Recently, researchers are diverted their attention towards the preparation of composite/mixed oxide electrodes for electrochemical capacitors and have been extensively demonstrated to improve the performance of ES electrodes, The properties of the pristine Co_3O_4, doped oxide of MnO_2: Co_3O_4 and RuO_2:Co_3O_4 can control some of the process parameters like the ingredients, film thickness, concentration of the solution, deposition time, annealing temperature and deposition scan rates.

Potentiodynamic electrodeposition process is a well-known technique which is easy for the deposition of Co_3O_4, Mixed oxide of MnO_2 : Co_3O_4 and RuO_2 : Co_3O_4 thin films by aqueous route. By using Electrodeposition technique pristine oxide, doped oxides or mixed oxide thin films can be prepared easily with fine control over preparative parameters. In our investigation, it was found that, the preparative parameters of the potentiodynamic electrodeposition technique such as type of ingredient, molar concentration of the ingredients, time for the deposition, deposition scan rate, annealing temperature etc. influence the XRD, SEM, TEM, AFM, elemental and electrochemical characterizations of the prepared cobalt oxide, manganese doped cobalt oxide and ruthenium doped cobalt thin film electrodes of (Mn: Co_3O_4 and Ru: Co_3O_4) using aqueous route by Potentiodynamic Electrodeposition.

The different phases of the present work were carried out in the laboratory is organized in VIII chapters. **Chapter-I** summarized general introduction to supercapacitor and its importance, literature survey regarding cobalt oxide, manganese oxide and manganese doped oxide, ruthenium oxide and ruthenium doped oxide and devices. **Chapter-II** describes the theoretical aspects of supercapacitor. It includes construction of supercapacitor, types of electrode and electrolyte used for the supercapacitor fabrication, types of supercapacitor and equivalent circuit representation for the same. In the last part of the chapter types of supercapacitive device were discussed in detail. **Chapter-III** explains detailed theoretical background of electrodeposition set up along with its three modes of deposition i.e. Potentiodynamic, Potentiostatic and Galvanostatic, thin film preparation using electrodeposition. This chapter is also concerned with different characterization techniques, such as, thickness measurement, X-ray diffraction (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), energy

dispersive analysis (EDAX), surface wettability test, transmission electron microscopy (TEM), SAED and atomic force microscopy (AFM). Last part of this chapter describes supercapacitive techniques such as cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy with equivalent circuit.

Chapter-IV elaborates the effect of ingredients, solution concentration, deposition time, annealing temperature and deposition scan rate on the properties of pristine Co_3O_4 thin films prepared via aqueous media. Prepared Co_3O_4 thin films have been characterized through structural, morphological and electrochemical characterizations. **Chapter-V** explains about the effect of equi molar percentage of manganese incorporation in Co_3O_4 on the properties of MnO_2: Co_3O_4 thin films prepared via aqueous media. Prepared thin films have been characterized through structural, morphological, elemental and electrochemical characterizations. **Chapter-VI** elucidates effect of equi (0.1 M) molar ruthenium incorporated Co_3O_4thin films on the properties of RuO_2: Co_3O_4 thin films prepared via aqueous medium. Prepared thin films have been characterized through structural, morphological, elemental and electrochemical characterizations were studied and their results are discussed well in detail.

Chapter-VII describes about the use of Mn incorporated cobalt oxide electrodes to fabricate symmetric liquid electrolyte device and its supercapacitive performance.

Chapter-IX summaries the results of the work as given below:

Synthesis of Cobalt oxide Thin Films by potentiodynamic Electrodeposition and their Electrochemical characterizations

In the pilot experiment different cobalt sources were used for the deposition of cobalt oxide thin films. All samples (0.1M) were deposited at the deposition scan rate of 100mV/s for 30 min. Prepared samples were annealed at 573 K for 1.5 hours. XRDs of annealed samples revels polycrystalline nature with face centered cubic crystal structure of Co_3O_4. Sample deposited using cobalt ingredient (cobalt chloride hexa hydrate) shows better result as analyzed from XRD, FESEM and cyclic voltammetery. The optimized ingredient (cobalt chloride hexa hydrate) was used to prepare cobalt oxide thin films using

different solution concentrations like 0.05 M to 0.3 M. The deposition scan rate and deposition time was maintained constant at 573 K and 30 min. Prepared samples were annealed at 573 K for 1.5 hour. Film deposited with 0.1 M solution concentration shows better results as analyzed from XRD, FESEM and cyclic voltammetry. The FESEM micrographic images of sample shows agglomeration of grains. Further improvement of optimized concentration (0.1 M) was used for deposition of Co_3O_4 films for different deposition times like 20 min to 60 min. Prepared samples were annealed at 573 K for 1.5 hour. The XRDs of all samples revels polycrystalline nature with good orientation along (400) plane having face centered cubic crystal structure. Film deposited for 30 min showed better results as observed from XRD, FESEM and cyclic voltammetry analysis. In morphological observation, optimized sample shows structural homogeneity and uniformity, which consists of fully covered agglomerated granular particles. Microstructure analysis of the same sample was carried out using AFM and TEM analysis. AFM shows that sample possess rough globular morphology while TEM shows granular agglomerated microstructure of the sample. Wettability test for the same sample shows hydrophilic nature with contact angle 50.1°.

The above optimized conditions were used for depositions of Co_3O_4 films using different annealing temperatures form 473K to 873K. The thicknesses of all samples were calculated using mass difference method. It was observed that with increase in annealing temperature film thickness goes on decreasing. XRDs of annealed samples show polycrystalline nature. From the XRD patterns, it is clearly observed that crystallinity of the samples increases with annealing temperature. FESEM images for the samples demonstrate that as temperature increases, there is increase in film cracks on the surface of sample. It may occur due to increased stress effect on the surface of samples at higher temperatures. Sample annealed at 473 K shows uniform and crackles surface morphology. Wettability for the sample clearly indicates hydrophilic nature of the electrode with contact angle of 45.95°.

Electrochemical characterizations of all prepared Co_3O_4 electrodes were carried out. The CVs of all cobalt oxide thin film electrodes prepared using different cobalt ingredients were taken. The sample deposited using cobalt chloride hexa hydrated shows

large area under the curve and SC is 237.38 F/g at scan rate 5mV/s in 1 M KOH at the potential window−0.92 to 0.45 Vvs Ag/AgCl. All CV shows mixed capacitive behavior. Two noticeable pairs of redox peaks are observed in the CV which corresponded to the conversion between different cobalt oxidation states. The optimized cobalt chloride source was used for the preparation of different molar concentration 0.05 M to 0.3 M samples. All deposited samples show mixed capacitive behavior in CV. Electrode deposited by 0.1 M solution concentration shows large area under the CV curve and SC is 237.68 F/g at scan rate 5 mV/s. in 1 M KOH at the potential window −0.92 to 0.45 V vs Ag/AgCl. The observed results are in consistence with XRD and FESEM etc. For further improvement in supercapacitive performance of Co_3O_4 electrode, electrodes were prepared for different deposition time at optimized molar (0.1 M) concentration. All CVs shows mixed-capacitive nature with redox peaks at the respective anodic and cathodic sweeps. From the CVs it was observed that electrode deposited for 30 min. Shows large value of SC 237.68 F/g at scan rate 5 mV/s. in 1 M KOH electrolyte at the potential window −0.92 to 0.45 V vs Ag/AgCl. This may be due to the uniform growth of granular type of morphology of the film as compared to other films. However electrode prepared for the time period of 60 min. shows larger current density but less SC. The weight of the deposited active material is much larger due to longer deposition time interval which affect on the electrochemical performance of the electrode.

The electrode deposited for 30 min. was further used to check the suitable annealing temperature. All electrodes show mixed capacitive nature. Electrode annealed at 473K shows large area under the curve and large current density. It has been observed that area under the curve and current densities goes on decreasing with increase in annealing temperature. Electrode annealed at 473K shows maximum value of the specific capacitance i.e. 251.11 F/g at scan rate 5mV/s in 1 M KOH at the potential window −0.92 to 0.45 V vs Ag/AgCl.

Electrode annealed at 473K is considered as optimized to check the effect of deposition scan rate by keeping all other optimized parameters constant. All the electrodes show mixed capacitive behavior with two pairs of redox peaks as observed in annealing temperature variation. CV depicts that electrode deposited at 80 mV/s shows higher area

under the curve and current density. Electrode deposited at 80 mV/s shows maximum SC i.e 372.41 F/g. at 5 mV/s.

The electrode was carried for scan rate variation from 2 mV/s to 100 mV/s in 1 M KOH electrolyte. Area under the curve and potential window goes on increasing with increase in scan rate with increase in long tail at negative potential. At lower scan rate (2 mV/s) it shows increase in SC and higher scan rate (100 mV/s) shows decrease in SC may be due to improper redox activity at higher scan rate. So 2 mV/s scan rate was used as optimized scan rate for further experimentation. Electrode was scanned in 1 M different electrolytes like, KOH, Na_2SO_4, $Na2SO_3$ and NaOH. Electrode scanned in 1 M KOH shows highest value of SC 441.17 F/g at 2 mV/s. It may be due to the fact that, conductivity and mobility of K^+ ions is more than Na^+ ions. The effect of optimized electrolyte was checked by varying different concentration of KOH electrolyte like 0.1 M to 2 M. It was observed that 1M electrolyte concentration provides maximum SC 441.17 F/g. The stability study of final optimized electrode was carried in 1 M KOH electrolyte and it shows better stability with retention of 87.88 % of the original capacitance after 1000 cycles. Charge-discharge analysis of optimized electrode was carried out for different current densities (mA/cm^2) in 1M KOH. Here it is observed that electrode carried at all the current densities shows nearly non-linear behavior of charge discharge curve. The highest calculated values of SE, SP and η are 20.98Wh/kg and 15.96 kW/kg and 86.63% respectively.

Using EIS technique the internal resistance of optimized electrode was carried out and is about 0.9435 Ω.EIS data was fitted with standard data to search an Randle's equivalent circuit using ZsimpWin software.

In the overall work it is observed that single aqueous route prepared electrodes shows little bit good supercapacitive performance it may be due to non supporting morphologies with increase in internal resistance etc. In order to enhance the supercapacitive performance of cobalt oxide thin film electrode Mn and Ru was tried to dope into cobalt oxide and effect for the same was checked.

Synthesis of Manganese Doped Cobalt oxide Thin Films by Potentiodyanamic Electrodeposition and their Electrochemical Characterizations

Mn doped cobalt oxide thin film electrodes were prepared using cobalt chloride hex hydrated and manganese chloride as a precursor in via aqueous route. Previously optimized parameters for cobalt oxide thin film that is equi molar 0.1 M conc., 80mV/s deposition scan rate, 30 min deposition time were used to prepare the thin film. The prepared samples were annealed at optimized annealing temperature 473K. XRDs of prepared samples confirms polycrystalline nature with good intense peak along (400) plane. XRD study shows face centered cubic and orthorhombic crystal structures for CO_3O_4 and MnO_2 respectively. The FESEM images of typical samples were taken to know the morphology variations with effect of Mn % incorporation. All the samples show porous granular surface morphology along with nanospikes / nanorods. Elemental analyses of all samples were confirmed using EDX technique. It was observed that composition shows proper increment in the Mn proportion in the film along with its percent wise addition. Contact angle measurement shows that with increase in doping % of Mn in the Co_3O_4 sample, contact angle goes on decreasing from 69.4° to 25.5°. This indicates that the electrochemical performance of the sample increases with increase in the doping % of Mn. 1% Mn doped cobalt oxide thin film shows super hydrophilic nature as compared to other samples.

Electrochemical characterizations of all aqueous route prepared manganese doped Co_3O_4 electrodes were carried using computer controlled potentiostat (H CH 600D spl. electrochemical analyzer / workstation) with standard three electrodes cell. In the supercapacitive study, the CVs of the electrode (size 1.5 cm x 1.3 cm) were carried out in 1 M KOH. The pristine Co_3O_4 and different percentage Mn (%) incorporated Co_3O_4 prepared electrodes were nomenclature as 'C_p' for pristine Co_3O_4, and $CM_{0.2}$, $CM_{0.4}$, $CM_{0.6}$, $CM_{0.8}$, CM_1 for 0.2 %, 0.4 %, 0.6 %, 0.8 % and 1 % addition of Mn. The capacitive performance of the pure and Mn doped (0.2% to 1%) cobalt oxide was evaluated by using cyclic voltammetry within a potential window −0.92 to 0.45 V at 2mV/s scan rate in 1M KOH. All the curves indicate mixed capacitive behavior of the electrodes endorsed by the redox

peaks observed on the respective anodic and cathodic sweeps. Electrode CM_1 (1% Mn incorporated cobalt oxide thin film electrode) shows maximum area under the curve and SC. The electrode CM_1 exhibits the maximum value of SC 605.39 F/g. It may be due to the more hydrophilic nature of CM_1 electrode.

1% Mn incorporated cobalt oxide thin film electrode was considered as optimized electrode to observe the effect of annealing temperature on crystallinity, surface morphology and electrochemical performance, the optimized electrodes were annealed at different temperatures 473 K, 523 K, 573 K, 623 K, and 673 K. Samples show strong orientations along (400) for Co_3O_4 or (202) for MnO_2 for low temperature annealing, but for high temperature annealing, orientations changes strongly. XRD reveals the increase in crystallinity with increase in annealing temperature. Co_3O_4 and MnO_2 shows face centered cubic and orthorhombic crystal structures respectively. FE-SEM images of manganese incorporated cobalt oxide samples annealed at 473 K shows porous nature with granular particles along with nanospikes/ nanorods feasible for supercapacitor application.

MnO_2 particles encapsulated in cobalt oxide thin film electrode shows strong influence on the electrochemical performance of pure cobalt oxide electrode as evidenced from TEM analysis. It shows formation of granular type of grains corresponding to pure cobalt oxide, along with the spikes originated from incorporation of Mn into the pure Co_3O_4 with average spike length 450 nm. SAED pattern of Mn incorporated Co_3O_4 confirms crystalline nature of the sample. AFM Micrograph reveals rough granular surface morphology with roughness 111nm.

Electrochemical characterization of CM_1 electrode annealed at different temperatures was carried out in 1M KOH and its CVs were carried out by varying scan rates. The optimized CM_1 electrodes were annealed at different temperatures 473 K, 523 K, 573 K, 623 K, and 673 K. All these annealed samples were nomenclature as MAT_1, MAT_2, MAT_3, MAT_4 and MAT_5 respectively.. It was evidenced that as the annealing temperature increases, the area under CV curves decreases. The maximum SC of 605.82 F/g was obtained for sample MAT_1 which was decreased to 214.58 F/g for the sample MAT_5. At lower annealing temperature, electrode shows maximum SC, it may be due to easy ionic intercalation.

The optimized electrode was carried for different scan rates 2 - 100 mV/s. At 2mV/s scan rate SC is 605.82 F/g and at 100 mV/s. scan rate SC 144.67 F/g in 1 M KOH electrolyte at potential window − 0.96 to 0.45 V vs Ag/AgCl. The optimized electrode was scanned in different1 M electrolytes like, KOH, NaCl, Na_2SO_3 and Na_2SO_4 etc. In all electrolytes, electrode shows the redox peaks at the respective anodic and cathodic sweeps of CV curves endorses for the mixed-capacitive nature. The calculated values of SC at 2 mV/s in 1M KOH, Na_2SO_4, NaCl, Na_2SO_3 and KCl electrolytes are 581.39 F/g, 57.56 F/g, 8.43 F/g, 6.02 F/g and 3.66 F/g respectively so the electrode carried in 1M KOH electrolyte shows maximum SC. The stability study of final optimized electrode was carried in 1 M KOH electrolyte shows better stability with 55.60 % capacity retention above 700 cycles. Using chronopotentiometry technique, charge-discharge of optimized electrode was carried out at different current densities (mA/cm^2). The calculated values of SE and SP and η are 67.42 Wh/kg, 31.7 kW/ kg and 73.89 %. Using EIS technique the internal resistance of optimized electrode was carried out and which is about ~ 0.78Ω. EIS data was fitted with standard data to search an Randle's equivalent circuit using ZsimpWin software.

Synthesis of Ruthenium Doped Cobalt oxide Thin Films by Potentiodynamic Electrodeposition and their Electrochemical Characterizations

Ru doped cobalt oxide thin film electrodes were prepared using cobalt chloride hex hydrated and ruthenium chloride as a precursor in aqueous route. Previously optimized parameters for cobalt oxide thin film that is equi molar 0.1 M conc., 80mV/s deposition scan rate, 30 min deposition time were used to prepare the thin film electrodes. The prepared samples were annealed at optimized annealing temperature 473K. All deposited samples were of polycrystalline nature having face centered cubic crystal structure for Co_3O_4 and tetragonal type crystal structure for RuO_2. Mostly all deposited samples grown along (400) plane for Co_3O_4 and along (210) plane for RuO_2. XRD patterns shows clear shifting of the peaks from larger 2θ values to smaller 2θ values due to incorporation of

ruthenium into cobalt oxide thin films. The FESEM images of all samples were taken to know the morphology variation because of Ru % incorporation in cobalt oxide. All morphology shows agglomeration of grain having mud type morphology with few surface cracks. The elemental analysis of the Ru incorporated cobalt oxide samples were carried out using EDX technique. It is found that all the samples show proper incorporation of Ru in cobalt oxide thin film.

Electrochemical characterizations of all aqueous route prepared ruthenium doped Co_3O_4 electrodes were carried using computer controlled potentiostat (H CH 600D spl. Electrochemical analyzer / workstation) with standard three electrodes cell. In the supercapacitive study, the CVs of the electrode (size 1.5 cm x 1.3 cm) were carried out in the potential window in 1 M KOH. The pristine Co_3O_4 and different Ru % incorporated Co_3O_4 prepared electrode were nomenclature as 'C_p' for pristine Co_3O_4, and $CR_{0.2}$, $CR_{0.4}$, $CR_{0.6}$, $CR_{0.8}$, CR_1 for 0.2 %, 0.4 %, 0.6 %, 0.8 % and 1 % addition of Ru. The capacitive performance of the pure and Ru doped (0.2% to 1%) cobalt oxide was evaluated by using cyclic voltammetry within a potential window −0.97 to 0.4 V at 2mV/s scan rate in 1M KOH. All electrodes CV curves show hybrid capacitive behavior with two redox peaks. In the fractional % incorporation of Ru, the CV curve of $CR_{0.4}$ electrode shows large area under the curve and current. The calculated value of SC for $CR_{0.4}$ electrode is maximum and it is 296.55 F/g at 2 mV/s carried in 1M KOH. It was observed that SC value of the pristine cobalt oxide is 441.17 F/g and decreases with increase in Ru incorporation beyond 0.4%. The decrease in SC may be due to decrease in porosity of the film compared to pristine cobalt oxide electrode.

The sample $CR_{0.4}$ showing highest SC was further treated at different annealing temperatures 473 K, 523 K, 573 K, 623 K, and 673 K for 1.5 hr. All these samples were nomenclature as RAT_1, RAT_2, RAT_3, RAT_4 and RAT_5.All samples show polycrystalline nature and increase in crystallinity with increase in temperatures. The FESEM images of typical samples were taken to know the morphology variations. All samples shows compact granular type morphology with few surface cracks. It was observed that with increase in annealing temperature sample shows compact mud type morphology.

From the TEM, it was observed that granular porous surface of prestine cobalt oxide thin film is fully covered with compact and mesh like structure due to Ru incorporation. From the 2D micrograph of AFM, it is clearly observed that sample shows rough granular morphology. The roughness of the sample was observed to be 5.2 µm.

This optimized $CR_{0.4}$ electrode was further annealed at different temperatures and its CVs were carried out by varying scan rates. Further $CR_{0.4}$ electrode was annealed at different temperatures 473 K, 523 K, 573 K, 623 K and 673 K. All these annealed samples were nomenclature as RAT_1, RAT_2, RAT_3, RAT_4 and RAT_5 respectively. It was evidenced that as the annealing temperature increases, the area under CV curves decreases. The maximum SC of 296.55 F/g was obtained for sample RAT_1 which was decreased to 158.76 F/g for the sample RAT_5. At lower annealing temperature, electrode shows maximum SC, it may be due to easy ionic intercalation.

The optimized electrode was carried for different scan rates 2-100 mV/s. at 2 mV/s scan rate SC is 296.55 F/g and at 100 mV/sec. scan rate SC 224.58 F/g in 1 M KOH at potential window − 0.97 to 0.4 V vs Ag/AgCl. The optimized electrode was scanned in different 1 M electrolytes like, KOH, NaCl, Na_2SO_3 and Na_2SO_4 etc. All CV curves show mixed capacitive behavior. Electrode carried in 1M KOH shows maximum area under curve and current density. The calculated values of SCs are 296.55 F/g for KOH, 15.94 F/g for NaCl, 72.23 F/g for Na_2SO_4, 45.37 F/g for Na_2SO_3, 20.70 for KCl. Effect of KOH concentration on the capacitive behavior of the electrode was also checked. Again the 1 M KOH concentration provides high area under the curve and maximum SC 296.55 F/g. It may due to proper ionic concentration and ionic size which may beneficial to improve the supercapacitive performance. The ruthenium incorporated cobalt oxide electrode shows excellent stability it may be due to high adherence of the film. Using chronopotentiometry technique charge-discharge behavior of the optimized electrode was studied for different current densities (mA/cm^2). The calculated values of SE, SP and η are 18.68Wh/kg, 43.07 kW/ kg and 70.51 %. Using EIS technique the internal resistance of optimized electrode was carried out and which is about ~ 0.88 Ω. EIS data was fitted with standard data to search an Randle's equivalent circuit using ZsimpWin software.

Electrochemical characterizations of Supercapacitor Device

MnO_2 : Co_3O_4 electrodes prepared via aqueous route using all optimized conditions were carried for two electrode system like, **symmetric** (two similar MnO_2 : Co_3O_4 electrodes). The calculated SC value is 115.76 F/g at the scan rate 2mV/s in 1 M KOH electrolyte at the potential window − 0.96 to 0.45 V vs Ag/AgCl. The prepared device shows better stability. Using chronopotentiometry technique charge-discharge of optimized electrode was carried out for different current densities (mA/cm^2). The calculated values of SE, SP and η are 215.81Wh/kg, 67.44 kW/ kg and 90.90 %. Using EIS technique the observed internal resistance of optimized electrode was~ 1.75 Ω. EIS data was fitted with standard data to search an Randle's equivalent circuit using ZsimpWin software.

Table 8.1: Optimized preparative parameters for different electrodes.

Sr. No.	Parameter	Optimized (Name/Value)
Electrode: Co_3O_4		
1	Cobalt Ingredient	Cobalt Chloride
2	Medium	Aqueous
3	Ingredient molarity	0.1 M
4	Deposition time	30 min
5	Annealing temperature	473 K
6	Deposition scan rate	80 mV/s
7	CV scan rate	2 mV/s
8	Electrolyte	KOH
9	Electrolyte concentration	1M
Electrode: MnO_2: Co_3O_4		
1	Manganese incorporation (%)	1%
2	Medium	Aqueous
3	Annealing temperature	473 K
4	CV scan rate	2 mV/s
5	Electrolyte	KOH
6	Electrolyte concentration	1M
Electrode: RuO_2: Co_3O_4		
1	Ruthenium incorporation (%)	0.4 %
2	Medium	Aqueous
3	Annealing temperature	473 K
4	CV scan rate	2 mV/s
5	Electrolyte	KOH
6	Electrolyte concentration	1M

Table 8.2: Supercapacitive parameters of different electrodes.

Sr.No.	Electrode	Scan rate (mV/s)	SC (F/g)	SE (Wh/kg)	SP (kW/kg)	η (%)	ESR (Ω)
1	**Co_3O_4**	2	441.17	20.98	15.96	86.63	0.9435
2	**MnO_2: Co_3O_4**	2	605.82	67.42	31.7	73.89	0.8157
3	**RuO_2: Co_3O_4**	2	296.55	18.68	43.07	70.51	1.87
4	**MnO_2: Co_3O_4 Symmetric device**	2	115.76	71.62	67.44	90.90	1.82