In this chapter, a literature survey on the synthesis and characterization of metal oxides and their supercapacitor applications are presented in detail. At the end of this chapter, scope of the present investigation is given.

2.1. INTRODUCTION

During the last few years, the electrode materials used for electrochemical supercapacitors have been extensively developed due to its high power and long cycle life than batteries for numerous applications such as power sources in next-generation electric vehicles, mobile electronic devices and the starting power for fuel cells. The energy storage in supercapacitors is usually based on the double-layer process due to the electrostatic force without phase transformation at the electrode–electrolyte interface and/or the faradaic redox reactions occurring near a solid electrode surface [1]. Based on the former mechanism of energy storage, the higher specific surface area of an electrode material has, the higher specific capacitance. In addition, the most promising materials for the application of supercapacitors should utilize both the fast and reversible Faradaic pseudocapacitance coming from the electroactive species and the indefinitely reversible double-layer capacitance at the electrolyte–electrode interface. Therefore, the development of electrode materials with the utilization of both double-layer capacitance and Faradaic pseudocapacitance becomes a subject of many electrochemists [2].
Active electrode materials for supercapacitors are broadly classified into three categories as (1) activated high surface area carbon (2) conducting polymers and (3) transition metal oxides [3]. Nanocrystalline metal oxides, which usually possess the characteristics of large surface area, high conductivity, electrochemical stability and pseudocapacitive behaviour. Among the various metal oxides, RuO$_2$ has metallic conductivity, high chemical and thermal stability, catalytic activities, electrochemical redox properties etc., in both crystalline and amorphous forms. Hence it gained importance with a large capacitance exceeding 700 F/g. Despite, the attainability of higher capacitance than all other oxide materials, the availability of the metal, cost and its probable toxicity have prompted to identify compounds to replace RuO$_2$ by cheaper materials [4]. Hence there is a need to have cheaper electrode materials for asymmetric supercapacitor applications.

2.2. LITERATURE SURVEY

B.E.Conway et al [5] developed cobalt oxide film with limited/unfavourable performance features: (a) a non-constant capacitance over its operable potential range; (b) possessing short (0.7V) range for reversible charge admission and withdrawal. J.H.Lim et al [6] reported the thin film sputtering process for the fabrication of RuO$_2$ electrodes for supercapacitors excluding the drawback of high cost. The capacitance fade was larger than the bulk supercapacitors due to its poor reversibility during charge-discharge process. Fei Cao et al [7] studied the synthesis of lead ruthenate pyrochlore (Pb$_2$Ru$_2$O$_{6.5}$) and used as electrodes for the fabrication of electrochemical capacitors. He found that the material exhibited high pseudocapacitance with improved specific energy, under constant-power discharge
of more than 5Wh/kg at 750 W/kg power level and significant saving in material cost compared to pure noble metal oxides.

Nae-Lih Wu [8] studied the two sets of SnO₂ based supercapacitors: one set comprised of Sb-doped SnO₂ nanocrystallites synthesized by sol-gel process with a specific capacitance of 16 F/g or 64 F/cm³ in 1M KOH and the other set comprised of nanocrystalline SnO₂ with Fe₃O₄ exhibited a capacitance of 33 F/g/130 F/cm³ in 1M Na₂SO₄. J.H.Park et al [9] reported the RuO₂ thin film electrodes prepared by heat treatment of metal alkoxide adsorbed onto carbon paper. Due to the porous graphite fiber substrate that acted to increase the contact area and allowed to complete the reaction between the RuO₂ and the electrolyte, this composite material possessed a specific capacitance of 620 F/g and good power characteristics. N.L.Wu et al [10] reported the improvement of SnO₂ electrodes with a maximum specific capacitance of 10 F/g in 1M KOH at 200 mV/s after firing at 800°C. The SnO₂ electrodes showed an enhancement with increasing charge-discharge rate due to improved oxide conductivity. W.Sugimoto et al [11] reported the electrochemical behaviour of a hydrous ruthenic acid consisting of an electroconducting crystalline network of ruthenium oxide layers nanometrically interleaved with a hydrous layer. The specific capacitances measured at 2 mV/s and 500 mV/s were 390 F/g and 330 F/g, respectively revealed excellent fast charge/discharge property.

Jong Hyeok Park et al [12] studied the electrochemical characteristics of RuO₂/multiwalled carbon nanotube (CNT) nanocomposite used as electrodes for supercapacitors. The specific capacitances reported for RuO₂/pristine CNT nanocomposites and RuO₂/hydrophilic CNT nanocomposite based on the combined masses and the mass of RuO₂ were 70, 500 F/g and 120, 900 F/g, respectively.
Thierry Brousse et al [13] reported the electrochemical characterization of a hybrid supercapacitor using a composite Fe$_3$O$_4$ negative electrode and a composite MnO$_2$ positive electrode in 0.1 M K$_2$SO$_4$. The specific capacitances of MnO$_2$ and Fe$_3$O$_4$ were found to be 150 ± 10 and 75 ± 8 F/g, respectively whereas the specific capacitance of the Fe$_3$O$_4$/MnO$_2$ capacitor was equal to about 20 F/g of the active material. It showed a real energy density of 7 Wh/kg with a power density of 820 W/kg when cycled between 0 and 1.8 V for over 5000 cycles. K.R.Prasad et al [14] reported the potentiodynamically deposited nanostructured SnO$_2$ onto an inexpensive stainless steel (SS) substrate for redox supercapacitor application in 1M Na$_2$SO$_4$. This nanostructured material showed a specific capacitance of 285 F/g and 101 F/g at the scan rates of 10 mV/s and 200mV/s, respectively with high stability of the material and high power density. Matheiu Toupin et al [15] synthesized MnO$_2$ powders by co-precipitation and adopted both thick and thin film electrodes for the supercapacitor applications. The specific capacitance of 1380 F/g was obtained for the thin film electrode involved one electron per manganese atom. The coulombic efficiency was about 100% indicating that all the MnO$_2$ material was taking part in the electrochemical process.

K.R.Prasad et al [16] also reported the nanostructured and nanorod-shaped three-dimensional In$_2$O$_3$ prepared by potentiodynamic method. A high specific capacitance of 190 F/g and 80 F/g was observed at the scan rates of 10 mV/s and 100 mV/s, respectively. These values of specific capacitances are higher than the other inexpensive oxides of much lower scan rates indicating the very high power characteristics of the material than RuO$_2$. He further studied the potentiodynamic deposition of mixed oxides based on MnO$_2$ namely nickel-manganese oxide (NMO)
and cobalt-manganese oxide (CMO) and characterized them for supercapacitor applications. The specific capacitance values of 621, 377 F/g and 498, 307 F/g were obtained with NMO and CMO electrodes, respectively at a cyclic voltammetric scan rate of 10 mV/s and 200 mV/s respectively, indicating high power characteristics of the binary oxides. These materials also showed long cycle-life and excellent stability [17]. Wang yong - gang et al [18] reported the RuO2 /TiO2 nanotubes composites. A maximum specific capacitance of 1236 F/g was obtained for the RuO2 with loading on TiO2 nanotube. The nanotube network of TiO2 provided a solid support to the RuO2 active material.

Thierry Brousse et al [19] designed a hybrid electrochemical capacitor using MnO2 and activated carbon (AC) as positive and negative electrodes, respectively in a mild aqueous electrolyte of 0.65 M K2SO4. This hybrid capacitor delivered a reproducible energy density of 10 Wh/kg and a real power density of 3600 W/kg. B-O.Park et al [20] prepared thin film ruthenium oxide electrodes by cathodic electrodeposition and used for supercapacitor applications in 0.5M H2SO4 electrolyte. This electrode with a thickness of 0.0014 g/cm² exhibited a maximum specific capacitance of 788 F/g. Yunhong Zhou et al [21] reported the capacitive characteristics of manganese oxides and polyaniline (M-P) composite thin film deposited on porous carbon in 0.1M Na2SO4 solution. The capacitance of M-P film materials reached a value of 500 F/g and it maintained 60 % of the initial capacitance after 5000 cycles. Han-Ki Kim et al [22] studied the characteristics of RuO2-SnO2 nanocrystalline-embedded amorphous electrode, grown by DC reactive sputtering method. The cyclic voltammogram obtained for RuO2-SnO2 nanocrystalline-embedded amorphous film in 0.5M H2SO4 liquid electrolyte was
similar to a bulk-type supercapacitor behaviour with a specific capacitance of 62.2 mF/cm² μm which was higher than the amorphous RuO₂ film.

Ji Yeong Lee et al [23] reported the fabrication of supercapacitor electrodes with nickel oxide (NiO)/carbon nanotubes (CNTs) nanocomposite formed by a simple chemical precipitation method. The specific capacitances reported for the bare NiO and NiO/CNT (10%) nanocomposite were 122 and 160 F/g, respectively with improved power density and cycle life. Fang Xiao et al [24] adopted the simple calcined method to prepare the brown-millerite type SrCoO₂.₅ and characterized by cyclic voltammogram and charge-discharge studies. It showed a maximum capacitance of 170 F/g and 168.5 F/g calculated from cyclic voltammetric studies respectively. Meigen Deng et al [25] studied the CNTs-MnO₂ nanocomposite prepared by coating MnO₂ on the surface of CNTs. The deposition of MnO₂ improved the specific capacitance of the CNTs from 49 to 146 F/g. It also showed an outstanding power performance and an energy density of 5.1 Wh/kg. Masaharu Nakayama et al [26] developed the manganese and molybdenum mixed oxides in a thin film form and used as electrode for supercapacitors. It exhibited a specific capacitance of 190.9 F/g and better reversibility compared to that of pure Mn oxide.

Chi-Chang Hu et al [27] studied an advanced electrode material with a 3D, arrayed, nanotubular architecture-annealed RuO₂.xH₂O based nanotubes with ultrahigh power characteristics and high capacity performances required for the next generation supercapacitors by using a very simple, one-step, reliable, cost-effective, anodic deposition technique. The specific power and specific energy of RuO₂.xH₂O nanotubular arrayed electrodes measured at 0.8 V and 4 kHz was equal to 4320 kW/kg and 7.5 Wh/kg, respectively. D.Rochefort et al [28] studied the
electrochemical behaviour of a thermally prepared RuO$_2$ in a proton exchange room temperature molten salt composed of 2-methyl pyridine and trifluoroacetic acid. The shape of the cyclic voltammograms obtained for the RuO$_2$ electrode in the protic ionic liquid was similar to that obtained in H$_2$SO$_4$ and showed distinct redox peaks due to Faradaic reactions across the electrolyte/electrode interface, giving rise to pseudocapacitance. The specific capacitance of the electrode in the protic ionic liquid (83 F/g) was in the same order of magnitude to that obtained in water-based electrolyte but was ten times higher than that in an aprotic ionic liquid composed of 1-ethyl-3-methyl imidazolium tetrafluoroborate. Jianguo Wen et al [29] prepared the hydrous ruthenium oxide (RuO$_x$.nH$_2$O) on titanium substrate by cyclic voltammetric method in the range of -100 to 1000 mV in 1 M H$_2$SO$_4$ electrolyte. The average specific capacitance was measured as 105 F/g.

Li-Ming Huang et al [30] reported a new composite film, (PEDOT-PSS-RuO$_2$ film) prepared by depositing hydrous ruthenium oxide (RuO$_2$) particles into a polymer matrix comprising of poly(3,4-ethylene dioxythiophene) (PEDOT) and poly(styrene sulfonic acid) (PSS). Specific capacitance of the PEDOT-PSS-RuO$_2$ composite was found to be 1409 F/g and the enhancement of capacitance was due to uniform distribution of hydrous RuO$_2$ into a three-dimensional conducting PEDOT-PSS matrix. D.Kalpana et al [31] studied the zinc oxide (ZnO) with carbon aerogel (CA) synthesized by a simple co-precipitation process and used as active material for symmetric electrochemical supercapacitor. The cyclic voltammetric studies showed a specific capacitance of 25 F/g in 6M KOH electrolyte and the charge-discharge measurement exhibited a maximum specific capacitance value of 500 F/g at 100 mA/cm$^2$ which was constant upto 500 cycles. V.Subramanian et al [32]
employed the hydrothermal technique to prepare nanostructures of MnO2 under mild conditions. The synthesized nanostructured MnO2 with a specific surface area of 132 m²/g showed a good pseudocapacitive behaviour with a specific capacitance of 168 F/g with a cycling efficiency of 83% for 100 cycles at fairly high current of 200 mA/g. Shin-Liang Kuo et al [33] synthesized the MnFe2O4-CB (carbon black) composite powders by a co-precipitation method and characterized for their electrochemical properties. The composite showed the highest capacitance of 56 F/g with NaCl and a lowest capacitance of 43.5 F/g with aqueous CsCl.

Mengqiang Wu et al [34] prepared the highly porous NiO was prepared by the combination of sol-gel process with supercritical drying method. The average specific capacitance of the aerogel like NiO was observed to be about 75-125 F/g between a potential window of 0-0.35 V vs SCE. V.Subramanian et al [35] studied the composites of amorphous MnO2 and single walled carbon nanotubes (SWNTs) at a high charge-discharge current of 2 A/g. He observed the typical capacitive behaviour of pure MnO2, the pure SWNTs and the composites by cyclic voltammetric studies. The EIS measurements showed a decrease in resistance with respect to the increase of SWNT content in the composites. The composites with 5 wt% SWNTs showed the highest specific capacitance during initial cycles. T.Cottineau et al [36] studied different transition metal oxides, namely MnO2, Fe3O4 and V2O5 as possible electrodes for electrochemical supercapacitors in natural aqueous media of 0.1 M K2SO4. He found that MnO2 and V2O5 hybrid devices exhibited a specific capacitance of 150 F/g and 170 F/g, respectively and Fe3O4 showed only 75 F/g of specific capacitance. Both MnO2 and Fe3O4 maintained its
specific capacitance values even after 1000 cycles whereas V_2O_5 electrode drastically faded after five hundred cycles.

Chin-yi Chen et al [37] prepared nanocrystalline MnO_2 powder by spray pyrolysis method using manganese acetate solution at 400°C. The as-obtained powders were subsequently coated onto graphite substrate via an electrophoretic deposition technique (EPD). This electrode showed the quite reversible electrochemical behaviour in aqueous electrolyte with a high specific capacitance of 275 F/g with a cycling efficiency of 85% after 300 cycles. The specific capacitance was found to decrease to 234 F/g after hundreds of CV cycles which was comparable to the value reported in the literature. E.C.Rios et al [38] prepared MnO_2 onto titanium substrate modified with poly(3-methylthiophene) (PMeT) and compared it with Ti/MnO_2 electrodes by electrodeposition method. He observed that the specific capacitance of Ti/MnO_2 was 122 F/g, while for Ti/PMeT_{250}/MnO_2 and Ti/PMeT_{1500}/MnO_2 the values were 218 and 66 F/g respectively in 1M Na_2SO_4.

Byung Jun Lee et al [39] prepared the amorphous RuO_2.xH_2O and a VGCF/RuO_2.xH_2O nanocomposite (VGCF= vapour grown carbon fiber) by thermal decomposition method. The specific capacitance of RuO_2.xH_2O and VGCF/RuO_2.xH_2O nanocomposite electrodes at a scan rate of 10 mV/s was 410 and 1017 F/g respectively, and at 1000 mV/s are 258 and 824 F/g respectively. Long-term cycle life tests for 10^4 cycles showed that the RuO_2.xH_2O and VGCF/RuO_2.xH_2O electrodes retain 90 and 97% capacity, respectively. Kuo-Hsin Chang et al [40] prepared RuO_2.xH_2O nanoparticulates in different crystal sizes by a hydrothermal synthesis route, demonstrating the independent control of crystal size and water content of RuO_2.xH_2O. The specific capacitance of RuO_2.xH_2O reached a
maximum of 540 F/g when the hydrothermal time was equal to 1.5 h, it then decayed monotonously to 390 F/g with prolonging the hydrothermal time from 1.5 to 24 h. Mahima Subhramania et al [41] prepared RuO2 nanoneedles by template-assisted electrodeposition method using aqueous RuCl3 solution under potentiostatic conditions at room temperature. The specific capacitance of these nanoneedles showed a higher value (3 F/g) compared to that of the bulk material (0.4F/g) which was explained on the basis of enhanced reactivity.

C.D.Lokhande et al [42] reported the supercapacitor performance of electrochemically deposited perovskite nanocrystalline porous bismuth iron oxide (BiFeO3) thin film electrode from alkaline bath. This showed comparable specific capacitance of 81 F/g and specific energy of 6.6832 J/g and specific power of 3.2958 W/g compared to other commonly used ruthenium based oxide perovskites. The perovskite BiFeO3 electrode was nanocrystalline with rhombohedral crystal structure showing porous surface morphology. Zhang Ying et al [43] prepared amorphous MnO2 by mechanochemical method was tested with cyclic voltammetry and constant current charge-discharge for the electrochemical supercapacitor performances. The positive electrode (PE) and negative electrode (NE) were investigated to find out their different performances in charge-discharge process. The capacitance of the NE was highly rate-dependent, decreasing from 12.3 to 53.1 F/g by 56.2 % over the range 5-25 mV/s. The PE appeared to be weakly dependent and its capacitance dropped only by 22%. The capacitive behaviour of CNT, V2O5, V2O5-CNT and SnO2-V2O5-CNT were studied by M.Jayalakshmi et al by cyclic voltammetry [44]. The V2O5 and CNT together gave a specific capacitance of 45-47 F/g on the 100th scan and the SnO2-V2O5-CNT electrode provided the best
performance value of 121.4 F/g, due to increase in the electronic properties of vanadium oxide by the presence of SnO$_2$ in the composite. This also included the capacitive behaviour of the composite.

Rak Young song et al [45] studied extensively the electrochemical capacitive behaviour of ternary composite (P-olyaniline/Nafion/hydrous RuO$_2$) in an aqueous electrolyte of 1M H$_2$SO$_4$. The ternary composite electrode displayed good cycleability and initial specific capacitance value of 325 F/g and 260 F/g after $10^4$ cycles with 80% capacitance retention for 50 wt% loading of hydrous RuO$_2$. At 100 mV/s the ternary composite showed specific capacitance of 475 F/g and at 1000 mV/s, it showed a specific capacitance of 375 F/g vs. Ag/AgCl. S.R.Sivakumar et al [46] reported the specific capacitances of (CNT/hydrous MnO$_2$/polypyrrole), CNT/hydrous MnO$_2$ and polypyrrole/hydrous MnO$_2$ in 1 M Na$_2$SO$_4$ electrolyte and are 281, 150, 32 F/g at 20 mV/s and 209, 75, 7 F/g at 200 mV/s for a fair MnO$_2$ loading of 0.64 mg/cm$^2$. The ternary composite showed much better electrochemical performances compared to binary composites. This was believed due to the good electrical conductivity of the composite and effective dispersion of hydrous MnO$_2$ in the composite electrode. The specific capacitance value of ternary composite showed 146 F/g which decreased rapidly during 500 cycles and ended with 35 F/g at 2000$^{th}$ cycle. A composite consisting of RuO$_2$.xH$_2$O particles deposited on carbon nanofibres had been prepared by accumulative treatment consisting of impregnation of carbon nanotubes with RuCl$_3$.0.5 H$_2$O solution, filtering to remove RuCl$_3$.0.5 H$_2$O excess and neutralization with NaOH solution to get RuO$_2$.xH$_2$O. The specific capacitance decreased from 840 to 440 F/g as the particle size increased from 2 to 4 nm [47]. Hydrous ruthenium oxides with the addition of carbon nanotubes (CNT) (0.0125 - 0.1 wt %) co-deposited on Ti substrate by cathodic deposition
method was studied by H.-S.Hwang et al [48]. The experimental results showed a maximum capacitance of about 719 F/g with the addition of 0.05 wt% of CNT and for a deposition period of 60 minutes.

X.Liu et al [49] constructed the hydrous ruthenium oxide electrodes for supercapacitor by sol-gel method. A high specific capacitance of 977 F/g was obtained for Ru oxide loading of 5 mg/cm² in 1M H₂SO₄ aqueous electrolyte. Their average power densities and energy densities exceeded 30 W/g and 30 Wh/kg, respectively during full discharge. This outstanding performance was due to the primary use of carbon fiber paper as a support for Ru oxide. Cobalt-nickel oxide/VGCF (vapour grown carbon fiber) composites were prepared by thermally decomposing cobalt and nickel nitrates directly onto the nickel foam substrate. Cyclic voltammetric studies exhibited the specific capacitance values of 1271 F/g at 5 mV/s and 955 F/g at 100 mV/s. The VGCF also played the role in reducing the interfacial resistance in the cobalt-nickel oxide to improve the capacitance performance [50].

Z.Fan et al [51] prepared MnO₂/graphite nanoplatelet (GNP) composites by hydrothermal method. The MnO₂ nanorods dispersed homogeneously on both surfaces of the GNPs and formed a coating structure indicating the excellent electrochemical properties. The specific capacitance of MnO₂/GNPs increased monotonously with increasing GNP content, and its maximum specific capacitance was 276.3 F/g. Additionally, the coating structure decreased the amount of conductive filler needed to meet the requirement of the electrode material. The specific capacitance based on the composite was 158 F/g by the addition of only 10 wt% GNPs.

Nanocrystalline iron-added manganese oxide powder was prepared by spray pyrolysis (SP) method by using manganese acetate and iron nitrate solutions at
400°C. The as-obtained powder was subsequently deposited onto graphite substrates via an electrophoretic deposition technique (EPD). The iron addition significantly improved the electrochemical properties of the Mn-oxide powder coatings. The specific capacitance of as-deposited Mn-oxide coating was increased from 202 F/g to 232 F/g when 2 wt% of iron was added. Even after 1200 cycles of life test, the iron-added coating exhibited higher cycling efficiency (~78% initial capacitance) than that of the unadded one (~60%). Wei-Chuan Fang [52] studied the capacitive properties of vanadium oxide on carbon nanotubes. The vanadium oxide uniformly deposited on carbon nanotubes gave rise to significant improvement in capacitive performance as compared with V₂O₅ film. Hence, the V₂O₅/CNT nanocomposite showed promise as an auxiliary power backup of hybrid electrical systems or consumer electronics. Menqiang Wu et al [54] reported the electrochemical performance of cathodically deposited amorphous SnO₂ onto graphite electrode. A maximum specific capacitance of 298 and 125 F/g was achieved from cyclic voltammetry at a scan rate of 10 and 200 mV/s, respectively. It also showed good cycle-life and stability. The specific capacitance of 265 F/g decreased to 95 F/g with increasing deposition rate from 0.2 to 6 C/cm². K.Karthikeyan et al [55] introduced ZnCo₂O₄/CNF as electrode material for supercapacitors. This material exhibited high specific capacitance and low impedance compared to pure metal oxide nanocomposites. The introduction of CNF in metal oxide increased the specific capacitance value by reducing the internal resistance of the electrode. It also showed a high capacitance of 77 F/g with long cycle life and high coulombic efficiency with minimum IR.
Hybrid films of polyaniline (PANI) and manganese oxide (MnOₓ) obtained by potentiodynamic deposition showed a 44% increase in specific capacitance from that of PANI (408 F/g) to 588 F/g, measured at 1 mA/cm² in 1M KNO₃ at pH 1. It also retained 90% of its capacitance after 1000 cycles with a coulombic efficiency of 98% [56]. Single crystalline Mn₃O₄ and MnOOH, successfully synthesized by hydrothermal process by Chi–Chang Hu et al [57]. The potentiodynamic activities for 200 cycles between 0 and 1V in 1M Na₂SO₄ at 25 mV/s showed relatively high capacitance of 170F/g with high power density and excellent stability for supercapacitor application. R.K.Selvan et al [58] reported the synthesis of hexagonal shaped SnO₂ nanocrystals and SnO₂/C nanocomposites for electrochemical redox supercapacitors. The material synthesized at 700°C has a specific capacitance of 37.8 F/g which is a suitable candidate for supercapacitor application. B.C.Kim et al [59] reported the capacitive properties of RuO₂ and Ru-Co mixed oxides prepared by potentiodynamic deposition on the surface of SWNT. Electrodes coated with the Ru-Co mixed oxide exhibited a specific capacitance of 620 F/g at low potential scan rates of 10 mV/s and 570 F/g at higher scan rates 500 mV/s. The increased capacitance at high scan rates is due to the enhanced electronic conduction of Co. Kentaro Kuratani et al [60] studied the RuO₂ electrodes prepared using a mesoporous silica, as the hard template. A specific capacitance of 200 F/g at the scan rate of 1 mV/s in aqueous H₂SO₄ was observed.

Te- Yu Wei et al [61-63] studied the supercapacitive properties of cobalt oxide aerogels prepared by an epoxide addition procedure. The specific capacitance of 623 F/g of cobalt oxide calcined at 200°C was much higher than those achieved by other mesoporous cobalt oxides, such as loose-packed cobalt oxide nanocrystals.
and the cobalt oxide xerogels. E. Beaudrouet et al [64] reported the low-cost layered manganese oxides with the ranciète structural type prepared by reduction of KMnO₄ or NaMnO₄ in acidic aqueous medium, followed or not by successive proton and alkali-ion-exchange reactions. Capacitances measured at 2 mV/s, for the different samples ranged from 7 F/g to 112 F/g in K₂SO₄ electrolyte. Qunting Qu et al [65] reported the electrochemical performance of MnO₂ nanorods prepared by a precipitation reaction and was investigated in 0.5 mol/L Li₂SO₄, Na₂SO₄ and K₂SO₄ aqueous electrolyte solutions. The nanorods showed the largest capacitance of 201 F/g in Li₂SO₄ electrolyte at slow scan rates. An asymmetric activated carbon (AC/K₂SO₄/MnO₂) supercapacitor could be cycled reversibly between 0 and 1.8 V with an energy density of 17 Wh/kg at 2 kW/kg and also it exhibited an excellent cycling behaviour with no more than 6% capacitance loss after 23,000 cycles at 10 C rate.

Torsten Brezesinski et al [66] reported the synthesis and pseudocapacitive characteristics of block co-polymer template anatase TiO₂ thin films synthesized using either sol-gel reagents or preformed nanocrystals as building blocks and the specific charge capacity was 168 mAh/g. Rajaram S. Mane et al [67] studied the use of low-cost electrochemically synthesized hydrophilic and nanocrystalline tin oxide film electrodes at room temperature in dye-sensitized solar cells and electrochemical supercapacitors. Cyclic voltammetric studies revealed the interfacial and specific capacitances as 118.4 µF/cm² and 43.07 F/g respectively in 0.1 M NaOH electrolyte. Rongrong Jiang et al [68] synthesized the nanostructured MnO₂ by co-precipitation method and found out a specific capacitance of 176 F/g when used as electrode material for supercapacitors. Gum-Jae Park et al [69] reported a
hybrid system consisting of KS6 graphite and Nb$_2$O$_5$ which delivered a highest initial discharge capacity of 55 mAh/g and a good cycle performance. G.Wang et al [70] synthesized nanoporous Co$_3$O$_4$ nanorods by a hydrothermal method and studied the supercapacitive performances by cyclic voltammetric measurements. The maximum specific capacitance of 281 F/g was due to the high specific surface area than the commercial microcrystalline Co$_3$O$_4$ powders that exhibited only 43 F/g of specific capacitance.

Yaohui Wang et al [71] reported the deposition of composite manganese dioxide – MWCNT films by cathodic EPD method. The pseudocapacitive behaviour of the films are tested in a potential window of 0-0.9 V vs SCE in 0.5M Na$_2$SO$_4$ solutions. The highest specific capacitance of ~650 F/g was obtained at a scan rate of 2 mV/s. Feng – Jiin Liu et al [72] demonstrated a novel and simple route for preparing a composite comprising of manganese oxide (MnO$_2$) nanoparticles and polyaniline (PANI) doped poly(4-styrene sulfonic acid-co-maleic acid) (PSSMA) by “electrochemical doping-deposition”. The specific capacitance of PANI-PSSMA-MnO$_2$ (50.4 F/g) in 0.5M Na$_2$SO$_4$ had improved values than PANI (18.5 F/g), when only the MnO$_2$ mass was considered, the composite had a specific capacitance of 556 F/g. Xuan Du et al [73] reported the activated carbon (AC)-Fe$_3$O$_4$ nanoparticles for asymmetric supercapacitors and were characterized in 6M KOH aqueous electrolyte. The asymmetric supercapacitor delivered a specific capacitance of 37.9 F/g at a current density of 0.5 mA/cm$^2$ and it also retained 82 % of initial capacity over 500 cycles. Po-Chiang Chen et al [74] developed a prototype, flexible and transparent supercapacitor from In$_2$O$_3$ nanowires/CNT heterogeneous films with a specific capacitance of 64 F/g. After 100 cycles, there is a little specific capacitance
decreased from 64 to 53 F/g, attributed to the dissociation of In$_2$O$_3$ nanowires during the redox process in GV measurements.

Hongfang Li et al [75] studied a mesostructured NiO/C composite with NiO nanoparticles studded in the wall of mesoporous carbon synthesized by a facile co-casting process. A large specific capacitance of 243 F/g for NiO/C composites and 456 F/g for the NiO nanoparticle were obtained. Gao-Ren Li et al [76] developed a simple and facile electrochemical deposition method for the preparation of mesoporous MnO$_2$/carbon aerogel composites and used as supercapacitor electrodes. The high specific capacitance of 515.5 F/g and good cycle ability coupled with the low cost and environmentally benign nature of the MnO$_2$/aerogel composite made them attractive for large applications. Katsutoshi Fukuda et al [77] studied the preparation and characterization of [Ru$^{3.8+}$O$_2$$^{0.2-}$] nanosheets with well-defined hexagonal symmetry via the soft-chemical delamination of an α-NaFeO$_2$ related layered ruthenium oxide. The restacked RuO$_2$ nanosheet electrode exhibited a high specific capacitance of ~700 F/g of RuO$_2$ in an acidic electrolyte, which was almost double the value of the non-exfoliated layered protonated ruthenate. Rong-Rong Bi et al [78] demonstrated the direct growth of RuO$_2$ nanoparticles on the CNTs surface with a simple and convenient solution-based method. The RuO$_2$/CNT composite with a mass ratio of 6:7 achieved a specific capacitance of 953 F/g, power density of 5000 W/kg and energy density of 16.8 Wh/kg.

Michael T. Brumbach et al [79] reported ruthenium oxide as a model pseudocapacitive material with good electronic and protonic conduction. The specific capacitance measured about 400-500 F/g for the ruthenium oxide material. A. Leela Mohana reddy et al [80] studied the multisegmented Au-MnO$_2$/carbon nanotube
hybrid coaxial arrays for high power supercapacitors. The material showed excellent electrochemical performance with a maximum specific capacitance of 68 F/g, a power density of 33 kW/kg and an energy density of 4.5 Wh/kg. Sheng Chen et al [81] demonstrated the graphene oxide (GO)–manganese dioxide (MnO2) nanocomposite prepared by a simple solution method of low temperature. The integration of GO and the needle like MnO2 crystals enable good electrochemical behaviour to use as electrode materials for supercapacitors. It showed a discharge specific capacitance of 216 F/g and retained about 84.1% of initial capacitance over 1000 cycles than that of MnO2 (69%).

Aurelien Du Pasquier et al [82] reported the electrochemically prepared poly(methylthiophene) as a cathode and Li4Ti5O12 anode in asymmetric hybrid supercapacitor. This hybrid device exhibited a higher specific energy of 10 Wh/kg and better cycle life than a Li-ion battery. Fang Chen et al [83] reported the randsellite, Li2Ti3O7 used as an anode material for asymmetric supercapacitors. A reversible specific capacity of 150 mAh/g in aqueous electrolyte and good cycleability was observed for 500 cycles. It also exhibited good rate capability.

Yong – Gang Wang et al [84] reported a new concept hybrid electrochemical super capacitor technology in which activated carbon was used as a negative electrode and a lithium-ion intercalated compound, LiMn2O4 as a positive electrode in a mild Li2SO4 aqueous electrolyte. The charge/discharge process was associated with the transfer of Li-ion between two electrodes. The hybrid cell exhibited a sloping voltage profile from 0.8 to 1.8 V, and delivers an estimated specific energy of 35 Wh/kg based on the total weight of active electrode materials. The cell exhibited
excellent cycling performance with less than 5 % capacity loss over 20,000 cycles at 10C charge/discharge rate.

Guixin Wang et al [85] prepared LiNi_{0.8}Co_{0.2}O_{2} by gel-like method to use as electrode material for supercapacitors. This was mixed with MWCNT to form composite electrodes, which showed a maximum specific capacitance of 271.6 F/g with 317.2 Wh/kg energy density and 96.7% coulombic efficiency.

Lian-Mei Chen et al [86] fabricated a hybrid electrochemical capacitor with LiCoO_{2} as a positive electrode and activated carbon (AC) as a negative electrode in various aqueous electrolytes. Pseudo-capacitive properties of LiCoO_{2}/AC were studied by cyclic voltammetry, charge-discharge test, and electrochemical impedance measurement. He observed that the potential range, scan rate, species of aqueous electrolyte and current density had great effect on capacitive properties of the hybrid capacitor. In the potential range of 0-1.4 V, it delivered a discharge specific capacitance of 45.9 F/g (based on the active mass of the two electrodes) at a current density of 100 mA/g in 1M Li_{2}SO_{4} aqueous electrolyte. The specific capacitance remained 41.7 F/g after 600 cycles.

J.-H. yoon et al [87] studied various methods of synthesis of layered Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2} cathode materials and used as a positive electrode for asymmetric electrochemical capacitor with activated carbon as negative electrode. Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2} prepared by the carbonate co-precipitation exhibited higher capacitance and better rate capability with stable cycling retention over 500 cycles than Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2} prepared by the hydroxide-co-precipitation. The asymmetric electrochemical capacitor cell, AC/ Li[Ni_{1/3}Co_{1/3}Mn_{1/3}]O_{2} had a voltage slope from 0.2 to 2.2 V and delivered a capacity of 60 F/g with a capacity retention of 88.4 % during 500 cycles based on the overall active materials weight. The leakage
current was largely decreased for the asymmetric electrochemical capacitor and the maintained voltage was 84.4 % during 3 days.

Y.Zhao et al [88] used LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ as positive electrode and activated carbon as negative electrode for asymmetric supercapacitor application. Their electrochemical properties indicated that the species of aqueous electrolyte, current density, scan rate and potential limit, etc. had influenced on the capacitance properties of AC/ LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ supercapacitor. The initial discharge specific capacitance of 298 F/g was obtained in 1M Li$_2$SO$_4$ solution within the potential range of 0-1.4 V at the current density of 100 mA/g and was cut down less than 0.058 F/g per cycling period in 1000 cycles and exhibited a good cycling performance.

Yun Xue et al [89] studied the supercapacitive performances of LiAl$_x$Mn$_{2-x}$O$_4$ synthesized by high temperature solid-state reaction was investigated by means of galvanostatic charge-discharge, cyclic voltammetry and AC impedance in 2M ($\text{NH}_4$)$_2$SO$_4$ aqueous solution. LiAl$_x$Mn$_{2-x}$O$_4$ showed rectangular shape performance in the potential range of 0-1 V. The capacity and cycle performance could be improved by doping Al and the composition of $x = 0.1$ was only about 14 % after 100 cycles.

Huiming Wu et al [90] studied the electrochemical performance of a hybrid asymmetric supercapacitor with activated carbon (AC) as anode and a lithium-ion intercalated compound LiNi$_{0.5}$Mn$_{1.5}$O$_4$ as cathode. The fabricated hybrid supercapacitor, AC/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in a non-aqueous electrolyte, 1M LiPF$_6$/EC-DMC exhibited a sloping voltage profile from 1.0-3.0 V and delivered a specific energy of ca. 56 Wh/kg. Moreover, it exhibited excellent cycling performance with less than 5 % capacity loss over 1000 cycles.

K.Karthikeyan et al [91] developed a novel hybrid supercapacitor with Li$_2$MnSiO$_4$ as the negative electrode and activated carbon as the positive electrode.
in 1.0 M LiPF$_6$/EC:DMC electrolyte. The initial specific capacitance obtained from the charge-discharge curve was 43.2 F/g at a current density of 1 mA/cm$^2$. The specific capacitance decreased slightly with increasing current density and thereby showed that the LMS/AC cell has a high charge-discharge rate capability. The hybrid supercapacitor retained approximately 85% of its initial capacitance and also exhibited a good cycleability with a high coulombic efficiency of greater than 99%, even after 1000 cycles.

R. Santhanam et al [92] reported the progress of high voltage spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ material because of its high voltage (4.7 V), acceptable stability and good cycling performance in the case of Li-ion batteries. He also reported the effect of doping, effect of coating on LiNi$_{0.5}$Mn$_{1.5}$O$_4$ material and its applications in asymmetric supercapacitors. This system exhibited excellent capacity retention even after 1000 cycles with high power density and high energy density.

2.3. SCOPE OF THE PRESENT INVESTIGATION

Numerous electroactive materials such as transition metal oxides and conducting polymers have been investigated extensively to enhance the capacitance and energy characteristics of supercapacitors. Recently, Lithium intercalated compounds such as LiCoO$_2$, LiNi$_{0.8}$Co$_{0.2}$O$_2$, etc. Has been used as cathode materials for supercapacitors to improve their energy and power densities [85]. In this direction, it is proposed further to prepare LiMn$_2$O$_4$ and doped LiMn$_2$O$_4$ nanopowders such as LiAl$_{0.3}$Mn$_{1.7}$O$_4$, LiCr$_{0.3}$Mn$_{1.7}$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, and LiSm$_{0.1}$Mn$_{1.9}$O$_4$ by low temperature combustion method using glycine as the fuel to use as used as cathode materials for asymmetric supercapacitor applications.
The thermal analysis (TG/DTA) will be used to understand the thermochemical properties such as decomposition temperature and phase formation temperature etc., of the prepared precursor samples.

The phase purity of LiMn$_2$O$_4$ based cathode materials will be confirmed by XRD studies.

The morphology and the average particle size of the prepared LiMn$_2$O$_4$ and doped LiMn$_2$O$_4$ nanopowders will be observed using scanning electron microscope (SEM) studies.

Finally, the asymmetric supercapacitors will be fabricated by using the synthesized LiMn$_2$O$_4$ and doped LiMn$_2$O$_4$ nanopowders as the cathode materials and the activated carbon as an anode and a porous polypropylene separator in 1M LiPF$_6$ - EC: DMC (1:1 v/v) as an electrolyte.

Cyclic voltammetric studies will be carried out in the potential range of 0.0 to 3.0 V at different scan rates of 5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s and 100 mV/s to find out the specific capacitance ($C_m$) of the capacitor cells.

AC impedance studies will be carried out on the open circuit potential (OCP) in the frequency range of 100 kHz to 1 mHz at the a.c. amplitude of 10 mV to find out the internal resistance ($R_i$) of the capacitor cells.

The charge-discharge studies will be carried out at a constant current density of 1mA/cm$^2$ to find out the discharge specific capacitance ($C_m$), coulombic efficiency ($\eta$), internal resistance ($R_i$), energy density ($E_d$) and power density ($P_d$) of the capacitor cells.

Finally, the synthesized LiMn$_2$O$_4$ and doped LiMn$_2$O$_4$ nanopowders will be selected based on their asymmetric supercapacitor performances.
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