There is huge demand for the energy producing mechanisms in the present situation of the enormous increase in the development activities across the world. It is true that, there is large number of the methods currently in practice including the thermal power plants, fuel energy, hydrothermal energy, etc. These sources of the energy though are of much importance, more or less causes the unwanted effects on the environment. The effects may be green house gases, pollution of the particulate matters. The nuclear energy is another option, which is supposed to deliver the requirement at the cost of the less environmental impact as compared to the traditional way of producing energy. The solar energy devices are among the important sources of the energy harvesting. This source is environmental friendly and could be projected as the sources of the wide utility all over the world. Now a day’s large number of countries are making use of the solar energy option for getting the electrical energy. However, still this technology of obtaining the electrical energy from the energy of solar type is in need of the research and development with respect to the best material.
On one hand the entire global population is looking for the generation of the energy especially the electrical energy, and fortunately the scientists and technologists have come with the great inventions for the production of the energy. It is true that all of sudden there is no need of the whole amount of the electrical energy produced. There is also the limitations in the use of the existing natural sources for the energy generation. Thus, the researchers and the technologists are looking for the methods of the energy production from renewable sources. But the limitation of the renewable energy sources are, they could not be constantly accessed throughout the year. There it becomes necessary to come up with the technology for the storage of the energy. Thus, one has to think over the mechanism by which we can store the energy for use in future applications, when needed. Right now, there are many solutions available for the choosing them for the storage of the energy, but these solutions need to be selected by considering many points such as environmental and the technical.

The fuel cell batteries and the supercapacitors are at the forefront among the systems available. When one compares the batteries and supercapacitors, then the preference now a days is given to the supercapacitors. The cheap and profound availability of the materials for the supercapacitors, is the main reason for the priority to the supercapacitors in energy storage systems. In addition there are great invention to prepare the supercapacitor devices which will not cause any harm to the environment. In spite of the excellent supercapacitive behavior including the cycle life and electrochemical stability. There are major two types of the mechanisms by which the supercapacitor stores the energy. These categories are dependent upon the reduction and oxidation mechanism which allows the freedom for transport of the ions called as the pseudocapacitors. And the energy storage other type of the device in the supercapacitor category takes the help of the interface interaction between the electrolyte and electrode called as the electrochemical double layer capacitors. The get rid of the fear of the situation that the fossil fuel on this earth is going to vanish with time period because of its excessive use for the purpose of the energy. And thus now in this world there almost all countries and labs are running behind the invention of the technology called as the renewable energy technology. The areas of the interest in this concern are the fabrication of the fuel cells, batteries, supercapacitors, and the solar cells. The supercapacitors are comparatively more preferred because those involve the electrochemical mechanism. These materials can deliver the
energy very quickly. Although there are many advantages of the supercapacitors, there is still the need of the inventions for the excellent material for the supercapacitors. The properties expected from the material to be used for this purpose must be capable of the things as good conductor and the good power density and the storage mechanism. While doing so the material selected must not harm the environment. Thus the transition metals which are supposed to be adherent with the requirement for the good electrode are at the forefront. In addition to the electrode material the component which is equally important in the supercapacitor study is the electrolyte. There are several options of the chemicals which could be used as the electrolyte. But, by concerning the various factors as environmental friendliness. The choice of the ionic liquid for this purpose is important. In case of the ionic liquids the ionic liquids which will work at the normal working conditions are called as the room temperature ionic liquids. These are at the top priority among the many types of the ionic liquids. Again there are many classes of the ionic liquids based on the functional groups present. The imidazolium based are comparatively good to be used as the electrolyte.

In our study we have focused on the pseudocapacitors mechanism by using the excellent electrode material as cobalt oxide with different morphologies. And also we have selected the electrolyte which are comparatively more suitable in the task to protect the environment especially the green organic chemicals in ionic liquid category.

6.1.2 Chapter 3 Summary

In the chapter number three syntheses of the cobalt oxide nanotubes is discussed in detail. The cobalt oxide is used as the electrode material in the supercapacitor studies. The method used of the synthesis of this electrode material isthe sol-gel deposition method. This method was little modified and the addition of the reflux mechanism was done. The substrate used is the stainless steel. The precursors chosen were of the analytical grade with respect to the purity of them. The chemical used as precursor was the Co(NO\(_3\))\(_2\).6H\(_2\)O and the NH\(_3\) was used for the complex formation in the procedure at basic pH. It is reported that the desired film formation takes place within about two hours of the time. To get the useful characteristics and the probable applications the synthesized films were annealed at the high temperature of 500 °C. Thereafter in the presence of the potassium hydroxide electrolyte the cobalt oxide electrode material was used
for the supercapacitance studies. The synthesized electrode material was characterized for various properties including the techniques as XRD, SEM, GCD, CV, EIS etc.

The formation of the cobalt oxide mechanism in detail is discussed, in which various reactions were taken into account. Initially the reaction of the precursor of cobalt, cobalt nitrate hexahydrate was reacted under controlled conditions with complexing agent ammonia to get the synthesis of the cobalt hydroxide at pH 9. The cobalt oxide on further addition of the ammonia is converted to the cobalt ammine for a while. The so synthesized cobalt hydroxide was then deposited by sol-gel method on stainless steel surface. Before the characterization of the deposited material it was annealed for about 500 °C to obtain the desired form of oxide cobalt oxide. For the confirmation of the structural nature of the cobalt oxide deposited material, by keeping the angle of between 20-80° as theta the technique used was the x-ray diffraction. And this was maintained throughout in this study. The x-ray diffraction study revealed the high purity material and the face centered cubic type structure which was inferred from the observations of the prominent peaks in the x-ray spectra.

The crystallite size is one of the important parameter for understanding the ability of the material to show the capacitance properties. The Debye-Scherrer’s formula was used in this chapter for the crystallite size of the Co$_3$O$_4$ was ascertained by and it is found to be 45 nm.

For obtaining the information of the surface properties as the surface shape the sophisticated technique employed was Microscopy Scanning Electron. The images obtained from the Microscopy Scanning Electron revealed the nanotubes like structure as the morphology of the cobalt oxide thin films. This morphology is responsible for the high surface area useful for better supercapacitance properties. The cobalt oxide nanotube are having the length of in the range of 250-300 nm. This morphology is responsible for the maximum interactions with the electrode of

The Co$_3$O$_4$ electrode was checked for the electrochemical properties and ascertained by the cyclic electrolyte ions including the hydroxides useful for the supercapacitance properties voltammetry studies. For this this study the KOH was used as the electrode, which indicated the potential window in the range from minus point five to +0.5 V/SCE. The cyclic voltammetry is the result of the redox reactions those takes place in the electrode/electrolyte system of cobalt oxide and the KOH, which led to the different scan rates. The redox peaks are
observed while scanning. There is the reaction of the cobalt oxide and the cobalt hydroxide system, there is the reaction of hydroxide ions with the cobalt oxide, resulting in the cobalt oxy hydroxide formation, and the electrons are liberated. These redox reactions are responsible for the capacitance observation. It is observed that there is regular increment in the current when the potential is applied for the supercapacitive behavior. The Co$_3$O$_4$ has shown the specific capacitance of 125.7 F/g at the scan rate of 20mV/s.

The possibility of the application of the cobalt oxide electrode material in the supercapacitor is tested by the galvonostatic charge – discharge study by maintaining the current at 2 mAcm$^{-2}$ in the presence of the electrolyte potassium hydroxide. It is observed that the electrode material cobalt oxide shows the large specific capacitance indicating its usefulness in the supercapacitors systems for high-performance. The discharge curve in the study is indicator of the relationship of the electrode the material with the potential. The morphology of the cobalt oxide also helps for the fast adsorption/desorption processes. The electron impedance spectroscopy study was carried out for the understanding of the supercapacitive bahaviour of the electrode material. By the implementation of this technique a Nyquist plot for the cobalt oxide could be generated and the observation of the slightly deviation towards the lower side tells us about the charge-transfer and diffusion resistance which are lowered. From the plot of the observations it is inferred that the point of the intersection the real axis is caused due to the linear component at low-frequency.

### 6.1.3 Chapter 3 Conclusions

- The sol gel technique is proved to be the most useful technique for the thin film synthesis.
- The various morphologies are possible to produce by optimizing the preparative parameters of the synthesis.
- The morphology obtained for the electrode material of our interest that is the cobalt oxide thin film was nanotube morphology.
- For better characteristic properties of the electrode material there is need of the removal of the volatile materials produced because of the ide reactions and also carried as it is
from the precursor chemicals. The to get rid of the these unwanted chemicals and also the interference caused due to this, the process of the heating the prepared sample thin film at the high temperature that Is the annealing is necessary. Here it is concluded that the annealing temperature of the 773 K is optimum.

To check the ability of the thin film electrode cobalt oxide nanotube material, the various characterisations needed to be carried out.

The cubic crystal structure of $\text{Co}_3\text{O}_4$ was confirmed by the application of the characterization technique X-ray diffraction. The X-ray diffraction is an excellent tool for the crystal structure determination.

The nanotube like morphology was confirmed by the implementation of the sophisticated microscopic technique called as the scanning electron microscopy.

The scanning electron microscopy images obtained revealed that nanotubes possess the 250-300 nm length, making available the maximum surface area, which is the requirement for the better supercapacitance.

The supercapacitance properties that is the behavior the cobalt oxide electrode material towards the electrochemical response is verified by keeping it for cyclic voltammetry studies. From this study which was also supported by the be concluded that galvanostatic charge-discharge observations it could the stability of the cycles of the capacitance are promising.

The conclusion about the consideration of the nanotube like cobalt oxide electrode material for the supercapacitors is done by the electrochemical impedance spectroscopy study.

Finally the thin film of the nanotube like morphology of the cobalt oxide in presence of the potassium hydroxide electrolyte has shown the maximum specific capacitance 125.7 Fg-1 at scan rate 20mV s$^{-1}$.

6.1.4 Chapter 4 Summary

The chapter number four is dedicated to the synthesis of the cobalt oxide, the application of the cobalt oxide as electrode in the supercapacitor. This chapter is also devoted to the synthesis of the new electrolyte namely the organic compound 1-butyl-3-methylimidazolium
tetrafluoroborate which is ionic liquid and its successful application as the electrolyte in the supercapacitor. In the synthesis of the cobalt oxide
the precursor chemical cobalt nitrate hexahydrate used was of the commercial grade and was applied as received without further purification. The other chemical used were including the strong basic solution called as the ammonia. The water solution of the cobalt nitrate hexahydrate was taken and reacted with the 28% water solution of ammonia to produce the complex of the cobalt and the ammonia. The solution of the cobalt oxide was then deposited on the zero grade polished stainless steel substrate. The formation of the well adhered film of the cobalt oxide with the physical properties as the uniform spread was resulted because of the deposition, with no cracks and is well adhered thin film of the electrode material.

In the synthesis of the methylimidazolium Tetrafluoroborate derivative with butyl functional molecule ionic liquid was done by taking the starting chemicals as 1-methylimidazole and 1-chlorobutane and in addition the other chemical required was the sodium tetrafluoroborate. The acetone, ethyl acetate, n-hexane and dichloromethane were used as solvents in the ionic liquid synthesis of. The synthesized ionic liquid is demonstrated as the efficient electrolyte for the supercapacitor studies. The ionic liquid so produced was applied in the form of the crystals and to get crystals the seeding was done by the addition of the chloride salt of the 1-butyl-3-methylimidazolium in the form of the crystals. The so produced compound is called as the imidazolium salt. Before the application of the ionic liquid in the supercapacitor system it was characterized for confirmation of the functional groups.

This chapter is also dedicated to the detailed studies of the electrode material for its nature and suitability as the material for supercapacitor application. The cobalt oxide obtained by this method of synthesis was of the nanostructured type. Especially the morphology of the cobalt oxide was the nanorod type.

The synthesis of the Co₃O₄ nanostructured material involved the water solution of ammonia addition to the metal precursor solution to produce the hydroxide of the cobalt. For further mechanism of formation the little excess of the ammonia was preferred to dissolve the intermittent precipitate of the cobalt hydroxide. Here the cobalt in the +3 oxidation state is reduced to the +2 oxidation state because of the interaction of the ammonia which provided the
highly basic situation. The surface of the stainless steel substrate is deposited with cobalt oxide which is well discussed, wherein the clear solution of the cobalt hydroxide with constant stirring at the room temperature followed by reflux heating at elevated temperature for couple of hours by dipping the substrate in it. This facilitated the deposition of the electrode material on the clean stainless steel surface in the form of the cobalt hydroxide. It is discussed well in this chapter as the synthesized material may be accompanied by the some other chemicals and thus before the characterization of the cobalt oxide thin film it was annealed at the 500 °C temperature to produce the pure form of the cobalt oxide.

During annealing the though the pure form of the electrode material was expected, then also to check the thermal stability of the material, it was characterized by the thermo gravimetric technique in air atmosphere by varying the temperature upto 1000 °C with the increments of ten degrees per minute. It is reported that the conversion of the cobalt hydroxide to cobalt oxide passes through the dehydration step upto the temperature range of 234 °C followed by the spinel Co$_3$O$_4$ formation at the cost of the total decomposition at around the 935 °C. At this high temperature the conversion of the cobalt oxide to CoO takes place.

The structural characterization of the cobalt oxide electrode material was done by using the X-diffraction technique in the in the 20 range of 10-80° angle. The observed are reported to be compared with the standards available in the form of the reference JCPDS cards. The scanning electron microscopy studies has given the morphological peculiarities. The images obtained by the scanning electron microscopy are observed to be of the nanorod type and also having good fixing with the substrate surface. It is predicted that the free transfer of the ions in the electrochemical studies is because of surface area made available by the nanorod morphology responsible for the excellent supercapacitor behavior.

Followed by the characterization, the thin films of the cobalt oxide were subjected to the electrochemical studies using the cyclic voltammetry equipment using the three electrode system including saturated calomel electrode as counter electrode and the graphite the reference respectively. It is well demonstrated that in the environment of the 1-butyl-3-methylimidazolium tetrafluoroborate electrolyte the performance observed was good, indicated by the voltage
window of the expected range. This observation of the cyclic voltammetry study was reported to supported by the galvanostatic charge and discharge study. For more precise discussion on the supercapacitance ability of the cobalt oxide electrode material, the sophisticated technique of the electrochemical impedance spectroscopy was implemented. This technique supported the availability of the large surface area as well as the pore size for the allowing the diffusion of the ions in the deep part of the material thereby improving the capacitance.

6.1.5 Chapter 4 Conclusion

For the electrochemical supercapacitor behavior of the cobalt oxide nanorods of the spine type the reflux modified sol-gel method prepared and deposited on the ultra-cleaned stainless steel substrate is successfully demonstrated in presence of the electrolyte environment of the tetrafluoroborate ionic liquid 1-butyl-3-methylimidazolium. The electrochemical system was reported to shown the maximum specific capacitance 70 Fg⁻¹ at the electrolyte BMIMBF₄ by maintaining the optimum concentration and the at 20 mVs⁻¹ scan rate.

6.1.6 Chapter 5 Summary

The chapter number five is devoted to the detailed explanation of the synthesis of the spinel cobalt oxide thin films prepared from the starting materials of the nitrate complex of the cobalt with water of dehydration along with the aqueous solution of the NH₃. By considering the environmental friendly approach the green electrolytes like the ionic liquid based on the imidazolium moiety was employed as the electrolyte in the electrochemical studies. It was demonstrated that the synthesis of the pure form of the large surface area cobalt oxide is possible by using the sol-gel technique and in this specifically the high basic pH is required to be maintained. The substrate employed was the stainless steel. By following the usual procedures of the cleaning of the deposited thin film the last treatment given was the heating at about 723 K to obtain the clearly formed cobalt oxide useful for the supercapacitor studies as an electrode material.

In this chapter the major attention is given on the synthesis and the application of the green electrolyte as the ionic liquid [HEMIM][Cl]. Especially in this synthesis the as procured
chemicals imidazolium and 2-chloroethanol were allowed to react with the methylimidazole at the reflux temperature of the 150°C in presence of the acetone as solvent. Followed by which the separation of the desired product from solvent was achieved. The characterization form the functional groups and the other properties leading to the confirmation of the ionic liquid were reported to be carried out. These characterization techniques included the nuclear magnetic resonance spectroscopy technique. From the peaks in the nuclear spectra it was inferred that the product obtained was the pure form of the ionic liquid [HEMIM][Cl]. The another ionic liquid, 1-methyl-3-ethylimidazolum bromide, which was equivalently demonstrated as the good electrolyte was prepared in the same way but by choosing the different molecules as the 1-bromoethane and the rest of the chemicals were those used in the synthesis of the earlier reported ionic liquid in this topic.

Thesuitability of the cobalt oxide electrode material for the supercapacitance study was confirmed by heavily characterizing the synthesized material after annealing. In the effort to understand the crystal structure of the cobalt oxide thin film the X-ray diffraction method was very effectively used, especially facilitated with the copper source. In this chapter it is discussed that the thin film annealed at the temperature of about 500°C was subjected to the XRD instrumentation at the range of the 15–80° angle of the 2θ. Very interestingly the morphology of the annealed electrolyte material was satisfying the cubic crystal structure properties when compared with the standards available internationally. And very important is the size of the crystals as the ten nanometer.

The porous nature of the surface of the cobalt oxide cubic structured material was verified by the implementation of the very decent technique as the microscopyscanning electron. The of the cobalt oxide thin film morphology surface nanocrystalline in nature and undoubtedly it was porous in nature with the size of the particles as the 40-45 nm which was indicated by the scanning electron microscopy results. Thus, this investigation as discussed in this chapter is supportive toward the possible applications of the synthesized electrolyte in supercapacitor applications for good capacitance. The good capacitance was due to the factors as the free movement of the ion and the electrons. For this the in detail information of the electronic situation is required of the material. The X-ray
photoelectron spectroscopy is the better instrumentation for this purpose. The amount and the configuration of the atom present as cobalt, oxygen and carbon is elucidated by the XPS study by using the binding energies of the atoms.

The applicability of the nanostructured cobalt oxide material is reported to be confirmed by the application of the techniques as the galvanostatic charge–discharge cyclic voltammetry. By using the various concentrations of the electrolytes and varying the scan rates the CV measurements are done. This study indicated the pseudocapacitive behavior of the cobalt oxide electrode that is there is an indication of the redox reactions. To support these inferences the galvanostatic charge-discharge studies were reported to be carried out in the atmosphere of the [HEMIM][Cl] and [EMIM][Br]ILs electrolytes at one mA.cm\(^{-2}\) current densities. The electrochemical impedance spectroscopy was electrode/electrolyte interface impact employed to study the on the capacitance.

**6.1.7 Chapter 5 Conclusion**

The work presented in the chapter number five is an excellent demonstration of the usability of the sol-gel synthesized nanostructured cobalt oxide deposition the stainless steel substrate for the electrochemical applications. The sol-gel technique has facilitated the formation of the desired morphology with greater surface area and also pore size. These properties are extremely useful for the supercapacitance. The morphology and the crystal structure and the cobalt oxide material were revealed by the scanning electron microscopy technique and the X-ray diffraction technique respectively.

The description of the various atoms of the materials with respect to the electronic state is confirms the atomic states of oxygen and cobalt. The Cv and GSd data helped to check the excellent behavior of the cobalt oxide towards the supercapacitance in presence of the ionic liquid electrolyte as [EMIM][Br] and [HEMIM][Cl]. The ability of capacitance was also supported by impedance electrochemical spectroscopy. The 32 F/g and 27 farad per gram were the values of the capacitance specific observed respectively in presence of the electrolytes 1-ethyl-3-
methylimidazoliumbromide and 1-(2-hydroxyethyl)-3-methylimidazolium chloride at 10 mV/s scan rate. This was confirmed by the application of the electrochemical impedance spectroscopy.

6.2 RECOMMENDATIONS

There is the observation that the supercapacitors can be used for the long life. The supercapacitors usually do not undergo the wearing process. These devices can show excellent life cycle. The mechanism of the charging of the supercapacitors is quite simple. It is also possible that the once can charge these devices quickly. Very important this is that the materials used in the fabrication of the supercapacitor could be selected which are cheap and available easily. The materials described in this thesis could be prepared very easily. The cobalt metal used has been shown the better performance when used in the form of the oxide form. The electrolyte chosen are the green chemicals and thus could be preferred over the other usual electrolyte materials. These device are very useful to cope up the to reduce the time required need for the charging of any equipment. In many countries there are large scale applications of the supercapacitors for very routine use green chemicals and thus could be preferred over the other usual electrolyte materials.

6.3 FUTURE SCOPE

In the need of the production of the energy from the available resources on this earth crust is about to vanish. The main reason for this the vast growing population of the human being on this planet. This much high number of the peoples on the earth is in need of the enough food, electricity and new amenities. It is evident that, for all these processes the energy is very primarily required. Thus all of us trying to take out the energy from natural sources as fossil fuel. But as it is very well known that the earth is having the limited sources of the fossil fuel. And one day all of us will be striving for the energy. Thus, one can think of the application of the scientific knowledge for the development of the new materials for the generation of the energy. In such cases the target is the energy emitted by the sun. This energy could be made use for many purposes. One of the important things is the conversion of it to the electrical energy. Thus one can opt for the fabrication of the equipments for this energy conversion.
The energy which is eventually prepared by different ways may be in the large quantity. Or it may be in more quantity than required at a particular place. Thus, we are in need of the supporting technology which will be useful for the storage of the energy. Till this date there are many optional equipment for the energy storage. But among those the target equipment is demand are the supercapacitors. On the mechanism two types of the supercapacitors are there based. These are the one which involves the oxidation reduction reactions called as the pseudocapacitors. And the other is the electric double layer capacitor.

The materials for the electrode formation is the topic of the current demanding research over the whole world because these materials are becoming the very useful for the storage of the energy in the specific equipments. For the purpose of the formation of the electrodes, the transition metal compounds are comparatively more preferred. This is because these metals possesses the required properties as thestability towards the chemicals and the heat, have mechanical strength and also good conduction ability. For the preparation of the supercapacitors the metals in the periodic table of the elements are most useful. To the point the transition metals of the first transition series are at the first preference. The metals could also be directly used. But if one prepares the compounds of the transition metals as the oxides or sulphides then it is observed that the performance of the device increases very quantitatively. Thus it is the great choice to go for the transition metals to be used as the electrodes. The other entity which is to be always accompanied with the electrodes is the use of the good electrolyte. The entire mechanism of the supercapacitance depends on the nature of the electrolyte. There are several ideas for the better electrolyte and those include the non corrosive materials for the environment, must be available at the lower cost. Thus, the green nature of the electrolyte material is welcome. And thus the selection of the ionic liquids is good.

6.4 LIMITATIONS OF RESEARCH WORK

It is true that the transition metal compounds are useful for the purpose of the electrode material. But for obtaining these metals in the expected pure form is complicated. The formation of the compounds say for examples the oxides and the sulphides there are methods, but most of the method suffer from some drawback as may be time consuming, lower efficiency. The most
important thing in the material synthesis is the production of the materials with porosity and hollow type interior. These type the formation is tedious, expertise of that kind along with the advanced instrumentation is must. Though the electrolytes as the ionic liquids are green chemicals. The cost of the synthesis is much more. Thus needs to develop friendly methods. The electrolyte ionic liquids has its own limitations as the toxic behavior. The synthesis is also a very tedious job. As the ionic liquids synthesized are always in the lower quantity, it is the another limitation about the availability.