

1.1 Introduction

1.1.1 About Supercapacitor

Today the whole world is in need of reliability in energy storage process and its conservation. The ever increasing cost of fuels, pollution, global warming and geopolitical concerns are also the key factors and issues is connected with the dependence of modern societies on fossil fuels. To reduce these issues, strong and reliable energy sources and storage technologies are required. As a result, recently there has been a growing interest in high power and high energy density storage systems in order to develop a sustainable energy model. Energy storage plays an indispensable part of this model. Currently, batteries are leading the energy storage market. However, batteries lack high power density, high number of charge-discharge cycles and high rates of charging and discharging. These deficiencies can be overcome with the use of supercapacitors. Supercapacitors have been known for more than fifty years and are considered as one of the potential energy storage systems in addition to batteries, fuel cells and normal capacitors. Supercapacitors are presently viewed as a novel kind of energy storage device.

There has recently been a growing demand for environment friendly hybrid electric vehicles. To pick up the efficiency of power system of hybrid electric vehicles, it requires kinetic energy to be stored somewhere whenever the vehicle slows down or stops. Although these operations are performed with batteries on low-power scale, new methods for efficiency enhancement will require large amounts of power that can only be provided by other energy storage technologies such as supercapacitors. These have attracted significant attention due to their high power capabilities and long cycle-life, giving a very good chance to build more advanced hybrid electrochemical supercapacitors, for both on-board and stationary applications. There are number of charge storage applications like hybrid electric vehicles, laptops, digital cameras, mobile phones, military, missiles etc.

ES must be pollutant free and inexpensive and have gained huge awareness in energy storage devices because of their high power density and high cycle strength. Their power density is higher than that of ordinary batteries, and energy density is higher than that of normal capacitors [1]. This can be graphically elucidated in a Ragone plot, in which the energy and power densities are represented in horizontal and vertical axes, also

showing the discharge time of the devices in diagonal lines ($E=Pt$). Different storage technologies are represented in a Ragone plot in Fig.1.1

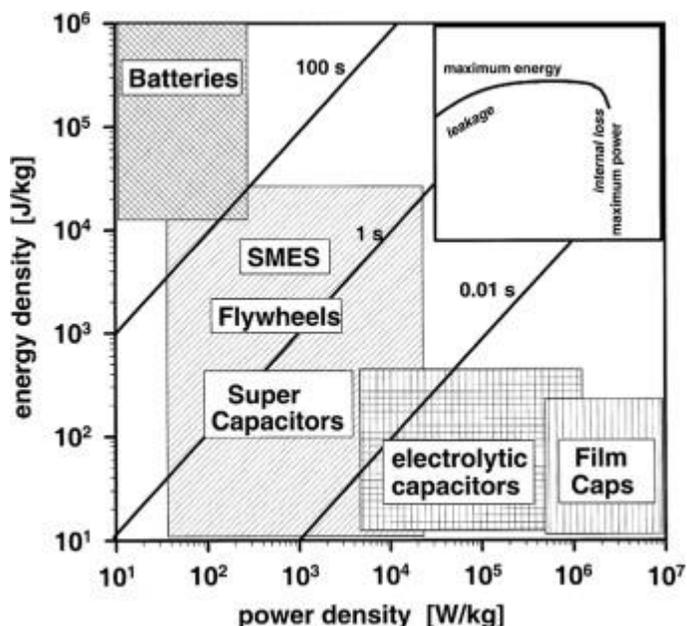


Figure 1.1: Ragone plot [2].

Supercapacitor charges in a short period of time and discharges in a matter of second. This is an important property for energy recovery system e.g. for dynamic braking of transport systems. Another great significance of supercapacitors is their cycle life. These devices can withstand millions of cycles that involve reversible chemical reactions.

A supercapacitor cell consists of two electrodes with a separator between them. The electrodes can be identical for symmetric cells or different for asymmetric cells. The separator is soaked in electrolyte and prevents the electrical contact between the electrodes. The separator material should be ion-permeable, to allow the ionic charge transfer, while at the same time possessing high electrical resistance, high ionic conductance, and low thickness in order to achieve the best performance. Usually, polymer or paper separators are used together with organic electrolytes while ceramic or glass fiber separators are usually coupled with aqueous electrolytes [3]. The electrolyte breakdown potential at one of the electrodes restricts the attainable cell voltage whereas the ESR of the cell will depend on the electrolyte conductivity. Aqueous electrolytes typically have a breakdown

voltage of around 1 V which is significantly lower as compared with organic electrolytes (around 3 V). The conductivity of aqueous electrolytes is higher than that of organic electrolytes which is desirable for high power devices. Aqueous electrolytes also attribute important assets such as low cost and easiness in handling.



Figure1.2: Diagram of symmetric supercapacitor [4].

Supercapacitor mainly consists of two types.

EDLSC, in which Energy is stored in the form of charges at the surface of electrode and electrolyte interface e.g. carbon.

Pseudocapacitor, in which energy is stored in the form of charges at the surface of the electrode e.g. transition metal oxides and electronic conducting polymers etc.

Hybrid supercapacitors, are the combination of both EDLSC and pseudocapacitor.

e.g. symmetric, asymmetric and solid state devices.

Helmholtz's double layer (HDL) occurring at the surface of the electrode-electrolyte interface leads to the principle of supercapacitor [1]. Various materials and methods were adapted in the development of supercapacitor electrodes. The materials include, **1) TMOs:** cobalt oxide, ruthenium oxide, manganese oxide, chromium oxide, iron oxide, nickel oxide, iridium oxide, titanium oxide etc. and their nano-composites [1].**2) Conducting polymers:** polypyrrole, polyaniline, polythiophene etc. and their nano-

composites[1] and **3) Carbon:** allotropes of activated charcoal, MWCNT, SWCNT, grapheme etc. and their nano-composites [1]. Various chemical and physical methods have been employed for the preparation of electrode material for the supercapacitor. Chemical methods include electrodeposition (both anodic and cathodic), spray pyrolysis, SILAR, CBD, sol-gel etc. and the physical methods include sputtering, pulse LASER deposition etc. Chemical methods are inexpensive, simple and environmental friendly. Chemically prepared materials show supporting morphologies and good crystallinity. Physical methods are costly and not environmental friendly. Moreover, different parameters are required to prepare the samples.

Synthesis of the materials having large surface area within the limited weight is the key aspect in developing supercapacitors. Electrochemical synthesis of oxide film is economical and effective for large-scale applications. It provides scope to deposit relatively uniform thin films onto large area substrates of complex shape. The thickness and morphology of the film can be easily adjusted by varying electrochemical parameters. The important aspect of the electrochemical synthesis is that it does not require too high temperature. The electrochemical reaction is a unique process occurring on the working electrode where either oxidation or reduction takes place without any chemical agent being required for the reaction. Electricity is accomplished by the oxidation and reduction and so there are no by-product species. Today, this is a very significant feature of electrochemical processes as far as the environmental protection and materials conservation is considered.

Nanostructured materials are the materials with microstructures having one of its dimensions in the nanoscale (1 nm to 100 nm).Physics and chemistry deal with the properties of solids which depend on the chemical composition(microstructure), the atomic structure (arrangements of atoms) and size of the solid particle in one, two or three dimensions. A good example showing relation between properties of solid and atomic structure is the variation of hardness of carbon when it transforms from diamond to graphite. Comparable variations have been noted if the atomic structure of a solid deviates from equilibrium or if its size is reduced to a few interatomic spacing in one, two or three dimensions. For example, CdS crystals show change in color if their size is reduced to few nanometers [5].

Nanostructured materials are found to demonstrate unique properties, in terms of electrode conductivity and particle-to-particle contact, due to their nanometer sizes where electron tunneling is quicker than micron-sized particles. The latter aspect is vital for supercapacitors as it directly influences the ESR of the cell. Therefore, the use of nanosized particle electrode for such an application would certainly help to achieve high rate capability within the cell. Obtaining uniform nanosized grains in metal oxide thin films is a crucial challenge for material scientists. This requires an appropriate synthesis approach. Therefore, the present work has been aimed at developing uniform sized cobalt oxide, manganese doped cobalt oxide, ruthenium doped cobalt oxide and ruthenium doped manganese cobalt oxide nanosized particles with a view to enhancing the electrode properties and characterizing its electrode active qualities in electrochemical supercapacitors. To prepare such nanostructured materials that have a large surface area within the limited weight is an important aspect while developing supercapacitors. Electrodepositing oxide film is economical and it enables us to deposit relatively uniform thin films onto complex shape of the substrates. One can also control the thickness and morphology of the samples by adjusting the preparative parameters.

1.1.2 Literature survey of

a. Cobalt oxide:

TMOs provide a variety of oxidation states for efficient redox charge transfer because of its high SC and excellent reversibility that arises from ideal solid state pseudofaradaic redox reaction occurring at the surface of electrode therefore they are considered as prominent electrode material for supercapacitor electrode. TMOs prepared electrode shows excellent value of SC over EDLSc electrode. The theoretical capacitance of Co_3O_4 electrode is~ 3560 F/g. It shows good structural properties, excellent electrochemical performance in alkaline solution due to its ability to interact with electrolyte ions not only at the surface but also throughout the bulk i.e. pseudocapacitive nature. The pseudocapacitive behavior of cobalt oxide itself confirms promising alternative material for supercapacitors. Cobalt oxide having different well-known forms like monoxide or cobaltous oxide (CoO), the cobaltic oxide (Co_2O_3) and the cobaltous oxide or cobalt cobaltite (Co_3O_4) forming at various deposition temperatures [6]. The prepared Co_3O_4 films were, semi-crystalline amorphous [7], nanocrystalline [8], porous [9],

hydrophilic [10] good conductive [6], of low ESR [11], p-type conductivity [12] etc. The different morphologies of Co_3O_4 like micro/nanostructures including one-dimensional (1D) nano-wires [13], nano-needles [14], nanobelts [15], nanorods [16], nanotubes [17], two-dimensional (2D) nanosheets [18], three-dimensional (3D) architectures [19], nanoparticles [20] and nanocubes [21] have been prepared by various methods. Among different transition metal oxides, Co_3O_4 is one of the promising electrode materials because of its high redox activity and strong reversibility [22]. It possesses multi-oxidation states, low band gap [23] and several morphologies with 3D architectures. It may play an important role in supercapacitor device applications [24]. Of all these, Co_2O_3 absorbs oxygen in adequate quantity and transforms into Co_3O_4 with no change in the lattice structure [25].

Cobalt (II, III) oxide is one of the two well-characterized cobalt oxides. As shown in Fig.1.3, cobalt (II, III) oxide is a mixed valence compound and its formula can sometimes be written as $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{O}_4$ and sometimes as CoO and Co_2O_3 . Similar to Co_3O_4 , it is of the spinel structure. Co^{2+} occupies the tetragonal 8(a) sites, and Co^{3+} occupies the octahedral 16 (d) sites, 32 (e) sites are occupied by 32 O^{2-} ions. As known, the spinel minerals have the generic formula AB_2O_4 , where A is a cation with +2 charge and B is a cation with +3 charge. Oxygen atoms in a spinel structure are arranged in a cubic close-packed manner and the cations A and B occupy some or all of the octahedral and tetrahedral sites in the lattice [26].

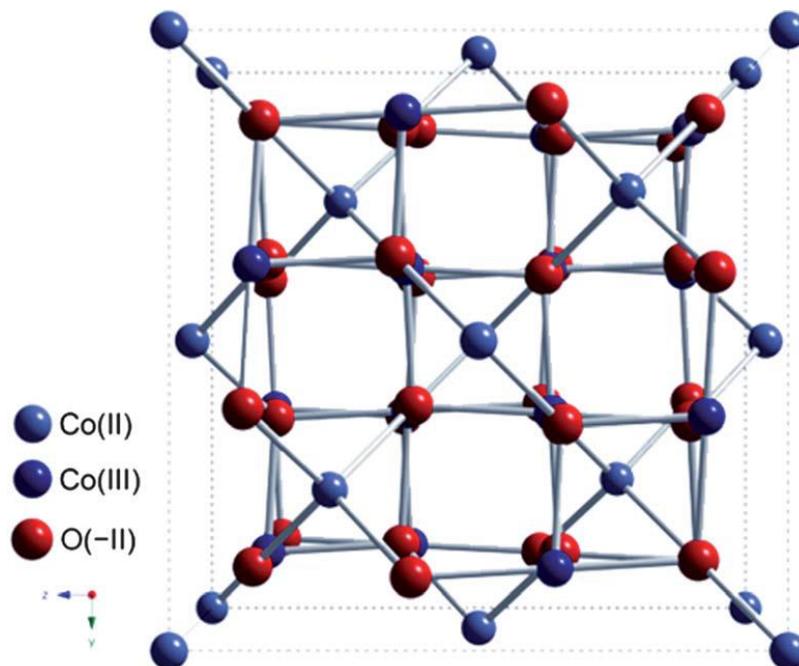


Figure1.3: Spinel structure of Co_3O_4 .

Nanocrystalline Co_3O_4 is capable of offering a large surface area, high conductivity, high electrochemical stability and pseudocapacitive behavior. Xia *et al.* [27] reported Co_3O_4 nanowire arrays grown on the nickel foam. The XRD shows polycrystalline nature with nanowire type morphology. The material was tested as a cathode electrode for supercapacitors by CV and charge-discharge in 1 M KOH. The self-supported hollow Co_3O_4 nanowire arrays exhibit superior supercapacitor performance with high SC (599 F/g at 2 A/g and 439 F/g at 4 A/g) as well as excellent cycle life. Moreover, the good corrosion stability of the Co_3O_4 electrode and its low cost high SC makes it promising candidate for the fabrication of supercapacitor device. Tummala *et al.* [28] reported Co_3O_4 preparation by plasma spray technique. The XRD showed polycrystalline nature with agglomeration of fused porous particles. The prepared electrode showed maximum SC 162 F/g at the scan rate 2 mV/s in 6 M KOH. The internal resistance observed using nyquist plot was about 2.5 Ω . Some authors reported non stoichiometric Co_3O_4 [29]. Cobalt has less affinity for oxygen than nickel [30]. It was also reported that Co_3O_4 exists only in hydrated form. Among all the metal oxides, cobalt oxide/hydroxide is the most prominent electrode

material for supercapacitors owing to their different attractive properties like good conductivity and good cycle stability [31].

Cui *et al.* [32] reported that hexagonal Co_3O_4 nano-sheets demonstrated a maximum SC of 227 F/g. Zhang *et al.* reported performance of the supercapacitor electrodes based on the $\text{Co}_3\text{O}_4/\text{C}$ core-branch nanowire arrays as cathode material. $\text{Co}_3\text{O}_4/\text{C}$ core-branch nanowire arrays exhibit outstanding electrochemical performance with high capacitance and good cycle life due to the unique core-branch architecture, and thus proving its potential application in electrochemical energy storage devices [33]. Gao *et al.* [34] reported Co_3O_4 nanowire arrays freely standing on nickel foam prepared via template-free growth followed by thermal treatment at 573 K in air. Electrode shows 746 F/g SC at 5 mA/cm^2 in 6 M KOH. The observed internal resistance from nyquist plot was around 0.75 Ω . Srinivasan *et al.* [35] reported nano-porous Co_3O_4 nanorods by facile hydrothermal method, provide maximum SC of 280 F/g at the scan rate 5 mV/s in 3 wt % KOH. Wei *et al.* [36] reported high SC 600 F/g for single-crystalline Co_3O_4 nanorods prepared on epoxide synthetic route. Shinde *et al.* [37] reported 74 F/g SC at the scan rate of 5 mV/s in 2 M KOH for Co_3O_4 thin films deposited on a glass substrate by spray pyrolysis. The prepared electrode shows direct band gap around 2.10 eV and indirect band gap around 1.60 eV with electrical resistivity of the order of 10^{-4} Ω . XRD shows cubic structure with reflection along (111) direction with overgrown clusters type morphology. In addition, Zheng *et al.* [38] synthesized mesoporous Co_3O_4 nanoparticles with the SC of 370 F/g. Due to high surface area and void interiors, it is believed that hollow structures are ideal electrode materials for pseudocapacitors. Kandlkar *et al.* [39] reported cobalt oxide electrode preparation using electrodeposition technique on copper substrate, obtained maximum SC was 235 F/g at scan rate of 20 mV/sec. in 2 M KOH with SE 4.0 Wh/kg and SP 1.33 kW/kg and excellent stability. The prepared samples show reflection along (111) plane and porous type morphology with fine particles. Hosono *et al.*[40] reported nanostructured CoOOH electrode prepared on a nickel foil exhibits maximum SC 200 F/g at the scan rate of 10 mV/s in 1M KOH. The prepared samples show polycrystalline nature with flowery, petal type morphology. Wang *et al.* [41] reported $\text{Co}(\text{OH})_2$ electrode exhibiting SC around 280 F/g at scan rate 5 mV/sec in KOH with redox reversibility. The peaks themselves indicate pseudocapacitive nature. Li *et al.* [42] prepared thin films of

Co₃O₄ by CBD on ITO. CV curve shows nearly rectangular behavior with maximum value of SC 227 F/g at 2 A/g in 6 M KOH and good stability. The observed internal resistance (ESR) from nyquist plot is around 2.3 Ω. The prepared sample shows reflection along (311) plane with spherical particles of 2 μm size and porous morphology. Thin films of Co₃O₄ prepared on copper substrate was reported by Kandalkar *et al.* [43]. The sample exhibits SC 165 F/g at 10 mV/s in 1 M KOH. The prepared sample shows reflection along (111) the plane with fine elongated composed morphology. Xia *et al.* [44] reported free standing single crystalline Co₃O₄ nanowire array of size 70 nm grown on nickel foam prepared by hydrothermal method. XRD shows reflection along (311) the plane with 1D nanowire architecture. The prepared electrode shows the maximum value of SC around 754 F/g at 2 A/g in 2 M KOH with good stability.

To enhance the supercapacitive performance of Co₃O₄, Yuan *et al.* [45] have intensively studied the whisker like Co(OH)₂ soft-template method. XRD reveals reflection along (001) plane with polycrystalline nature. The prepared electrode shows SC 279 F/g at 80 mA/cm² in KOH with a good stability and the CV curve shows redox peaks indicating pseudocapacitive behavior. From the nyquist plot, the observed internal resistance was around 0.4 Ω. The SC associated with the electrode that was calculated from impedance was around 177 F/g. Kandalkar *et al.* [46] reported cobalt oxide thin film electrodes prepared on copper substrate by using SILAR technique. The prepared sample shows agglomerated particles with small porous type morphology. The maximum value of SC was around 118 F/g at 50 mV/s in 1 M KOH. The calculated values of SE, SP and η were 5.8 Wh/kg, 0.33 kW/kg and 93.44 % respectively. Xu *et al.* [47] reported Co₃O₄ nanotubes successfully synthesized by AAO templates method and then thermally annealed at 773 K. XRD of the prepared sample shows reflection along (311) plane. The sample exhibits nanotubes type morphology. The calculated value of SC was ~ 574 F/g at the current density 0.1 A/g in 6 M KOH. The observed CV curve demonstrates mixed capacitive nature (i.e. nearly rectangular with peaks) with good stability. Using nyquist plot, the internal resistance was around 0.4 Ω.

The growth of cobalt oxalates was observed through the water-controlled precipitation process reported by Wang *et al.* [48]. The XRD pattern shows anisotropic crystal structure with reflection along the (311) plane. The SEM reveals nanotubes type

morphology. The observed pore size was around 17.28 to 8.58 nm while the maximum value of SC was 202.5 F/g at current density 1 A/g in 2 M KOH, the CV curves indicate pseudocapacitive nature. Du *et al.* [49] reported a facile synthesis of hollow Co_3O_4 boxes for high capacitance. The XRD shows polycrystalline nature. The calculated value of SC was 278 F/g at current density 0.5 A/g in 3 % KOH. Yang *et al.* [50] reported a unique hierarchical porous architecture of nanosheet @ nanowire arrays synthesized by using facile hydrothermal process. The prepared films annealed at 120 °C for 9 hrs. The XRD shows reflection along (311) plane with nanowire - array type morphology. The prepared electrode shows maximum 715 F/g SC on nickel foam at current density 5 mA/cm² in 1 M KOH.

In current years, researchers have switched towards the preparation of mesoporous cobalt oxide. Ultra layered Co_3O_4 electrodes have been synthesized by a homogenous precipitation method under hydrothermal process by Meher *et al.* [51]. The prepared electrode shows well-arranged nano-crystalline rectangular micro sheets. The Maximum value of SC (548 F/g) was observed at the current density 8 A/g in 1 M KOH with high stability and pseudocapacitive nature. The observed internal resistance is very less as observed from the nyquist plot. Rahki *et al.* [52] synthesized the substrate depended self-organization of mesoporous cobalt oxide electrodes by substrate assisted solvothermal synthesis method. The XRD spectra of the samples show reflection along (311) plane. Sample exhibits the morphology of Co_3O_4 nanowires having average length ranging between 1-10 μm . The prepared electrode shows maximum SC around 911 F/g at the current density 0.25 A/g in KOH with good stability over 5000 cycles. The internal resistance observed from the nyquist plot was 0.33 Ω for flower-like morphology of nanowires. The nyquist plot itself indicates pseudocapacitive nature of the deposited material. Recently, researchers have planned the preparation of symmetric devices using same kind of electrodes for supercapacitor application. Jagadale *et al.* [53] reported cobalt oxide electrode preparation on SS by potentiodynamic electrodeposition technique. The prepared electrode shows hexagonal crystal structure with nanoflakes. The observed maximum value of SC was around 44 F/g in 1 M KOH at the scan rate 5 mV/sec with pseudocapacitive nature. The observed internal resistance from the nyquist plot was ~ 2.3 Ω . To avoid the leakage, corrosion problem and to increase the power/energy density of

supercapacitor, researchers planned to set up some solid-state devices. Yu *et al.* [54] reported synthesis of carbon nanocomposite electrodes using PVA/phosphoric acid showing maximum value of SC around 115.83 F/g at scan rate 2 mV/s.

In the overall literature it is observed that very little attention has been given for the preparation of cobalt oxide supercapacitor electrodes using potentiodynamic electrodeposition. The prepared cobalt oxide electrode shows limited potential window and less SC. To increase the supercapacitive performance of cobalt oxide electrode i.e. to increase the potential window, SC, stability, crystallinity and decrement in the internal resistance it requires the doping of other elements.

b. Manganese doped cobalt oxide:

Manganese oxide can exist in variety of stable states MnO, Mn₃O₄, Mn₂O₃, MnO₂ and several oxidation states, including Mn(0), Mn(II), Mn(III), Mn(IV), Mn(V), Mn(VI), and Mn(VII) [55-56]. Some reported crystal line phases of manganese oxide are MnO, Mn₂O₃, MnO₂ and Mn₃O₄ [57]. Mn₃O₄ is one of the most stable forms at lower temperature as reported earlier. It plays an important role in catalysts [58], elemental biogeochemical cycles [59], electrode materials [60 (A, B)], and soft magnetic materials [61]. Mn₃O₄ is a potentially interesting electrode material for electrochemical supercapacitors because of its low cost, environmental compatibility and intrinsically high capacity [62]. The prepared manganese oxide shows unique structure and novel morphology such as nanoroads/nanowires [63], nanoparticles [64], nanoplates [65], mesoporous/ macroporous structures [66], hydrophilic nature [67], moderate ESR (1.05 Ω) [68] and p-type conductivity [69]. Guo *et al.* [70] reported the microstructure of Mn₃O₄ prepared on SS substrate by solvo thermal treatment at 393 K. The XRD indicates reflection peak along the plane (211) with tetragonal crystal structure and SEM shows novel microsphere like morphology with average diameter around 2 μm. The XPS analysis showed that the prepared sample possesses binding energy (BE) around 284.6 eV and maximum value of SC around 219 F/g at the scan rate of 10 mV/sec with good stability in 1 M Na₂SO₄. Lee *et al.* [71] reported amorphous nanostructured manganese oxide prepared on SS substrate and obtained SC around 190 F/g in 1 M Na₂SO₄ due to utilization of both its electric double layer and Mn (Mn₂O₃III)/ Mn (Mn₃O₄IV) redox transition. To carry faradaic redox reactions of cobalt

oxide, alkaline electrolytes such as aqueous KOH/ NaOH, Na₂SO₄ etc. were used which have a limited potential window of 0.4 to 0.5 V. Yuan *et al.* [72] reported MnO₂ pillared layered manganese oxide via delamination/ reassembling process followed by oxidation reaction exhibiting SC value of 206 F/g. To study the supercapacitor devices, Dubal *et al.* [73] reported symmetric type of supercapacitors using SS substrate. The prepared electrode shows reflection along (211) plane with tetragonal crystal structure and nanopetal/ nanowire type morphology. The maximum value of SC of symmetric Mn₃O₄ - Mn₃O₄ electrode was 72 F/g in 1 M Na₂SO₄ electrolyte. Beguin *et al.* [74] reported the preparation of asymmetric supercapacitors of carbon/ MnO₂ electrode. The observed value of SC was 113 F/g at the scan rate 2 mV/s in 0.5 M Na₂SO₄. The calculated energy density was 13.9 Wh/kg.

Fan *et al.* extensively demonstrated the manganese-cobalt oxide nano composites doping/ mixing electrodes for electrochemical capacitors. For example, the three-dimensional tubular arrays of MnO₂ - NiO nanoflakes, hybrid structures of Co₃O₄ nanowire@MnO₂ ultrathin nanosheet core/ shell arrays and cobalt monoxide nanowire@nickel hydroxide nitrate nanoflake aligned on nickel foam can be used for high-rate supercapacitors [75]. Prasad and Miura *et al.* [76] deposited microporous and nanostructured cobalt - manganese oxide (CMO) onto SS substrates by potentiodynamic methods. It is found that the addition of Co oxide has a positive impact on improving SC of MnO₂. Yan *et al.* [77] reported mesoporous Mn - Co oxide for supercapacitors derived from a mixed oxalate Mn_{0.8}Co_{0.2}C₂O₄ H₂O, synthesized by a solid-state co-ordination reaction at room temperature. The prepared samples show tetragonal crystal structure having SC 383 F/g at scan rate 2 mV/s in 6 M KOH. Chang *et al.* [78] reported that the addition of Co causes change in surface morphology from a fibrous to smooth which may account for the significant reduction in the SC of the as-deposited mixed Mn-Co oxide with a high Co content. Recently, Pang *et al.* [79] reported the porous nanocubic Mn₃O₄ - Co₃O₄ nanocomposites. The XRD spectras of the prepared samples shows cubic crystal structure forming porous structure of nanoparticles that offer high surface areas as well as good electrolyte/ ion access. The prepared electrode shows SC around 336 F/g at the scan rate of 50 mV/s in 1 M Na₂SO₄. The internal resistance associated with the electrode observed using the nyquist plot was around 1.05 Ω. Pang *et al.* reported the coordination complexes

of Mn have been used as a nanostructured precursor to prepare mesoporous metal oxides. More importantly, when calcining the nanostructured precursor, there were large number of released gases from decomposed organic ligands and new pores were generated, finally resulting in a novel porous structure. The decomposition products retain both micro/nano and porous structures [80-81]. Yu *et al.* [82] also reported Hierarchical NiCo₂O₄@MnO₂ core-shell hetero structured nanowire arrays on Ni foam by two-step solution route coupled with a post calcination treatment. The XRD spectra of prepared samples show reflection along (311) plane with crystalline birnessite type MnO₂ along with nanowire type morphology. The reported SC was around 1471.4 to 1273.8 F/g at the scan rate of 2 to 20 mV/s in 1 M LiOH exhibiting good stability. Luo *et al.* [83] reported the nanostructured Mn - Ni - Co oxide composites prepared by thermal decomposition of the precursor obtained by the chemical co-precipitation method. The prepared samples show nanostructured networks of solid rods and pore size around 200 nm observed from SEM. The reported SC was around 1080 F/g at the scan rate of 5 mV/s in 6 M KOH. The nyquist plot indicates pseudocapacitive behavior of the electrode and gives internal resistance around 0.43 Ω . This is less as compared to pristine Mn₃O₄ electrode. Yang *et al.* [84] investigated the cobalt doped manganese oxide by pulse laser deposition on silicon wafer and SS substrate. The prepared electrode shows nearly rectangular behavior and SC 99 F/g at the scan rate of 5 mV/s in 1M K₂SO₄. Toupin *et al.* [85] reported poor electronic and ionic conductivity of the prepared manganese oxide. Wei *et al.* [86] written a critical review on manganese oxide (nanostructured and amorphous) based materials/ composites for electrochemical supercapacitor electrodes by different methods. Review reports the highest value of SC 389 F/g at the scan rate of 10 mV/s. The high viscosity processed electrode using KMnO₄ + MnCl₂ + PG + PAM, 65 1C80 shows rod-shaped morphology with α -MnO₂, γ -MnO₂ structure.

c. Ruthenium doped cobalt oxide:

Ruthenium oxide: Amorphous, nanocrystalline and hydrous RuO₂ is considered to be one of the promising candidates for supercapacitor electrode due to its high SC, low ESR [87]. It has great advantage in terms of wide potential range and highly reversible redox reaction with high SE and SP. It exhibits excellent pseudocapacitive behavior with

excellent reversibility and high stability. The only disadvantage is it is costly. The hydrous ruthenium oxide is mixed electronic - protonic conductor [88, 89]. However, it is very expensive, less abundant and having high cost. Therefore, it has lot of major limits for commercial applications. The benefit of the use of amorphous, porous material is that they have high charge discharge rate [90]. This gives us a better quantitative insight in to the supercapacitive nature of an electrode material as compared with CV measurements. The straight line characteristic in charge-discharge curves indicates the ideal capacitive nature of the active material, which is feasible for supercapacitor electrode [91]. Hydrous ruthenium dioxide, $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ is the most promising electrode material for electrochemical supercapacitors due to its intrinsic reversibility of surface redox couples [92, 93] and ultrahigh pseudocapacitance [94, 95]. Since the superficial redox transitions of RuO_2 involve a proton-electron double injecting/ expelling process [93], crystalline $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ not only reduces the electronic resistance but also promotes the rate of proton diffusion /exchange for high-power operations [96-99]. Such excellent performance is maintained for $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ films [100], especially for the high-power application. This phenomenon is commonly found for the most electroactive materials due to longer diffusion lengths of ions/electrons [101-104]. Thus three-dimensional (3D), mesoporous, orderedperiodic architectures are desirable for improving such an issue [105-109]. In order to develop advanced electrode materials for electrochemical supercapacitors, several desired 3D mesoporous architectures have been developed [110], which could reduce the ESR by simultaneously maintaining facile electrolyte penetration, fast proton exchange, and good metallic conductivity. As a result, achieving the ultrahigh-power purpose and retaining a high capacity for supercapacitors became possible.

Ambare *et al.* reported non-aqueous route spray pyrolyzed $\text{RuO}_2 \cdot \text{Co}_3\text{O}_4$ thin electrodes for supercapacitor application. The XRD and SAED studies confirm polycrystalline deposits of nanoparticles. The SEM and TEM reveal granular porous and rough morphology with mixed microstructures. The observed band gap of the optimized $\text{NCR}_{0.6}$ electrode is well in reported range 1.45 eV. The XPS study reveals proper oxidation state. The CV curves show mixed capacitive behavior with good stability in early cycles with maximum observed value of SC 628.3 F/g at the scan rate of 1 mV/s in 1 M KOH for 0.6 % Ru incorporation in cobalt oxide[111]. Lang *et al.* successfully synthesized Co_3O_4 /

MWCNT composites by chemical co-precipitation method [112]. The prepared electrode shows maximum value of SC around 418 F/g in 2 M KOH with good stability. The internal resistance observed from the EIS plot is 0.87 Ω for Co_3O_4 and 0.71 Ω for $\text{Co}_3\text{O}_4/\text{MWCNT}$. Lang *et al.* also showed that Co_3O_4 can interact with ions not only at the surface but also throughout the bulk. However, when a thick-and-compact cobalt oxide film is used for electrode fabrication, its poor electronic conductivity limits charge-transfer-reaction kinetics tremendously and difficulty occurs in the penetration of electrolyte into it. Therefore, the present drawback of cobalt oxide electrode is to increase the conductivity and potential window, using supported the 3D morphology. The 3D morphology enhances the surface area. Kim *et al.* [113] reported RuO_2 and Ru - Co mixed oxide deposited by electrochemical deposition of RuO_2 or the co-deposition of Ru - Co mixed oxides on the surface of single-walled carbon nanotubes using styrene butadiene rubber as a binder. The prepared electrode shows maximum value of SC 620 F/g at scan rate of 10 mV/s in 3 M NaCl. Lee *et al.* reported the change in value of SC of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ and VGCF/ $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ nanocomposite electrodes. At the scan rate of 10 mV/s the value of SC's were 410 and 1017 F/g and at 1000 mV/s were 258 and 824 F/g in 1M H_2SO_4 [114-116].

Recently, the uses of composite electrodes containing RuO_2 and carbon nanotubes have shown much higher SC after the use of either component individually [117-119]. On the other hand, it has been known that the incorporation of Co element in some metal oxides be able to improve the electrochemical properties [120]. For example, it was observed that the incorporation of cobalt atoms affects the structure and electrochemical behavior of nickel hydroxides [121]. Presently Wang *et al.* [122] reported review on electrode materials for aqueous asymmetric supercapacitors. Wang et al [123] reported preparation of an asymmetric supercapacitor using $\text{RuO}_2/\text{TiO}_2$ nanotube composite and activated carbon and their characterization like CV, CP, and EIS. The results show that the asymmetric supercapacitor has electrochemical capacitance performance within potential range 0 to 1.4 V. A power density 1207 W/kg was obtained with an energy density of 5.7 Wh/kg at charge - discharge current density 120 mA/cm². The supercapacitor also exhibits good cycling performance and maintain 90% of initial capacity over 1000 cycles. Dubal *et al.* [124] reported preparation of solution based, binder free synthetic approach of RuO_2 thin films for solid state supercapacitors. The XRD shows amorphous nature and

SEM shows nanosized smooth rounded nano grain type morphology. The calculated value of SC was 234 F/g at 5 mV/s scan rate in H₂SO₄ - PVA gel. The internal resistance observed from the nyquist plot was around 0.63 Ω/cm².

Ternary oxides also play vital role in order to improve the performance of the supercapacitor electrode. Some of the authors reported nanocrystalline and amorphous ternary oxide thin films with different supporting morphologies prepared by different materials and methods. Taniguchi *et al.* [125] reported the spray pyrolytic synthesis of nanostructured LiFe_xMn_{2-x}O₄ materials for lithium ion batteries. The XRD spectra of the prepared samples reveals single-phase of cubic spinel structure and porous surface morphology. Taniguchi *et al.*[126] reported powder properties of partially substituted LiM_xMn_{2-x}O₄ (M, Al, Cr, Fe and Co) synthesized by ultrasonic spray pyrolysis technique. The prepared sample shows pure cubic spinel structure and morphology changes from spherical porous to spherical dense with increasing metal substitution. Yu *et al.* [127] reported Hierarchical NiCo₂O₄@MnO₂ core-shell hetero structured nanowire arrays on Ni foam as high-performance supercapacitor electrode and desirable cycle life rates. The calculated value of SC was around 1471.4 F/g at 2 mV/s in 1 M LiOH.

In the overall literature it is observed that a very little work was carried out in the preparation of cobalt oxide, manganese doped/mixed cobalt oxide, ruthenium doped/mixed cobalt oxide and ternary oxide thin film electrodes by Electrodeposition and preparation of symmetric and asymmetric devices.

1.2 STATEMENT OF THE PROBLEM

Electrochemical energy storage systems are highly indispensable in today's information rich modern society and technology. Electrochemical storage device in particular meet all the requirements needed for energy and power applications. Supercapacitors have been received a lot of attention due to its applications in the field of energy/ power storage of hybrid electrical vehicles, digital communications, military, missiles etc. To improve the performance of supercapacitor electrode, preferably it requires conducting current collectors and coated material which is preferred with multi oxidation states, good electrical conductivity, mixed capacitive behavior, semi crystalline

(amorphous as well as crystalline), porous and hydrophilic nature, ideal polarizability, low ESR etc.

The aim of present dissertation is to carry out the systematic study which is essential to improve the performance of cobalt oxide electrode prepared by potentiodynamic electrodeposition.

In the *1st phase* of the work, thin film electrodes of cobalt oxide will be prepared via aqueous route by potentiodynamic electrodeposition technique. The deposition will be carried out on 304 no. SS substrates. The good quality samples will be decided on the basis of molar concentration, deposition time, annealing temperature, deposition scan rate and the CV measurements etc. The prepared samples will be optimized by considering physical characterizations like XRD, FESEM / SEM, EDX, AFM, TEM, contact angle measurement and electrochemical characterizations like cyclic voltammetry for SC measurement. Chronopotentiometry technique will be used to study the charge-discharge behavior and to calculate the SE, SP, and η values of the electrodes. Stability testing of the prepared electrode will be carried using CV. The internal resistance and capacitive nature of the final optimized electrode will be carried out using EIS technique. The nyquist plot will be used to search an equivalent circuit.

In the *2nd phase* of the work, systematic study has been planned to prepare manganese doped cobalt oxide thin film electrodes by potentiodynamic Electrodeposition via aqueous route using equimolar solutions of cobalt chloride and manganese chloride. The preparative parameters will be kept same as that of cobalt oxide. The prepared thin film samples will be characterized and optimized by considering physical and supercapacitive characterizations as made in phase 1.

In the *3rd phase* of the work, ruthenium doped/mixed cobalt oxide thin films will be deposited using potentiodynamic electrodeposition technique via aqueous route by using equi-molar solutions of cobalt chloride hexa-hydrate and ruthenium trichloride. The % incorporation of Ru is followed in the preparation of different samples. The prepared films will be characterized and optimized by considering physical and supercapacitive characterizations as made in the phase 1.

In the *4th phase* of the work, study is diverted towards preparation of symmetric and solid state devices. The optimized sample electrodes from the past work will be used for

the fabrication of supercapacitor devices. The prepared devices will be characterized by electrochemical characterizations like cyclic voltammetry, chrono-potentiometry and impedance spectroscopy.

In short, the present dissertation aiming preparation of cobalt oxide, manganese doped cobalt oxide, ruthenium doped cobalt oxide thin film electrodes by potentiodynamic electrodeposition technique via aqueous route. Structural, morphological, elemental and supercapacitive characterizations will be used to finalize the samples. By using the optimized electrode, devices will be prepared and their electrochemical characterizations will be explained in depth.

The purpose of the dissertation work is to improve the capacitive performance of cobalt oxide by incorporating multi - valency, morphology supporting manganese oxide and conducting ruthenium oxide by a potentiodynamic electrodeposition technique.

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