The current situation at the world level is the fast development in all sectors. Such fast development always makes use of the huge amount of the energy of all kind. On the other hand, our planet is having the limited sources, which will get depleted soon. In addition, the attempts to extract energy form the resources sources including the artificial strategies, causes the enormous effect on the environment such as unexpected enhancement in the pollution level is one big problem. The industrialization leads to the greenhouse effects. The whole world is looking for the solution to get rid from the green house effects. By taking in consideration all these effects, all the scientific community is working hard to search for the clean energy sources. The another thing to be taken in consideration is the source of the energy must be renewable. Looking at the long lasting life of the entire planet, the searched energy sources must be sustainable. This requires the innovations and additions of the technologies energy conversion and storage devices [1]. Supercapacitor, a new energy storage device, as an intermediate system between dielectric capacitors and batteries. The service lifetime for enough time is one of the important characteristics of the supercapacitor. In comparison with the other energy storage devices the...
supercapacitors can hold the power at very high density level. From the application point of view, one needs the important characteristic property form the energy storage devices as the processes of charge and discharge to be fast enough. The supercapacitor materials of new kind can also be developed, which will cause very less or negligible effect on the environment. All these factors are ever attracting the researchers towards the energy and energy storage devices development of the conversion[2]. The double-layer electric capacitors (EDLCs) is one of the class of the supercapacitors on the the energy storage basis of the mechanism.The other class which has again the same energy storage mechanism and also the concern of the reduction and oxidation reactions, is the electrochemical pseudocapacitors (EPCs). These are the two classes of the supercapacitors. The electrolyte and electrode concept of the charge separation at the interface of the is concern of the mechanism in the capacitance characteristics in case of the EDLCs. Whereas, the faradic reduction and oxidation reactions in the electroactive material are the cause to go for the electrochemical pseudocapacitors. Here the reduction and oxidation reactions are of the reversible type as well as those are fast in nature [3].

The electrode materials for the supercapacitors must be able to show the high performance. And such a requirement has triggered the interest in this field in this decade. For the electrode to show good efficiency in the form of supercapacitance, there are few materials which are recommended. These materials include the conducting polymers, transition metal oxides and the graphite or more simply the carbon. Among the promising electrodes materials for supercapacitors, the Co$_3$O$_4$ is posses one of the best electrodes material. Along with the reversibility, the cobalt oxide has high reduction and oxidation activity. For the deposition of the cobalt oxide on pre-cleaned glass substrate the chemical solution method is being reported. The deposited film of the cobalt oxide was annealed for four hours by keeping the temperature of about 350 °C. This annealing has produced the formation of the structure of the cobalt oxide as amorphous in nature. The cobalt oxide so produced was showing affinity towards the water molecules indicating the probability to make use of it in the supercapacitors. The formation of the amorphous cobalt oxide was supported with the confirmation from Raman spectroscopy studies [4].

In some of the cases the metal oxides from the second and the third transition series of the periodic table are tested for the supercapacitor applications. Those metals include ruthenium
and rhodium. These lead to the production of the amorphous materials and are able to show the good storage capacity. But, it is well known that the extraction and availability of these metals is comparatively very less that limits their use. So as to replace these metals the other options are check the possibility of the use of first transition series elements in the periodic table. It is observed that the elements form the groups VIII of the periodic table seems to potential. To name the oxide of the cobalt and nickel are at the top. These oxides also show the corrosion stability along with the good performance for long time [5]. In one report it is justified that the other method such as hydrothermal method supported with microwave techniques is successful in the cobalt oxide electrode material formation for electrochemical supercapacitor. The combination of the microwave and hydrothermal mechanism is helpful to produce the cobalt oxide with rod shaped crystals. These types of the mechanisms may be referred to as template mechanism as in such case the chemicals as surfactant cetyltrimethyl ammonium bromide. It is in true sense is positively charged in nature which conveniently reacts with the precursors. The electrode synthesized in this way of the cobalt oxide could show the high performance for specific capacitance of 456 F per gram of electrode material accompanied by the stability to repeat the cycle for hundreds of the time [6].

The sol-gel method is reported to be used for the synthesis of the sol followed by its deposition on the substrate. By this method first of all the cobalt hydroxide is prepared at the temperature of about 150 °C. This method allows the formation of the material with the surface of large pore volume and the surface of the large area. This cobalt hydroxide was then converted to the cobalt oxide at the enhanced temperature above two hundred degree centigrade, causing the changes in the surface dimensions. This step has resulted in the formation of cobalt oxide from cobalt hydroxide, This cobalt oxide has some characteristics useful for supercapacitors. Here, cobalt metal oxidation state changes in the leads to the formation cobalt oxide in which the oxidation state of the cobalt was plus two. This oxidation and reduction reactions at the surface are the properties of material to be useful for the better supercapacitor performance of about two hundred ninety faraday per gram [7].

The indium doped tin oxide glass substrate was employed for the cobalt oxide deposition of the thin film for capacitance studies. The method employed was the solution method in which the bath containing the precursor chemicals was used to deep the substrate. The deposited film
was containing the particles in the size ranging from ten two few tens but below the hundred nanometers. These dimensions facilitate the point electrode material of free contact of the electrolyte. As the surface is having the pores, it allows the ions in solution to get diffuse inside. This situation is found to be promising for the supercapacitance performance [8].

The electrochemically deposition is one another method reported in the literature for the efficient cobalt oxide films deposition. The application of the different voltages gives the results predicting that storage capacity of the charge was considerable. In comparison with the positive electrode the application of the cobalt oxide as negative electrode resulted in the observation of the better supercapacitance [9]. By sputtering technique the cobalt oxide was grown as electrode material on platinum substrate. Cobalt metal was first sputtered in argon atmosphere followed by deposition on the platinum substrate in the absence of any contamination. Here the sputtering at radiofrequency was recommended [10].

In more interesting report the growth of the cobalt oxide on the surface of the nickel substrate is obtained by solvothermal process. Here large number of the morphologies were obtained. The solvothermal process requires different solvent. Including the ethyl alcohol, glycol and glycerol. In the study of the solvotherm process the effects of the solvent son the surface morphology are studied. The properties of the solvents as viscosity and some physical properties are also considered.

The capacitance of the synthesized cobalt oxide electrode of the porous nature was observed to be promising with the important specific characteristics as electrochemical stability and cycle rate [11]. In one another method called spray pyrolysis the synthesis of the oxide of the cobalt and nickel cobalt is achieved [12]. The environmental benign synthesis of the cobalt oxide nanoparticles in the atmosphere of the waste parts of the plants is also useful technique. Such produced cobalt oxide has also shown the pseudocapacitive properties [13]. The sol–gel reflux method is a widely applied for preparation of metal oxide thin film because of its well-known advantages, such as better stoichiometric control, lower calcination temperature, shorter sintering time, finer particle size with homogeneous distribution and high surface area [14]. Many researchers have developed various Co$_3$O$_4$ nanostructures: nanoparticles [15], nanosheets [16], nanotubes [17], nanowires [18], and nanoflowers [19].
Recently, ILs poses the very useful electrolyte properties over the usual molecular liquids. Such properties as less volatile and good conduction of the charges or ions leads the ionic liquids to be considered for the supercapacitor applications. [20]. Room Temperature Ionic liquids (RTILs) have many advantageous properties like voltage window with big range and the conductivity to the higher side essential for electrochemical applications. RTIL have been used as solvent free green electrolyte for hybrid supercapacitors, ionic liquid gel in electrochemical double layer capacitors, many reports have been found in literature of IL based supercapacitor studies [21-27].

For designing the supercapactiros of kind lightweight and flexible is to replace the usual and common electrolytes as hydroxides of the s-block elements in periodic table. In such case we have a choice to search for the electrolytes with polymer structure as well as the solid or highly dense liquids called as the ionic liquids. This new ideas definitely helps us to restrict us from the fabrication of the common setup

for the electrolytes [28]. The organic chemistry ahs gifted the material science a kind of the liquids of gel type electrolytes behaving as polymers in structure. These gels are of both types soluble in water as well as organic solvents [29-31].

The aqueous electrolytes of the kind basic as well as acidic could be of use to produce the electrolyte gels with the higher alcohols and other hydrocarbon families such as the poly(-methylmethacrylate), polyvinyl alcohol [32-34]. These electrolytes possess the ions for free movement, can show good conductivity of ions which is remarkable. The aqueous medium has, in general the low stability towards the electrochemical reactions, thus small window of stability, showing poor performance of supercapacitance. In contrast to the aqueous electrolytes, the organic electrolytes which are not soluble in water, has the polar nature and the compound s are the derivatives of the polyethylene. Both these aqueous and the polymer based electrolytes are poor to show the large potential window and thus becoming the materials of low priority. The polymers structures with the less volatile ionic liquids, called as the ionogels, and showing the more stable electrochemical nature are at the forefront [35,36]. The applications of the ionogels are due to the many useful characteristics such as mechanical acceptable properties, electrochemical and stability of thermal and components resistant to the flames and with high evaporation temperature [37]. The ionogels used in solid state supercapacitors could be
synthesized by the combination of the polymers as poly(vinylidenefluoride-hexafluoropropylene) with the ionic liquids as 1-ethyl-3-methyl imidazolium tetrafluoroborate [38, 39].

In one of the study the solid state supercapacitor was fabricated from the polymer developed from the combination of the imide derivative of the trifluoromethanesulfonyl ionic liquid of methylpyrrolidinium derivative. This supercapacitor has shown the better performance in capacitance[ 40]. The new kind of the materials just as the hollow carbon spheres, which possess the properties as specific area of large size and also have very low resistance of the transport of the ions. Because of the creation of the numerous pores in the structure these materials show low density of the material [41–45]. All these properties are needed for their applications in the field of the supercapacitance [46-48]. The modification of the electron donation characteristics and to get increased efficiency of the hollow carbon spheres the addition of some specific gases as nitrogen could be done [49, 50].

The ionic liquids with particularly no vapour pressure and comprising of the cations and anions of both the inorganic and organic origin, could be taken for our help for the introduction of the nitrogen in the hollow carbonspheres. In the formation of carbon materials of functionalized nature, the precursor role is played by the templates of ionic liquids [51-53]. In the formation of the mesoporous and microporous carbons with nitrogen content on its surface the ionic liquids with the carbon-nitrogen functionalities are preferred[54]. By sol-gel process the synthesis of the hollow carbon spheres with nitrogen doping is achieved with the porous morphology. The 1-alkyl-3-methylimidazolium bromide and the structure supporter tetraethyl orthosilicate are applied as the precursors of nitrogen and carbon. There is great scope to control the morphology of the materasil by varying the 1-alkyl-3-methylimidazolium bromide amount in synthesis. Overall the synthesized material possesses the all required properties for the better performance in supercapacitor ability [55]. For the capacitors based on the carbon materials, the energy density could be increased by the electroactive species dissolution in the electrolyte by the mechanism of the reduction and oxidation reactions and thus leading to form a redox supercapacitors [56, 57].

In these redox active supercapacitors, the modification in the carbon electrodes is achieved by the addition of the additives in those. For example the, enhancement in the capacitance of pure benzoquinone was found to be three hundred twenty faraday per gram, whereas the if hydroquinone is oxidized in benzoquinone, the system containing the potassium
hydroxide electrolyte and carbon electrode shows the capacitance of the nine hundred farady per gram[58, 59]. The other additives those are reported to be used in the literature are methylene blue, phenylenediamine and potassium iodide [60-62]. The redox active supercapacitors are highly soluble in the water, and this ability is used to classify those materials. Similarly the ionic liquids are also soluble in the water, which is disadvantage of tit for not much preferred for the supercapacitor studies. The ionic liquids produced from the imidazolium base are being used for the capacitance study of the carbon electrodes copper ions as the cationic electrode and the as the negatively charged electrode. This system was based on the solubility of the molecules of ability to undergo the reduction and oxidation as well as the ion transport mechanism. These limitations are very well overcome by the use of the redox active centers in the presence of the ionic liquids of electroactive type allowing the linkages with the ions [63-65]. Ferrocene is one of the important organometallic compound, that could be explored for the modification of the anions and cations of the ionic liquids. These types of the redox ionic liquids with the ferrocene shows the self discharge mechanism [66].

The supercapacitors have limitations in the energy density which is comparatively low as that of the fuel cells and batteries, which are very commonly, used conventional energy storage devices. Those devices includes different types of the capacitors asymmetric capacitors, pseudo-capacitors, and electric double-layer capacitors. Thus, it is very hard to think of the total replacement of the fuel cells and batteries with the use of the supercapacitors, considering the requirement of the power and energy. Thus, in urge to the applications of the supercapacitors as the substitutes for the earlier devices it is necessary to go for the research of the technology for the materials of the synthesis for supercapacitors and also to design the materials for the electrolyte to obtain the voltage window wide enough and the to fabricate the electrode materials with the optimized structures and integrated systems, so that the large surface area will made available [67, 68]. It is observed that the past few years has witnessed the supercapacitor electrolyte development of the various forms such as the reduction oxidation type, viscous organic compounds called as the ionic liquids, other organic and the aqueous as well as solid type [69-71]. By this a we are now with the sufficient knowledge to proceed with the new developments in this rear of the energy conversation. The inorganic electrolytes are generally
having the lower voltage windows, whereas the materials of from the organic category possess the comparatively large voltage window. This property of the organic materials facilitates with the high density of the energy because of the high cell current. In addition the other property of the electrolyte whether soluble in water of not also plays an important role, here the water insoluble electrolytes are preferred, because of the ability to show large voltage window. Thus, in the development of the good supercapacitor, such electrolytes are preferred. In the energy storage devices, it is the common observation that such devices are gets heated while in use. This is because of the resistance of the electrolyte materials. Thus, if the supercapacitor system is applied at temperature of some higher degrees, there will be much better performance due to reduction in the electrolyte resistance. If the supercapacitors working in such situations are developed, then automatically the set of the confinement of such system will not arise. However, in the development of the such supercapacitors, one should take in mind that the cycle life the supercapacitor decreases down, which limits the usual protocols for the synthesis of the new supercapacitors. For the solution of the problem, one should think of using some other alternatives of the electrolytes which will allow the high temperature at the same time the life of the cycles remains at the good enough number. The best alternative is make use of the stable and having capacity to be in the liquid state for at least one hundred degree centigrade temperature are the ionic liquids [72]. As the ionic liquids can with stand high temperature, these chemicals generally does not undergo the decomposition. Taking in consideration of the limitations of the ionic liquids as the lower conduction properties, we need to modify the application strategies. The strategies must allow the additional extra amount of the organic solvents and the operating temperature for the supercapacitor involving the ionic liquids be the higher [73 - 76].

In some of the reports there is application of the mixture of the ionic liquids at the higher temperature so that the conductivity of those both ionic liquids will add up for the total performance [77]. In an attempt to obtain the promising supercapacitance by using the mixtures of the ionic liquids, the electrolytes were modified and applied at the temperature of the 333 °. This resulted in the good performance of the supercapacitor. The ionic liquids of the ethyl methyl imidazolium based derivatives containing the fluorine as N-propyl-N-methylpiperidinium, trifluoro-methane sulfonamide and the combination of these both ionic liquids were applied in the two cell systems of the supercapacitor solutions. The typical supercapacitance study of these
mixtures was carried out and the results were recorded at the various temperatures from 293 ° to 333 °. The supercapacitor performance of the individual ionic liquids at the higher temperature of 333 ° was low but with the use of the mixtures of the ionic liquids the synergistic effect was in power showing the enhanced performances. The supercapacitance behavior of the materials containing carbon shows the influence of the presence of the fluoride anion along with the ionic liquids has influence on indicting the applications at the excellent life time of 10,000 cycles with minimum degradation required characteristic for good supercapacitor to work at the elevated temperature [78].

If the phenomenon conversion of the liquid electrolyte in the solid starts to take place, there come the limitation of the movement of the ions causing the declination in the electrochemical performance of the system. To overcome this formation of the solid in the electrolytes, the excellent option is the making use of the gel type materials as electrolyte. This type of the materials are always posses the characteristics of facilitating the excellent stability as far as the mechanical strength is considered as well as that of the dimensions also. In the preparation of the polymer containing the gel materials uses the little percent of the polymers. As a result the so produced electrolyte has nature of both kinds as that of the liquid and also the solid, which is advantageous for the transport of the ions easily. Some literature studies shows the applications of such type of electrodes in the electric double layer capacitors, though with comparatively low specific power in spite of the specific energy and capacitance of the high value [79 - 81]. It is evident that some of the characteristics of the polymer supported gel electrolytes such as the less ionic conductivity and the viscosity comparatively high, adversely reflects in the performance of the supercapacitor with respect to the temperature range and also the specific power. In such case the examples are the poly(vinylidene) and poly ethylene oxide fluoride-co-hexafluoropropylene) polymer in the ionic liquid capable of working at the room temperature [82]. However, high viscosity and low ionic conductivity comparing to the conventional liquid electrolyte is an issue limiting the power and temperature range of gel electrolyte based supercapacitors [83].

The butanedinitrile in the form of the crystal nature and plastic like is reported as used in the synthesis of the electrolyte of solid form and allowing the exceptionally good movement of
cations and anions during the mechanism of the supercapacitance [84 - 86]. The structural feature of this type of the polymer allows the high diffusion of the ions than those of the other electrolytes. The properties such as ability to dissociate and the cationic and anionic centers useful for the expected conduction are there with the butanedinitrile solid-solvent. In spite of the fare properties as mechanical, these materials show good conductivity of ions [87]. In case of the double layer capacitors of electric type and the lithium ion batteries, the properties such as mechanical could be improved by preferring the combination of the polymer and the electrolyte material [88]. The organic compound butanedinitrile could be used for the formation of the electrode of the gel type to increase the mechanical strength. The hexafluoropropylene derivative of the polymer containing the vinyl groups are preferred in some cases for the formation of the electrolyte along with the ionic liquid. However, the butanedinitrile could not produce ions the resistance is more in the conduction mechanism [89, 90]. In a typical synthesis of the polymer supported gel electrolyte, the complex molecule of co-hexafluoropropylene of the polyvinylidene fluoride polymer was allowed to mix along the, tetrafluoroborate1-butyl-3-methylimidazolium ionic liquid derived from the imidazolium. This entire process does not make use of the solvent and leads to the supercapacitors of solid type. In contrast to the common electrolytes the polymer based gel type electrolytes allows the working of the supercapacitor at the wide temperature range and also the output is good conduction properties and stability electrochemical window was also appreciable. It is to be noted that at the higher temperature also there is no any change in the phase of the electrolyte gel. The electrode material was fabricated from the activated carbon material and applied in the electric double layer capacitors. The specific capacitance observed was 176 F/g from this system with eighty percent retention for over 10000 cycles with respect to good cycling stability [91].

In recent years voluminous efforts are taken to produce the electric double layer capacitors which will work at the operative voltage of the high value. In these attempts the focus was given on the electrolytes. The case where the organic compounds such as ionic liquids are preferred then there are many chances to get the desired properties from the electric double layer capacitors. The ionic liquids are such salts in the molten stage, which allows the easy movement of the ions in the surrounding so that there will be generation of system where the high operative
potential could be achieved such as three point five volts, though there is some limitation to show high conductivities because of the more viscous nature [92-93]. Thus these systems will not work appreciably at lower temperature. To overcome this type of the limitation and to get the better performance in terms of the operating voltage, one can prefer to take the more than one ionic liquid, and this mixture may prove better properties towards the capacitance studies in case of the double layer capacitorselectric. In spite of these speculations, the applications of the ionic liquids as electrolyte has economical limitations, thus many research groups are designing the ionic liquids and accordingly synthesizing the same for the purpose of the capacitance studies [94-95]. In the search of the better entities for the expected synthesis of the ionic liquids the organic compound as hexamethyleneimine, the compound of the nature polymer, are the forefront in the devices used for the storage of energy as supercapacitors [96]. If these nitrogen containing moieties, such as hexamethyleneimine, are taken as the resources for the synthesis of the ionic liquids, then this mechanism will serve many purposes including the environmental concern that ecofriendly approach and much cheaper also compared to the synthesis of the usual ionic liquids for the applications in the energy storage devices especially the electrolytes in supercapacitors. There are several reports on the applications of the ionic liquids which are fabricated from the hexamethyleneimine compounds. The electrolyte produced from the combination of the hexamethyleneimine with other entities leading to the hexamethyleneimine-based ionic liquids are found to show large electrochemical window, in case of especially lithium ion batteries, when supported with electrodes made up of the carbon materials [97-99]. In one of the attempt to synthesis the desired electrolyte, the precursors as derivatives of the hexamethyleneimine in which mostly the different alkyl groups are varied from one carbon alkyl to four carbon alkyl. And the other compounds being reported in these synthesis are the imide derivatives of the fluoromethanesulfonyls. These hexamethyleneimine based ionic liquids have shown the promising performance of electric capacitors of double layer type. The selection of the particular ionic liquids based in the hexamethyleneimine has shown appreciable cyclic voltammetry characteristics with the potential window of about the 3.5 volts as an operating potential and also there is no appreciable decomposition of the electrolyte [100 -101].

In case of the electric double layer supercapacitors the preparative voltage increases which reflects in the power and energy at the higher values. These energy and power values take
in account the parameters of the device as capacitance and resistance. Though there is limitation of the electrolyte system and thus it shows the lower life cycle at the potential of 3 V [102, 103].

To overcome this limitation in obtaining the high values of voltage that is operative, tremendous efforts are put by the researchers especially in the case of double layer the electricsupercapacitor electrolytes. The excellent options for these achievements are the applications ions of the ionic liquids as electrolytes which possess promising properties required for good supercapacitance including the more stable electrochemical window and remarkable conductivity [104-106]. The electric double layer supercapacitors have reported to be shown the 3.5 V as operative voltage, when applied the ionic liquids as electrolytes [107]. But the applications of the ionic liquids at room temperature are not much promising and are showing the low power densities owing to the lower conductivities and higher viscosities of these electrolytes. As compared with the common electrolytes. The basic characteristics of the ionic liquids which become the hurdle in their applications as electrolytes in the supercapacitors can be get read if you choose one ionic liquid and appropriate organic solvent and make use of their mixture in the electric double layer supercapacitors. But the care has to be taken about the costs of the ionic liquids and thus, accordingly the researchers are looking for the comparatively low cost ionic liquids. One can design the expected ionic liquids as per requirement in the supercapacitance applications, and by selecting the low cost precursors those could be synthesized in the research laboratories, which in turn will act as the good electrolyte materials in the technology of supercapacitors [108, 109]. The ionic liquids are composed of the cations and the anions. The alkys substituted two atoms of the nitrogen are more preferred in the case of the for example the azepanium compounds in ionic liquid synthesis. This precursor leads to the multi-member ring compounds, useful for the better supercapacitance and also represent the example of the green approach. The cost of the ionic liquids synthesized by this approach are comparatively cheaper than those of the ionic liquids based on pyrrolidinium[110]. And also can act as good electrolytes for the storage of the electrochemical potentials. These ionic liquids are capable of showing the large potential stability windows on the substrates coated with carbon batteries as well as finds the lithium ion applications in [111-112]. The reports are there in the literature about the applications in supercapacitors of the azepanium-based ionic liquids electrolytes.
The imide derivatives of the azepanium bis (trifluoromethanesulfonyl) containing the methyl and butyl functionalities are synthesized and applied in the studies of the electric double layer supercapacitance and electrochemical performance. This type of the electrolyte contains the bigger cations causing the decreased conductance and the increased viscosity, but this hardly affects the observations at low currents of the energy storage capability and the cycle stability.

By taking the propylene carbonate as the starting chemical the synthesis of azepanium based ionic liquids was carried out. It is recommended to use the commercial active carbon, conducting chemical and the binder materials in the proportion of the 90:5:5 and applied on the foil of aluminum. So produced material possesses the surface area little more than one centimeter square and considerable mass loading capacity. The entire study was done for about 50000 cycles and at 10mA/cmgalvanostatic charge-discharge. The good retention of the cycle stability was observed for the capacitance as 80 % after varying the cycle number upto 55000 and the observed operative potential was 3.5 V [113].

In the supercapacitors studies the material graphene is mush important because of its properties as low resistivity and high theoretical specific surface area such as ten ohm centimeter and two thousand six hundred thirty meter square per gram respectively accompanied by stability and strength [114, 115]. This attracted the researchers to study in detail the structural aspects of the graphene-based materials and graphene itself [116 - 118]. The graphene materials electrode could be well used in the solvents as organic as well as water and capable to show the good capacitance about two hundred faraday per gram [119-122]. For the efficient application of the graphene materials for supercapacitor properties, one need to take concern about the lower capacitance especially volume wise for applications in smaller devices [123].

It was observed that there is need of the grapheme with the more surface area which could be achieved by the not more orderly arrangement on the structure of the grapheme but with dense nature. If one uses the low evaporating solutions as electrolytes for the preparation of the gel films of the grapheme, this lead to synthesis of the grapheme with non-orderly arranged grapheme layers. The working voltage window of the ionic liquid electrolytes is large up to the four volt [124, 125]. The characteristics as non-flammable nature, negligible vapor pressure and high chemical stabilityuseful for better supercapacitors and batteries are rendered by the promising electrolytes as the ionic liquids[126]. Recently there finds the applications of the
alternative electrolytes to be applied with graphene. Among those are the ionic liquids, which shows remarkable properties and also shows the capacitance performance of specific nature in terms of the value is seventy five faradays per gram at the voltage window of 3.5 volt [18]. The choice of the mechanism of obtaining the nitrogen doped graphene, especially reduced graphene, before its application as electrode material enhances the supercapacitance to the value of about 258.0 F/g [127]. In one another investigation the graphene is activated by functional groups to get the very large surface area more than three thousand meter square per gram of material. If this high surface area electrode material is used in the presence of the ionic liquid, imidie derivative of theethyl-methylimidazolium bis(trifluoromethylsulfonyl) as electrolyte, this high surface area enables the synthesized material to show specific capacitance of the 200 F/g [128]. The functinoalised ionic liquids applications is the challenge at the different working temperatures of the supercapacitors fabricated from the activated graphene. The reasons for this limitation are the characteristics of the ionic liquid as the lower melting points and viscosity to the high value [129, 130]. To get the remedy over, some investigations are come up with the modifications of the ionic liquids so that they will be in the liquid state at the working temperatures of the supercapacitors and voltage window of 3.7 V as up to more than 350 degree kelvins. In this case the options are to select more than one ionic liquid and take the mixture of them, which again essentially contains the pyrrolidium and piperidinium derivative cations and imide derivative anions. This also helps to reduce the viscosity of the ionic liquids as comparatively smaller molecules are involved. The effect of the presence of the smaller molecules is that, those facilitate the avoidance of the rigid structure formation and thus there is decrease in the melting point, by maintaining the solubility properties as required. The less viscous nature again is responsible for the good conductions as expected [131].The equimolar proportion of the nitrogen derivative of the butyl and methylpyrrolidinium fluorosulfonil imide and another ionic liquid nitrogen derivative of the methyl and propylpiperidinium fluorosulfonilimide ionic liquids as electrolyte was taken for the supercapacitance studies of the graphene materials. In this specific investigation the starting material was the powder of graphite. It was converted to the graphite oxide with the help of the potassium permanganate and sulphuric acid-phosphoric acid mixture followed by the stirring at slightly high temperature. Another chemical hydrazine was applied to get the graphene then
produced is obtained in the form of the film with good porosity [132]. The so produced graphene film is allowed to interact with the ionic liquid of choice so that there is the insertion of the ionic liquid molecules in the graphene material. This graphene film was then applied in the studies of the electrochemical performance. In the supercapacitance studies the three electrode system was reported to be used. The working electrode was the film of the graphene. The electrolyte was the mixture of the equimolar proportion of the two ionic liquids butyl nitrogen derivative of the ethylpyrrolidinium fluorosulfonyl tris imide and methyl, propylpiperidinium bis fluorosulfonyl imide. For collection of the current the materials such as gold and oxide of the aluminum as applied. The system was tested at high temperature around 350 degree kelvins. The study was covered the techniques as cyclic voltammogram for capacitance study, for impedance measurement the electrochemical impedance spectroscopy. The capacitance observed was about 175 F/g. at the temperature of the system of 350 degree kelvins [133].

The molten salts of the specific chemical retaining their properties at the room temperature are called as the aprotic ionic liquids. These types of the ionic liquids can be good alternatives for the routine electrolyte materials in supercapacitors as per the recent investigations [134]. The composition and the properties of these electrolytes give excellent efficiencies in case supercapacitance when accompanied by the electrodes of the non-porous nature. In the energy storage system with combination of the fuel and battery mechanism, the characteristics of the ionic liquids to exhibit the vapour pressure at lower side as well as the anti-flammable nature, leads those to be important candidates [135-136]. In the usual applications of ionic liquids, the cationic electrode material is some polymer supported material and the anionic electrode is the carbon material [137, 138]. At high temperature that is about sixty degree celsius, in comparison with the organic materials for the applications in the supercapacitors the, aprotic ionic liquids are also playing the important role with the ability to show good performance [139], though those are having limitation because of the more viscous nature and the poor conduction properties [140]. By considering these limitations the researchers have come up with the applications of the more suitable electrolyte materials such as the protic ionic liquids which shows better conduction at range of the temperature, the voltage window with good stability and can be used with the less porous materials [141-142]. The protic ionic liquids as the name itself
is self-explanatory, contains the positively charged hydrogen ions, which takes part in the reduction and oxidation processes leading to the faradic reaction and also pseudocapacitive mechanism, this fusion of the two mechanisms is especially taking place at the electrolyte and electrode touching points [143]. The faradic reaction and

also pseudocapacitive mechanism actually enhances if the oxygen from the oxygen containing functional groups present on the surface is being used in the redox mechanism along with the positively charged hydrogen ions thereby cumulatively increasing the specific capacitance to the remarkable value. In a study on the ionic liquids application of the of the protic type, the electrolytes used are with the groups on the surfaces responsible for the transportation of ions and the specific area

enough for the better capacitance with the moderate porosity. These materials are used in the three electrode system in the electrochemical studies. The presence of the H$_2$O molecules in the protic ionic liquids, has significance in addition to the acidic-basic condition and the various positively and the negatively charged ions [144]. In case of the protic ionic liquids the removal of the water molecules is difficult even in heating because of the hydrogen bonding among themselves, which cause the challenge in its efficient application. The very important strategy is to make use of the electrode materials containing the maximum porosity and expected active functional groups on the carbon material to obtain the better supercapacitance. If the carbon material required is synthesized with the very small pore sizes may be to the nano level, such material of the pyrrolidium based protic ionic liquids are capable to show the specific capacitance of very high value. At the neutral pH range the capacitance obtained is 200 F/g and in strong alkaline medium the observed specific capacitance for the selected system is 121 F/g. the limitation created by in the electrolyte the presence of the water molecules, could be overcome if one choses the another material, especially organic materials, say ionic liquid, then the voltage window could be remarkably widened.

In a typical application, the carbon is first activated by the xetogel. The xerogel of the material composing of the formaldehyde and resorcinol was obtained by adjusting the precursor at the slight acidic pH range, to get the material with the 200 M$^2$/g of the surface area. And density of above one gram per centimeter cube. The surface area was found to be the very high when studied at the various temperatures in nitrogen and carbon dioxide atmosphere as well. The
supercapacitance values indicate that the material used in this study can very well work at the 2.5 as cell voltage [145].

The need of the small sized and transportable electronics equipments is ever increasing and to supply the electrical support to such equipments is the challenge now a day. This challenge in some way is accepted by the researchers and come up with the energy storage devices with excellent performance that is nothing but a supercapacitor. The supercapacitors exist in very small dimensions and are the excellent energy storage devices performance wise. The materials with abilities as following the mechanism of the charging and discharging at the fast rate, and good cycle life called as the electrochemical double layer capacitors are the very god alternatives in the energy conversion and storage equipments [146]. There are several things to be thought of while preparing for the best possible materials as electrode as well as the electrolyte, so that those could be easily implemented in the micro-supercapacitors. One of the important dimensions to be thought in this direction is the nanostructured materials. Especially the carbon based materials are gaining the importance in this case. These carbon based materials can possess the high ratio of the volume to surface, which is in demand for the better supercapacitor properties. The various dimensions which are reported in the literature are as carbon nanotubes [5] and graphene [147]. In addition the compact carbon materials like allotrope of the carbon diamond is at the top priority in the nanostructured materials derived from the carbon. This type of the materials are of much importance in the supercapacitor devices research field [148, 149]. One of the important characteristics of the carbon materials is their inertness towards the chemical environment, wide electrochemical windows, and high overvoltage. These characteristics are responsible for the supercapacitors good performance energy density in terms of the densities power [150]. In diamond, many shapes could be articulated by varying the preparative environments. The most attracting shapes are the porous diamond, diamond nanowires, and nanocrystalline diamond [151] etc. However, to obtain the excellent supercapacitance, it was recommended to have the modifications of the diamond nanostructures. These type required modifications could be achieved by the process of the doping the materials. Some of the p-block elements in the periodic table of the elements such as boron could be doped in the diamond to observe the poor density above eight hundred watts per centimeter cube and 1000 V/s as the discharge rate [152]. The reports are available on the
synthesis of the material with various functional groups on the carbon allotrope diamond. The functional groups which are attracting in such cases are the hydroxide groups. These hydroxide groups are not directly attached as a functional group, but the hydroxides of the transition metals are preferred. In one report the application of the nickel hydroxide for the fictionalization of the diamond has achieved the nanowires of diamond with power density of the three into ten to the power five watt per kilogram and 1600 F/g mass specific capacitance [153]. On the line as similar application to that of the carbon materials some other materials are also tried including the third row element in the elements table of the long form of the chemical elements table the silicon. The nanowires of the silicon have recently attracted the researchers to check the possibility of it use in the supercapacitors [154]. It is well known that silicon and silicon materials are the very important entities in the micro-devices of many kinds in electronics. Similarly the silicon has great potential in the storage devices for energy because of its properties as density of power to the high level, reasonable cycle stability and good capacitive behavior [155-158].

In one of the investigation the researcher have reported the synthesis of the silicon nanowires coated on the diamond to be used in the supercapacitance study with three electrode system [159]. This configuration has shown excellent stability of the cycles for about 10000 cycles and over one hundred micro-faraday per centimeter square capacitance. In one of the report the microwave technique accompanied by the deposition chemical vapor was employed for the applying the layer of the silicon nanowires on the surface of the diamond which was previously made to the crystalline form. Here, homogenized, well adhered and evenly coated film was obtained. This film was applied for the electrochemical studies, where this material acted as the electrode. For this electrochemical studies the hydrogen ion containing the ionic liquids was reported to be used.

In a typical synthesis of silicon nanowires, the substrates used were imide derivative of the triethylammonium bis (trifluoromethylsulfonyl) ionic liquid, and the silicon doped p-type impurities. The synthesized material was subject to the various characterizations including the morphology. The system to study the electrochemical properties was followed the mechanism of the electric double layer supercapacitor in presence of the hydrogen ion containing the ionic
liquids as electrolyte. This materials has reported be working well at the reasonably high temperature and with the electrochemical window with wide in nature [160-163].

In supercapacitor devices there are several including the electrode and electrolyte components. The efficiency of the supercapacitor is greatly dependent on electrolyte material; it also governs the mechanisms of the density of the energy to be stored in supercapacitor, the operating voltage etc. and ultimately the overall performance of the supercapacitor. There are several inorganic chemicals such as potassium hydroxide used as electrolyte. But now the increase demand is there for the environmental friendly chemicals to be used as electrolytes, and in this especially the ionic liquids are playing an important role. In fact till today the science of the electrolyte has progressed much so as to get the maximum performance of the supercapacitor. In this remarkable contribution is because of the application of the mixtures the organic solvents and of the ionic liquids and are recommended in the electrochemical studies [164 - 173]. The ionic liquid facilitates the higher energy densities and also the operating potential, which is definitely higher if one compares with the routinely used organic and aqueous electrolytes. Though, there are limitations for use of the ionic liquids because of their application strategies, the researchers have come up with solution as to convert the ionic liquids liquid status to the solids materials as polymers. In this case the polymers are synthesized of desire by taking the precursor as imidazolium based ionic liquids and fixing them in to the polymer structures of the polyacrylonitrile, polyethylene glycol, polyvinyl alcohol, and polymethyl methacrylate polymers etc. [174 - 183]. It is observed that not all the ionic liquids show better performance with respect to cycle rate capability and specific capacitance due to their limited conductivity properties. To avoid the limitations of the liquid states of electrolytes, the good option is to go for the solid state supercapacitor systems. Efforts are also made to insert the higher boiling molecules from organic nature in the polyer matrix, but with no much improvement [184, 185]. The poor conductivity is not the only issue, but in addition the attention is also to be paid towards the hazardous nature and the mechanical properties. In one of the attempt the imidazolium based tetrafluoro borate ionic liquid was employed to the supercapacitor and interestingly the results showed that there is observation of the significant capacitance. Especially the ionic liquid embedded in the polysaccharide has shown the supercapacitance at
the operating voltage 2.5 V was observed to be the value 130 F/g [186-188]. This is kind of the example of solid state electrolyte. Many efforts are made in the development of the polymer based ionic liquid electrolytes from the imidazolium ionic liquid, these are showing the promising properties towards the supercapacitance [189 - 192]. The best reported example in the category of the polymer based ionic liquids, was prepared from the precursor ionic liquid mixture prepared from the nitro-butyl-nitro-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide and poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide. In the typical synthesis the solvent acetone was used to dissolve the polymer based ionic liquid and stirred for defined duration. By using the physical method the film was allowed to adhere on the substrate followed by drying at 400 kelvins, to get all state electrolyte. Simultaneously the electrode from carbon material was prepared using the active carbon material and the current collector aluminum. This combination at the end is resulted in the solid form and possess the electrochemical window with great stability and is also remarkably wide in nature. In the synthesis of this kind of the electrode material the carbon is being used as active material. This material when tested for the supercapacitance showed the 100 Fg\(^{-1}\) specific capacitance at ambient temperature [193].

The supercapacitance properties are greatly governed by the shapes of the electrode materials. In this concern various attempts are made to achieve the synthesis of the electrode material with various morphologies. The large varieties of the morphologies are also having impact on the conductivity and the stability of the cycles in the supercapacitors [194–199]. Appearance of the specific morphology of the electrode material facilitates the large surface area and is the very important aspect that leads these materials to be used in the electrical double layer capacitors [200]. In case of interface the charge at the electrolyte the electrical double layer capacitors, and electrode separation takes place. This mechanism could be enhanced if large surface is there of the electrode material. To increase such surface area the application of the activated carbon is very common in the electrical double layer capacitors. The performance of the supercapacitor is interpreted on the basis of the wideness of the potential window of the electrolyte used and also on the electrode material. In early literature the applications of the aqueous electrolytes is reported, but those have the limitations because of the specific energy
cause by the less wide potential window [201, 202]. In contrast to this, though more volatile but with wide voltage window materials as organic electrolytes could be preferred are preferred over the aqueous electrolytes in the applications of supercapacitors [203, 204]. There are many characteristic properties accompanied in the ionic liquids those leads the greater applications of these materials in the electrochemical studies [205–209]. In spite of the general chemical characteristics of the ionic liquids to be nit working at the high temperatures, a special class of the ionic liquid electrolyte is recognized as the hydrogen ion containing ionic liquids. The ionic liquids of this type can allow the working of the supercapacitor at the room temperature and above also upto 80 °C. In the formation of the hydrogen ion containing ionic liquids, one of the hydrogen is transferred from acid to base [210, 211]. Because of the presence of the positively hydrogen ion, there occurs the mechanism of the acceptor and donor in the bond formation of the hydrogen [212] and thus behave as good electrolytes for conduction and accordingly finds many applications [213–223]. In addition to the protic ionic liquid that is positively charged hydrogen ion containing material, the aprotic materials, though they have low viscosity and conduction properties are also reported to be used as useful entities in the electrochemical studies of the electrode materials. The mixture of the two different aprotic ionic liquids and also in the battery applications, the combination with the some s-block elements in the periodic table of the elements as lithium is also reported for energy storage [224- 227]. If one choses to the described combination of the aprotic ionic liquids, it is observed that the performance is better because of the fast phenomenon of the discharging and charging leading to potential window wide enough [228]. To avoid the solid nature hindrance in most of the applications, some typical solvents are being reported to be used to decrease the viscosity and the application at higher temperature is also investigated.

One of the alternatives for the highly viscous nature is to select the solvents which gets solution form at the defined temperature and also converts to solid at one temperature value. These types of the solvents, helps to maintain the characteristics of the ionic liquids to store energy at the ambient temperature also. In one typical investigation for the supercapacitor, two ionic liquids were selected containing the positively charged hydrogen ion containing ionic liquid as the electrolyte medium in the cationic form and the electrode was the carbon containing material. At the 2 volt potential, there are chances of the insertion of the anions in empty spaces.
in the layers as well as the lattice of the crystal. This insertion gives the observation of the capacitance of 200 F/g. But, there is observation of the decrease in the insertion and also the removal of anions from the sites if the potential is increased over 2.5 V. Thus, at optimum voltage the retention of the capacitance was observed to be more than eighty percent for the long duration of the time, almost one hundred hours at room temperature. These observations indicted the usability of the eutectic ionic liquids for electrochemical studies. The imide derivatives of the triethylammonium and pyrrolidinium based ionic liquids were prepared by taking the initial quantities of the precursors in similar proportion. The round bottom flask of the three neck facility was applied to accommodate the pyrrolidinium based ionic liquid at the freezing temperature followed by the addition of the mineral acid containing nitrate ions with swirling for a while. The system was added with the dichloroethane before reflux and evaporation. By considering the exothermic nature of the reaction the low temperature was facilitated for the system. The further reactions were of the base and acid reactions with the addition of the HCl [229]. The cobalt oxide deposition of thin films is demonstrated in the present work. The bath for the deposition was maintained with high pH values that is alkaline in nature. The precursor chemical used was cobalt nitrate. The process of the deposition was carried out using the sol-gel reflux method.

These films are characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques for structural and morphological investigation. For electrochemical performance of Co$_3$O$_4$ are studied by Electrochemical impedance (EIS), Galvanostatic charge/discharge (GCD) and Cyclic voltammetry (CV), techniques and in 0.1M 1-ethyl-3-methylimidazolium bromide [EMIM][Br] and 1-(2-hydroxyethyl)-3-methylimidazolium chloride [HEMIM][Cl] ILs used as electrolyte and we got very impressive results with Co$_3$O$_4$ electrode.

5.2 EXPERIMENTAL DETAILS

5.2.1. Chemicals

In our experiment, the chemicals used were already of the considerable purity, thus purification step before their application was avoided. Cobalt nitrate hexahydrate,
(Co(NO$_3$)$_2$.6H$_2$O) (Thomas baker, Marine Drive, Mumbai, India, Analytical Reagent Grade), Ammonia (Runa Chemicals, Dombivali, Mumbai, India, Laboratory Reagent grade), 1-methylimidazole, 1-Bromoethane 2-chloroethanol (Spectrochem Ltd., Kalbadevi, Mumbai, India), while solvents used acetone, ethyl acetate, n-hexane, AR grade were purchased.

5.2.2 Synthesis of Co$_3$O$_4$ Thin Film

The formation of the cobalt oxide (Co$_3$O$_4$) thin film by simple sol-gel reflux method involves the addition of ammoniato the 0.1M cobalt precursor solution with constant stirring and pH was adjusted to ~12. The reaction mixture was refluxed at 80°C in round bottom flask by keeping stainless steel substrate in it. Prior to deposition SS substrate polished zero grade polish paper. On the stainless substrate the uniform, crack free deposition of cobalt hydroxide (Co(OH)$_2$) was obtained within 2 hours. It was then annealed at 500°C for pure Co$_3$O$_4$.

5.2.3 [HEMIM][Cl] Ionic Liquid Synthesis

In a typical synthesis a starting chemical 1-methylimidazole was taken in round bottom flask. To this imidazolium, 2-chloroethanol was added in excess. The whole mixture was allowed to reflux at 150 °C for an estimate time of the 48 hr. The liquid phase was maintained by the use of the acetone as solvent. After reflux the mixture was allowed to cool down. This resulted in the observation of the two separate layers in the flask. Then the solvent layer was discarded. The remaining component in the flask is nothing but the expected ionic liquid [HEMIM][Cl]. This product was then washed with the ethyl acetate for three times by using the quantity of ten milliliters each. In the later stage the same product was again washed with the other solvent n-hexane. The whole product was then kept in vacuum at low pressure for the purpose of the drying. The formation of the ionic liquid [HEMIM][Cl] was then confirmed by the characterization using proton magnetic resonance spectroscopy instrument.
1HNMR Data for [HEMIM][Cl] IL

Structure of the synthesized IL is confirmed by NMR.

The obtained 1HNMR data is as follows,

$^1$HNMR [HEMIM][Cl] (DMSO, 300 MHz): $\delta$ (ppm)=2.50 (2H, s), 3.85 (2H, s), 4.21 – 4.23 (2H, d), 5.28 – 5.34 (1H, d), 7.70 (1H, s), 7.74 (1H, s), 9.20 (1H, s)

5.2.4 Synthesis of [EMIM][Br] Ionic Liquid

In the 1-methyl-3-ethylimidazolium bromide ionic liquid synthesis, the starting material taken was methyl derivative of the imidazolium, 1-methylimidazole. It was taken on the round bottom flask. To this imidazolium derivative, 1-bromoethane was added in equimolar concentration. The whole mixture was then refluxed at 65-70°C for 48 h. The solvent used during reflux was acetone. After the reflux was over, the reaction mixture was allowed to remain as it is for some time. The two separate layers are the result of the above steps which are formed. The solvent layer of the acetone was then removed. The remaining component was the ionic liquid, 1-methyl-3-ethylimidazolium bromide. This crude product was then washed by the solvent ethyl acetate to get the purified ionic liquid. The washed product was again treated with another solvent n-hexane to remove all the impurities in the ionic liquid. After drying in the vacuum under reduced pressure the ionic liquid was ready to use in further applications. For the detailed characterization and confirmation of the structure of the ionic liquid, the proton nuclear magnetic resonance spectroscopy was employed.
1-methyl imidazole + Bromoethane $\xrightarrow{\text{Acetone}}$ Reflux 48 h $\rightarrow$ [EMIm][Br]

**Scheme 1** Synthesis of [EMIM][Br]

1HNMR Data for [EMIM][Br] IL

Structure of the synthesized IL is confirmed by NMR.

The obtained $^1$HNMR data is as follows,

$^1$HNMR [EMIM][Br] (DMSO, 300 MHz): $\delta$ (ppm)=1.37–1.42 (3H, t), 3.84 (3H, s), 4.15–4.22 (2H, q), 7.60–7.65 (1H, t), 7.73–7.74 (1H, t), 9.08 (1H, s)

5.2.5 Characterization Techniques

The powder X-ray diffraction (XRD, X’pert Pro) using Cu Kα radiation was employed for the determination of the crystal structure of the Co$_3$O$_4$. The scanning electron microscope with the field emission add on (S-4700, Hitachi) was used for the morphological investigation of the deposited cobalt oxide film. The aluminium Kα radiation ($h\nu=1486.6$eV) was used as an X-ray source in the characterization of the surface chemical state of Co$_3$O$_4$ thin films. The technique used is X-ray photoelectron spectroscopy (HRXPS, VG Multilab 2000, Thermo VG Scientific and UK) and the system temperature was room temperature. The normalization with respect to the C1s peak at 285.0 eV was used for the correction of the energy spectra. For the electrochemical studies the electrolytic bath containing three electrode system was used. All the observations were recorded at the ambient temperature. The deposited cobalt oxide was acting as the working electrode. The reference electrode was the saturated calomel electrode (SCE). The carbon in the form of the graphite was used as the counter electrode. The interesting part of this study is that, we were employed the 0.1M [HEMIM][Cl] and [EMIM][Br] ionic liquids as the electrolytes. The supercapacitance properties of the Co$_3$O$_4$ electrode was studied by applying various techniques as Cyclic Voltammetry (CV), Galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) at Metrohms AUTOLAB 32 FRA module.
5.3 RESULTS AND DISCUSSION

5.3.1 Formation of Film and Reaction Mechanism

In the present case, Co$_3$O$_4$ thin film was deposited on SS substrates. The 0.1M Co(No$_3$)$_2$. 6H$_2$O solution was used as source of cobalt. This is a starting material for the synthesis. In the conversion of the cobalt nitrate to cobalt hydroxide the basic medium is necessary. To maintain the basic medium diluted ammonia was drop wise added to the starting solution. Throughout the addition of the ammonia the arrangement is made to stir the whole solution constantly. The formation of cobalt hydroxide needs the situation of the saturation at basic condition. The ions such as the cobalt in plus two oxidation state and the negatively charged hydroxide ions will be at the maximum possible level. This situation is achieved by the addition of the ammonia in the cobalt nitrate solution. This proceeds to the Co(OH)$_2$ nuclei formation and starts the formation of the precipitate of Co(OH)$_2$ at pH-9. The following reactions can be represented as below;

$$NH_3 + HOH(aq) \rightarrow NH^+(aq) + OH^-(aq) \quad \ldots(5.1)$$

$$Ca(NO)_3(aq) + 2OH^-(aq) \rightarrow Ca(OH)_{2(aq)} + 2NO_2^{-} + 6H_2O(aq) \quad \ldots(5.2)$$

The cobalt ion could be reduced by the excess addition of ammonia. The reduced form of the cobalt produces Co(NH$_3$)$_4^{2+}$ complex ion. The presence of the ammonia in excess quantity increases the pH of the solution at which, this complex containing solution now appears as clear and transparent solution.

Following reaction represents the reaction mechanism,

$$Co(OH)_2 + 4NH^+_4 \rightarrow Co(NH_3)_4^{2+} + 2H_2O + 2H^+ \quad \ldots(5.3)$$

By maintaining the room temperature the so produced Co(NH$_3$)$_4^{2+}$ complex ion was stirred for several minutes. The reflux was done at the temperature of the 178 $^0$ for 2hon the whole solution. The attractive forces as cohesive forces as well as vander Walls forces are responsible for the deposition of the Co(OH)$_2$ complex on the surface of substrate stainless steel.
In the mechanism deposition there is also a role of the chemical bonds. Then the Co(OH)$_2$ was annealed at 500°C to get Co$_3$O$_4$ in pure form.

$$\text{Co(OH)}_2 + O_2 \xrightarrow{500\degree C} \text{Co}_3\text{O}_4$$  \hspace{1cm} (5.4)

### 5.3.2 X-ray Diffraction Pattern (XRD)

Structural properties of Co$_3$O$_4$ thin film annealed at 500°C were analyzed at the 2$\theta$ angle in the range of 15–80° by using XRD. The XRD spectrum of the Co$_3$O$_4$ thin film deposited on SS substrates is shown in the Fig. 5.1. It showed that Co$_3$O$_4$ with cubic crystal structure (JCPDS card number-01-074-1656). The stainless steel substrate also shows the three diffraction peaks in the XRD spectrum. The major diffraction peaks occur at angles 2$\theta$ of 19.04°, 31.34°, 36.93°, 38.64°, 44.92°, 55.79°, 59.51° and 65.40° are assigned to the (111), (220), (311), (222), (400), (422), (511) and (440) planes of the Co$_3$O$_4$ crystal lattice, respectively. No peaks of other Co$_3$O$_4$ phases occur. The Scherer formula was for calculation of the crystallite size;

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (5.5)

In the equation 5.5 the crystallite size is indicated by D, the full width at half maxima is $\beta$, the wavelength of the X-ray used is $\lambda$ and the angle of the diffraction is $\theta$. It is found to be 10 nm.
Fig. 5.1 XRD pattern of Co$_3$O$_4$

5.3.3 Scanning electron Microscopy (SEM)
For the study of the surface morphology of the Co\textsubscript{3}O\textsubscript{4} thin film deposited by the sol-gel reflux method, the scanning electron microscopy instrumentation was used. The SEM images of Co\textsubscript{3}O\textsubscript{4} thin film are shown in the Fig. 5.2. The formation of the nanocrystalline micro grains with clusters is confirmed from the SEM image. It looks like porous in nature. The average range of cobalt oxide grains was observed to be 40-45 nm. It is inferred from the SEM studies that the observed morphology of surface indicating the nanoparticles is present in the deposited material. For supercapacitor applications such morphology with the higher surface area favours for better capacitance ability.
Fig. 5.2 SEM image of Co$_3$O$_4$

5.3.4 XPS Spectrum of Co$_3$O$_4$
A reliable method for investigating the detailed information on the electronic structure in the surface of the thin film is the X-ray photoelectron spectroscopy (XPS). The presence of cobalt, oxygen and carbon is confirmed by the XPS study of cobalt oxide, is observed over a wide binding energy region in the spectrum. The presence of elemental carbon is seen from the presence of the peak at 284.59 eV signal [230]. The C(ls) photoelectron peak (285 eV) has been used as an energy reference. The photoelectron peaks C(ls), O(ls), Co(2p\textsubscript{1/2}) and Co(2p\textsubscript{3/2}) have been recorded.

![Fig. 5.3 XPS spectrum of Co\textsubscript{3}O\textsubscript{4}](image)

The airannealed Co\textsubscript{3}O\textsubscript{4} thin film annealed was used for the study of the XPS spectrum and the observed spectrum is as seen in the Fig. 5.3. The cobalt oxide material phase is stable in
the nature and there is the presence of the compound $[\text{Co}^{2+}\text{Co}_2^{3+}\text{O}_4]$ with mixed valence. This is the composition of the $\text{Co}_3\text{O}_4$ stable phase and has indicates the spinel structure. There is also existence of the XPS spectrum for the Co $2p_{3/2}$ and Co $2p_{1/2}$ electrons. The XPS binding energy peak centered at 794.79 eV is of Co $2p_{1/2}$. And the XPS binding energy peak at 779.77 eV is of the $2p_{3/2}$. These peaks are called as the is spin-orbit peaks as shown in the Fig. 5.4 [231].

Fig. 5.4 Core level spectrum of cobalt atom
Fig. 5.5 core level spectrum of oxygen atom
The peak at the binding energies of 530.1±0.1eV is of the O1s and can be assigned to oxygen in Co–O bond in Fig. 5.5. Moreover, weak shake-up satellites peak occurs centered at 790.5 and 805.6eV from the main bands.

5.3.5 Cyclic Voltammetry (CV) Study

In the study of the measurements of the electrochemical parameter are done by using the different electrodes in one system. These three electrodes are of the three different materials. The electrode on which the reaction of the interest is expected is made of the cobalt oxide material deposited on the substrate. The electrode of which the potential is very finely maintained is the saturated calomel electrode, which has the task to be used in reference measurement to other electrodes in the system used as a reference for measurement by other electrodes. There is the possibility of the parallel reaction those may take place in addition to the expected reaction in the bath.

To take the cognizance of such additional reactions the system called as the counter electrode is used, which is normally made up of the carbon. By maintaining the room temperature the study of the cyclic voltammetry was performed at the room temperature. The electrode system containing the three electrodes was demonstrated that the synthesized cobalt oxide material has potential of the supercapacitance behavior, which is confirmed by the and Galvanostatic charge–discharge (GCD) and Cyclic Voltammetry (CV) studies. For checking the capacitance ability of the deposited cobalt oxide material the electrochemical impedance spectroscopy (EIS) study was also supported. In this study the electrolytes used were the synthesized ionic liquids [HEMIM][Cl] and [EMIM][Br] prepared at the concentration of the 0.1molar.

The behavior of the electrode materials capacitiveis studied by the important technique as CV. At the different scan rates CV curves of the Co$_3$O$_4$ electrode in 0.1M [HEMIM][Cl] and [EMIM][Br] ILs were observed as shown in the Fig. 5.6. The cobalt oxide electrode has shown the pseudocapacitive behavior. This is indicated by the reduction and oxidation reactions and reflected in the broad peaks in the CV curves. There are this type of two peaks are present. However the ideal rectangular shape is not observed for the peaks obtained due to the reduction
and oxidation. The pseudocapacitive behavior of the Co$_3$O$_4$ electrode is indicated by the deviation in the CV curves.

The cathodic sweeps is observed from the curves and the not entirely symmetric anodic sweeps of CV curves are each other. The kinetic irreversibility in the reduction and oxidation reactions may be because of the faradaic process polarization and ohmic resistance [232]. The fast charge and discharge signals are due to the increasing scan rate and represented by the increase in current also.
Fig. 5.6 Cyclic Voltammetry (CV) of Co$_3$O$_4$ in [EMIM][Br]
The specific capacitance decreases as the scan rate increases show in Fig. 5.7 and Fig. 5.8. If the electrolyte ions in and the surface of the host material are allowed enough time for the interaction, and then there is possibility of the entry of the ions into the host material. This happens in case of the cobalt oxide material facilitating the availability of the active surface taking part in the reactions of the electrode material [233].
Fig. 5.8 Specific capacitance versus scan rate of Co$_3$O$_4$ in [EMIM][Br] and [HEMIM][Cl] ILs

5.3.6 Galvanostatic Charge-Discharge (GCD) Study
Fig.5.9 shows the GCD curves of the Co$_3$O$_4$ electrode in at galvanostatic current densities of 1 mA/cm$^2$ in 0.1M [HEMIM][Cl] and [EMIM][Br]ILs. A good symmetry is maintained in the charge-discharge process. There is a sudden The potential drops fast and then the decay in the potential in the discharge curve is observed.

The incremental voltage drop is shown by the activity of the initiation of the potential drop. This is result of the resistance shown by the material nature. The corresponding behavior of the domination of faradaic reduction and oxidation reactions with the CV test is the next decay in the potential. The good capacitive and reversible behavior of Co$_3$O$_4$ is confirmed by the symmetric nature of charge-discharge curves.
5.3.7 Study of the electrochemical Impedance (EIS)

Information about kinetic features of the ions and electrode-electrolyte interface electron in the electrode are attained from EIS spectra. Fig. 5.10 shows the Nyquist plots of Co$_3$O$_4$ thin film electrode in 0.1M [HEMIM][Cl] and [EMIM][Br]
ILselectrolytes. The intrinsic resistance of substratecurrent collector, contact resistance between the active material and electrolyteionic resistance of are the three types of the resistances which are shown by the system. The results in the intercept $Z'$ at real part of the combination thee resistances the resistances in the high frequency range.

The double-layer capacitance in combination of the charge-transfer resistance caused by faradaic reactions and on the grain surface layer is shown by the semicircle in the region of high frequency. Lower the resistance value for the charge-transfer, higher the specific capacitance of the electrode. Lowest charge-transfer resistance is shown by Co$_3$O$_4$ electrode in the electrolyte [EMIM][Br] ionic liquid. Whereas the in the case of the [HEMIM][Cl] ionic liquid electrolyte slightly higher resistance. The charge-transfer resistance, the electroactive surface area is responsible for. In the surface of the electrode and the electrolyte and to the the ionic diffusion / transport is indicated by a straight line at low frequency region[233, 234].
Overall the importance of the oxide of the cobalt was traced in this chapter. It is discussed in terms of the chemistry of the cobalt oxide. The oxidation states variability was the point of the concern towards the applicability of the cobalt oxide for the energy storage application. The various possible structural types of the cobalt oxide structure are also focused. And among the various types of the structures the spinel type are found to be very effective. The chemistry of the
thin film formation is also discussed well. There are large number of the materials are available for the purpose of the use in the deposition of the material so called as the substrates. Though there are many materials available, the selection of the stainless steel was done in this study. Purposefully the choice of the nitrate compounds of the cobalt was done as the initial chemical in the formation of the deposition of the film. The water solution of the ammonia was used for facilitation of the pH between seven to twelve that is higher than the acidic one. There was very good observation that the evolution of the aqueous solution of the starting chemical was fixed on the surface of the solid material. Now by this way the formation of the film has taken place. For the growth of the material film on the sold use of the method called as the sol gel was done effectively.

The next job as far as the application studies of the synthesized films was taken in consideration. The main aim was to why not make use of the thin films of the cobalt oxide for the specific application. Although there are many applications of such type of the material. But as per the objective the films were applied for their response in the energy storage mechanism. And in this application the synthesized material will act as the electrode. As per vast studies so far by scientists across the world, in the energy storage, it is very necessary to have the some solution so called as the ions containing liquid which when allowed to have contact with the current undergoes the decomposition and very precisely nowa day’s called as the electrolyte. If one looks at the large array of chemicals available, many are useful as the electrolytes. But the big problem is that the amongst these chemicals many gives excellent results towards their applications in variety of the energy applications, at the same time cause unrecoverable damage to the environment. This damage may be because of the corrosive nature of the chemical in use. There are also certain other reasons including the addition of the pollutant in the environment.

Thus what is reported here in this chapter is, instead of the use of the non-friendly chemicals why not use the friendly chemicals with respect to the environment etc. Thus, if we look towards the large number of the chemicals available and synthesized in the various laboratories worldwide, the chemicals of the specific type which are so called as the ionic liquids are playing the crucial role. These organic chemicals are supposed to be very useful as far as their potential application level in the large number of the mechanisms in various fields. Thus, as a wise decision the selection of the imidazolium containing ionic liquids were synthesized.
Certainly the all possible study for the characterization of these chemicals was carried out using the sophisticated technique. Before the application of the electrode in the ionic liquid, it was heated at about seven hundred twenty three degree celsius temperature, to produce the expected structural parameters useful for the good performance.

About the electrolytes much is discussed here. The possible reaction path for the synthesis of the expected chemical which in turn will act as the electrolyte was designed. AS per the defined protocol the derivative of the imidazolium was selected and allowed it to react with the ethyl alcohol derivatised with the chlorine atom. As this reaction was not possible at the temperature of the ambient atmosphere. It was decided to make use of the higher temperature of about one hundred fifty degree celsius. This reaction mechanism was involving the reflux for few hours. Thus to maintain the liquid state for the reactants the other chemical called as the neutral one and is nothing but the acetone was added the flask of the reaction. Once it is confirmed that the reaction is over the acetone was taken out and the product of interest that is the ionic liquid was used further. As a trial and to elaborate the study to involve some other ILs, instead of the chlorine derivative of the one of the initial chemical was chosen and allowed to react in similar manner to produce bromide IL.