next diagrammatic presentation indicates the next step which is nothing but the annealing at elevated temperature. Then at last the representative output from the characterization studies is shown.

Co$_3$O$_4$ thin films were analysed by XRD, SEM. The electrochemical performance in supercapacitor applications of Co$_3$O$_4$ electrode in aqueous solution of 1.5M KOH as an electrolyte by CV, GCD, and EIS measurement.

3.3 RESULTS AND DISCUSSION
3.3.1 X-ray Diffraction Study
The deposition of the Co$_3$O$_4$ thin films was done on the stainless steel substrates. Here the technique sol-gel reflux method called as the was preferred to be employed. The source of the cobalt used was cobalt (II) nitrate hexahydrate. The diluted water solution of the ammonium hydroxide was then added to the precursor solution to form the precipitation of Co(OH)$_2$. Now, the solution appeared become turbid at pH ~9 is due to the solubility product and ionic product of Co(OH)$_2$ exceeds the and the possible reaction is,

$$Co(NO_3)_2 \cdot 6H_2O + 2NH_4OH \rightarrow Co(OH)_2 + 2NH_4 + 2NO_3 \quad \ldots(3.1)$$

The above equation states that the reaction between the cobalt nitrate hexahydrate when reacted with the ammonium hydroxide at the optimum reaction product formation conditions leads to the composed of the cobalt hydroxide. The other products liberated are the ammonia and the nitrate. Followed by excess addition of the water solution of the ammonia, the reduction of the Co$^{2+}$ ion is achieved. This proceeds further to produce the Co(NH$_3$)$_y$$^{2+}$ complex ion which clear and transparent solution results from the formation of at higher pH. The entire mechanism of the formation of the Co(NH$_3$)$_y$$^{2+}$ is represented by chemical reaction,

$$Co(OH)_2 + 4NH_4^+ \rightarrow Co(NH_3)_y^{2+} + 2H_2O + 2H^+ \quad \ldots(3.2)$$

The above equation that is the equation 3.2 indicates the clear mechanism of the formation of the ammonium cobaltate. In which the oxidation state of the cobalt is +2. The other products which are produced in this equation are water molecule and the hydrogen ion. The existence of the chemical attractive forces, cohesive forces and effect of the Vander Walls forces the Co(OH)$_2$ complex gets deposited on steel substrate. Further, the Co(OH)$_2$ on annealing at 773K to form pure Co$_3$O$_4$ shown below,

$$Co(OH)_2 + O_2 \rightarrow Co_3O_4 + H_2O \quad \ldots(3.3)$$
The cobalt hydroxide which is now on the substrate in the form of the film is then employed as the electrode in the supercapacitance studies. The stability of the material used for the electrode purpose is of the great importance. Thus, the heat treatment is given to the film called as the annealing. The equation 3.3 indicates the reaction that takes place when the film is subjected to the annealing treatment. Here

the oxidation of the cobalt hydroxide takes place in presence of the oxygen. And the conversion of the cobalt hydroxide to the cobalt oxide takes place. The other products which are of the less important in this study are the water molecules, which re removed in the heating process.

The annealed film of the cobalt oxide was then subjected to the characterization by various techniques. The structural properties were estimated by the use of the analysis by X-ray diffractometer. In this study, the of the θ angle X-ray diffracotmeter was varied to the values as the 20°, 30°, 40°, 50°, 60°, 70° and 80°. This array of the detailed study gives the account of the structural properties of the synthesized Co₃O₄ as shown Fig.3.2.

It exhibits major X-ray diffractometer peaks of Co₃O₄ phase due to the diffraction peaks at different angles (2θ). It is observed that the peak at the 2θ angle of 19.05° is attributed to the plane of the cubic crystals lattice of Co₃O₄ matching with the (111) plane. The peak at the 2θ angle of 31.34° is due to the plane of the cubic crystals lattice of Co₃O₄ matching with the (220) plane. The peak at the 2θ angle of 36.93° is because of the plane of the cubic crystals lattice of Co₃O₄ matching with the (311) plane. The (400) plane of the Co₃O₄ cubic crystals lattice is responsible for the observation of the peak at the 44.92° angle that is the 2θ angle. Finally the peak at the 2θ angle of 59.54° is the result of the matching plane (511) existing in the cubic crystals lattice of Co₃O₄. FCC type Co₃O₄ is in good agreement with (JCPDS- 01-074-1656). No other peaks are observed indicating high purity Co₃O₄.
The Debye-Scherrer’s formula is the excellent tool for the calculation of the crystallite size. In our case also we have used the same formula and the Co$_3$O$_4$ crystallite size was calculated, and it was calculated to be 45 nm.

\[ D = \frac{0.89 \lambda}{\beta \cos \theta} \quad \text{...(3.4)} \]

where, the crystallite size is denoted by the symbol ‘D’, the half maxima full-width at is indicted by the symbol ‘B’, ‘\( \lambda \)’ is the wavelength of X-ray and ‘\( \theta \)’ is diffraction angle respectively.

3.3.2 Scanning Electron Microscopy Study
In the microscopy scanning electron the electrons of the high energy are produced because of the gun of the electron. A beam of the electrons is produced as a result. This beam of the electrons then scans the material surface under investigation. There is creation of the various interactions of the electrons form the beam those takes place with the surface of the material. These interaction leads to the production of the various types of the electrons as the absorbed, secondary and the backscattered etc. The unit in the scanning electron microscope that is the detector reads the electron samples. Then this detector then send information in the form of the signal to the amplification system. These signals are seen on the screen.

The SEM image of Co$_3$O$_4$ thin film is shown in the Fig.3.3. It shows the nanotubes like structure, which is used for supercapacitor application. The well adherent and nanotube like formation was developed of the cobalt oxide which could be ascertained form the images obtained from the Scanning Electron Microscopy Study. These nanotubes are with evident length of tube in the range of 250-300 nm.

![Fig. 3.3 SEM image of Co$_3$O$_4$]
This type of morphology allows the accessibility of OH ions of electrolyte by the electrode. This way of the permission of the interaction of the ions the most important requirement for application of supercapacitor materials.

### 3.3.3 Cyclic Voltammetry Study

The Co$_3$O$_4$ electrode shows certain electrochemical properties. These properties are studied by the cyclic voltammetry experiments. This CV study is carried out in the electrolyte potassium hydroxide of the concentration 1.5M. The range of the potential window was from -0.5 to +0.5 V/SCE. This CV study is as shown in the Fig. 3.4.

![Cyclic Voltammogram of Co$_3$O$_4$ at different scan rate](image)

Different scan rates were followed for recording the Co$_3$O$_4$ electrode CVs. In the mechanism the oxidation and reduction reactions takes place. The CV study shows the reduction and oxidation peaks, which are observed while scanning. In the sequence of the oxidation and reduction reactions the formation of the CoO$_2$ is resulted. On the electrode external surface, that is in this case, Co$_3$O$_4$ the hydroxide
ions in presence of the water molecules reacts with the cobalt oxide. This then follows the formation of the cobalt oxy hydroxide along with liberation of the electrons. The so produced cobalt oxy hydroxide in further sequence of the reaction reacts with the another hydroxide ions to obtain the formation of the expected cobalt oxide molecule along with water molecule and free electrons. These oxidation and reduction reactions are responsible for the observation of the capacitance. Thus we observe that the shapes of the CV curve are of different shape than those of the observed from the electric double layer capacitance.

The above described reaction sequence, involving the reduction and oxidation reaction of at the cobalt oxide electrode in alkaline electrolyte is given below [13].

\[
Co_3O_4 + OH^- + H_2O \rightarrow 3CoOOH + e^- \quad \ldots(3.5)
\]

\[
CoOOH + OH^- \rightarrow CoO_2 + H_2O + e^- \quad \ldots(3.6)
\]

For supercapacitive behavior we need to observe the steady increment in the current when we apply the potential. In the case of the cobalt oxide, as shown in the Fig. 6.4, the curves clearly shows that the with the increased scan rate the current under curve slowly increases. From this we can draw inference that the supercapacitive behavior is clearly observed as the scan rates are I direct proportion to the voltammetry current [104, 105]. If we try to relate the different parameters as average as specific capacitance along with scan rate and weight of the deposition, we can make use of the certain equation for calculation of the specific capacitance, as shown in equations 6.7 and 6.8.

\[
C = \frac{I}{dV/dt} \quad \ldots(3.7)
\]

\[
C_s = \frac{C}{2W} \quad \ldots(3.8)
\]

where,
average capacitance = \( C \)

specific capacitance = \( C_s \)

scan rate = \( \frac{dV}{dt} \)

weight of deposited material = \( W \)

The Fig. 6.5 shows the plot of the changes in the values of the specific capacitance versus scan rate. From this it could be concluded that the cobalt oxide electrode has capacity to show the specific capacitance at higher side. Particularly the values of the specific capacitance observed in this case for cobalt oxide at the rate of scan 20mV/s is of 125.7 Fg\(^{-1}\). Whereas in literature the value for the supercapacitance of the cobalt oxide electrode is 74 Fg\(^{-1}\) when we study at scan rate 5mVs\(^{-1}\) [106].

![Fig. 3.5 Variation of specific capacitance with scan rate](image)

**3.3.4 Galvonostatic Charge – Discharge Study (GCD)**
The galvanostatic charge – discharge study gives us the information of the possible application of the electrode under study for the supercapacitor. In our case the galvanostatic charge – discharge curves of the cobalt oxide electrode at 2 mAcm$^{-2}$ were obtained at galvanostatic current densities in 1.5M KOH electrolyte. Fig. 3.6 shows that the charge-discharge curves which remain undistorted and symmetric. The Co$_3$O$_4$ gives a large specific capacitance, promising for the development of high-performance supercapacitors. The internal resistance and followed by the potential decay is responsible for sudden potential drop. And this sudden potential drop is clearly indicted form the discharge curve. This whole phenomenon clearly indicates that the electrode material is having the promising capacitive behavior.

The typical morphology obtained for the cobalt oxide electrode due to the synthesis method in this case chemical deposition by sol-gel technique leads to provision of the large electrochemical active surface for electrolyte. It improves the desorption surface adsorption processes.

![Graph of galvanostatic charge-discharge of Co$_3$O$_4$ at a current density of 2 mAcm$^{-2}$](image.png)
3.3.5 Electron Impedance Spectroscopy (EIS) Study

The very primary and important characteristics of electrode materials for supercapacitors could be evaluated using an excellent technique as electron impedance spectroscopy studies. This method is the prominent method for this evaluation. The Nyquist plot of the Co$_3$O$_4$ electrode. It shows the inclined line which indicates a lower diffusion resistance and charge-transfer resistance. In the impedance spectra of cobalt oxide, the spectra is represented by plot which is drawn by considering the real axis, $Z'$ and the imaginary part of $Z''$ as shown in the fig. 3.7.

From the spectra it is observed that there is an intersection point on the real axis which is because of at low-frequency the linear component. The electrode resistance of internal type in an condition is open circuit indicated by the intersection point on the real axis in the high frequency region. In the system to study the electron impedance, the electrolyte suffers the ionic resistance. The active material exhibits an intrinsic resistance in this system. There is contact of the active material and the current collector. This contact creates some interface. Thus these three processes lead to the internal resistance in the system [107, 108].

To observe the supercapacitive behavior, the observation of the linear spectrum in the impedance study is must. And it must also correspond to the Warburg impedance. In case of the impedance spectrum study of the cobalt oxide, a linear part is observed in it. This linear part is because of the dependence of frequency of the ionic transport followed by the diffusion of ions in the electrolyte and to the electrode surface. The Warburg impedance corresponds to the linear part. These observations are the capacitive behavior characteristics.
Fig. 3.7 EIS plot of Co$_3$O$_4$