ABSTRACT

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, MnO_2: Co_3O_4 and RuO_2:Co_3O_4 can control some of the parameters like the ingredients, film thickness, solution concentration, deposition time, annealing temperature and deposition scan rates.

. **Chapter-I** summarized general introduction to supercapacitor and its importance, literature survey regarding concerned materials. **Chapter-II** describes the theoretical aspects of supercapacitor. It includes construction of supercapacitor, types of electrode and electrolyte used for the supercapacitor fabrication. **Chapter-III** explains theoretical background of electrodeposition set up, thin film preparation using electrodeposition. This chapter also explains with different characterization techniques.

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. Intialy Co_3O_4 thin films were synthesized by potentiodynamic electrodeposition technique using variations in the parameters such as ingredient, solution concentration and deposition time. The prepared samples were analyzed using XRD, FE-SEM, TEM, cyclic voltammetery, chronopotentiometry and electrochemical impedance spectroscopy. Optimized ingredient, Molarity and deposition time were Cobalt chloride, 0.1 M and 30 min. respectively. Crystallographic study shows polycrystalline FCC structure of the deposit. Cyclic voltammogram reveals pseudocapacitive behavior. The calculated highest value of SC at the scan rate 5 mV/s was 237.68 F/g in 1 M KOH, within the potential window - 0.92 to 0.45 V vs Ag/AgCl. The calculated maximum value of SE, SP and η were 4.91 Wh/kg, 28.69 kW/kg and 94.78 % respectively. The internal resistance observed using EIS was ~ 3.55 Ω.

To check the effect of annealing temperature and deposition scan rate, Co_3O_4 thin films were deposited potentiodynamically on SS substrate using finally optimized parameters. Prepared samples were annealed from 473K to 873K by the interval of 100. Optimized annealing temperature and deposition scan rate was 473 K and 80 mV/s

respectively. XRD study reveals cubic crystal structure of Co_3O_4. FE-SEM showed compact agglomerated granular type morphology. Optimized Scan rate, electrolyte and electrolyte concentration are 2mV/s, KOH, 1M respectively. Electrochemical characterization of electrodes showed pseudocapacitive behavior. Maximum value of SC (441.17 F/g) was achieved at the scan rate 2 mV/s in 1M KOH with 87.88 % stability. Charge-discharge curves showed nonlinear behavior and used to calculate the SE, SP and columbic η which were 20.98 Wh/kg, 15.96 kW/kg and 86.63 % respectively. EIS of complex impedance spectra shows internal resistance ~0.9435 Ω.

Chapter-V explains about the effect of Mn (%) incorporation in Co_3O_4 on the properties of MnO_2: Co_3O_4 thin films prepared via aqueous media. Mn doped cobalt oxide thin film electrodes were prepared using cobalt chloride and manganese chloride as precursor via aqueous route. Previously optimized parameters for cobalt oxide thin film i.e 0.1 M conc., 80 mV/s deposition scan rate, 30 min deposition time were used to prepare the thin film. The pristine Co_3O_4 and different 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 prepared samples were annealed at optimized temperature 473 K. XRDs of prepared samples confirms polycrystalline nature with intense peak along (400) plane. XRD study shows FCC crystal 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 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.

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 FCC 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.

TEM 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.

Cyclic voltammetery curve of 1% Mn doped cobalt oxide electrode annealed at different temperature evidenced that as the annealing temperature increases, the area under CV curves decreases. The maximum SC of 605.82 F/g was obtained. 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. It was observed that 1M KOH electrolyte with 2mV/s scan rate is suitable for the electrode. 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. 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 ~ 0.78 Ω. EIS data was fitted with standard data to search an Randle's equivalent circuit using ZsimpWin software.

Chapter-VI elucidates effect of equi (0.1 M) molar ruthenium incorporated Co_3O_4 thin films on the properties of RuO_2: Co_3O_4 thin films prepared via aqueous medium. Ru doped cobalt oxide thin film electrodes were prepared using cobalt chloride hexa hydrated and ruthenium chloride as a precursor in aqueous route. Previously optimized parameters for cobalt oxide thin film that is 0.1 M conc., 80 mV/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. 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 respectively. All deposited samples were of polycrystalline nature having FCC crystal structure for Co_3O_4 and tetragonal type crystal structure 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. FESEM images shows agglomeration of grain having mud type morphology with few surface cracks. The elemental analysis of the Ru incorporated cobalt oxide samples show proper incorporation of Ru in cobalt oxide thin film.

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.

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 show 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 with roughness 5.2 µm.

CV study 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. At lower annealing temperature, electrode shows maximum SC, it may be due to easy ionic intercalation.

It was observed that 1M KOH electrolyte for the scan rate 2 mV/s is more suitable for the optimized electrode. All CV curves show mixed capacitive behavior. The calculated maximum value of SC is 296.55 F/g. The ruthenium incorporated cobalt oxide electrode shows excellent stability. The calculated values of SE, SP and η using chronopotentiometry are 18.68Wh/kg, 43.07 kW/ kg and 70.51 %. Using EIS showed ~ 0.88 Ω internal resistance of optimized electrode.

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

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. The calculated values of SE, SP and η using chronopotentiometery 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.

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

Table 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 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