Oxide Materials used for Supercapacitor Applications: A Comprehensive Review

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***Abstract*—Supercapacitors are an emerging class of energy storage devices combining high power density, long cycle life, and rapid charge–discharge rates. Electrode material selection critically commands their efficiency. Efficiency of supercapacitor is multifaceted, depending on a material's capacitance, energy density, power density, rate capability, electrical conductivity, cyclability, and manufacturing feasibility Current research has explored the sustainable synthesis of Metal oxides emerged as promising materials for supercapacitor electrodes owing to their high theoretical capacitance, multiple oxidation states, and better chemical stability than polymers. This review confers information about supercapacitor's performance formed by metal oxides. Detailed about preparation methods and supercapacitor properties are discussed.**

***Index Terms*—metal oxides, supercapacitors, performance and efficiency**

I. INTRODUCTION

As considering the energy shortage and environment destruction, there is an increasing interest in high-power and high-energy density storage systems [1]. There has been great interest in developing more efficient energy storage devices. Batteries, fuel cells and supercapacitors are typical non-conventional energy devices, which are based on the principle of electrochemical energy conversion. They find tremendous applications in consumer electronics ranging from mobile phones, laptops, digital cameras, emergency doors and hybrid vehicles etc [2-4]. The origin of capacitor was introduced by famous Leyden jar experiment in 1745 [5]. The experiment gave new avenues for capacitive charge storage. The first device to work double layer charge storage mechanism was described by General Electric in 1957. However, the device was not practical for commercial application. After that, SOHIO, standard oil company of Ohio applied for a patent for invention of a device able to store higher charge. The capacitance achieved by this device was much larger than that of previous result. The Nippon Electric company obtained the license in 1975 and came up with a device in 1978 which they name as Supercapacitor. Supercapacitors have great potential in the area of portable electronic equipment, renewable energy systems, and hybrid power cars [6-8]. Supercapacitor is a typical energy storage device (similar to secondary battery) which possess high specific capacitance, high power density and long cycle life [9-13]. Supercapacitor consists of two identical electrodes with a separator immersed in an electrolyte. Electrode material plays an important role in supercapacitor. There should be an active contact between the electrode materials and the electrolyte to attain good supercapacitive properties

Types of Supercapacitors

Depending on the type of energy storage in supercapacitors, they are classified as in to electrical double layer capacitors (EDLC) and pseudo-capacitors. Electrochemical supercapacitors occupy a unique space in energy storage, offering very high power density and long cycle life compared with batteries, while generally having lower energy density.

Electric Double Layer Capacitors (EDLC)

Electric Double Layer Capacitors store the electric charge directly across the double layer of the electrode. This EDLC is termed as a true capacitance effect since there is no charge transfer across the interface. The capacitance contributed by EDLC is similar to that of a parallel plate capacitor. EDLC is based on principle of adsorption. EDLCs are made up of two carbon based porous electrode material which are separated by an insulator. In EDLC the charge is stored in a non-faradaic manner. The charge storage mechanism is based on the electrostatic charge accumulation at the electrode-electrolyte interface. Symbolically it is

represented as shown in Fig. (1). In EDLC generally electrode material is activated carbon [14-16].

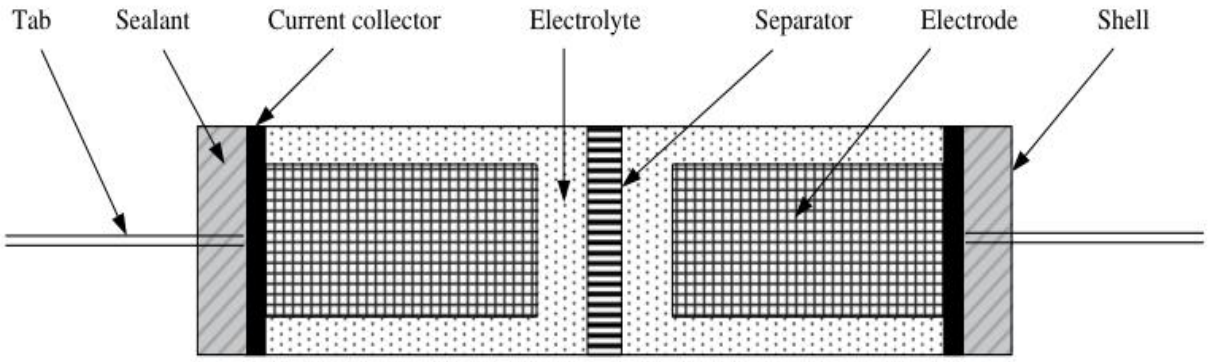

Fig. 1 Schematic diagram of Electric Double Layer Capacitors

Pseudo-capacitors

Pseudo-capacitors electrostatically store the charge and the faradaic charge transfer occurs at electrode-electrolyte interface. It has high specific capacitance and high energy density than the electrical double layer capacitance. The mechanism that allows pseudocapacitors to store energy is a faradaic redox reaction that occurs close to the surface between the electrode materials and the electrolyte ions. This reaction is both quick and reversible. Pseudocapacitors typically have a higher capacitance per gram than EDLCs, but their kinetics are slower. Reaction mechanism in pseudo capaciotrs is shown as in Fig. (2). RuO_2, Transition metal oxides [17, 18] and conducting polymers [19-21] are good examples of pseudo-capacitors or redox capacitors.

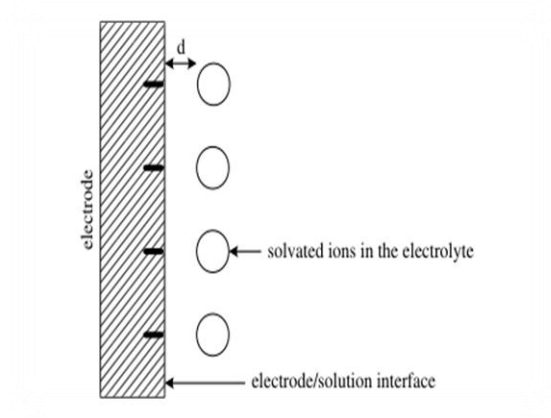

Fig. 2 Reaction Mechanism in Pseudo-Capacitors

Hybrid Electrochemical Capacitors

The hybrid type supercapacitors combines the advantages of EDLC and the pseudo capacitors. The combination of EDLC and pseudocapacitors results in high energy density and better cycle stability in supercapacitors. This form a device with better performance. Hybrid supercapacitors are combination of both EDLC and pseudocapacitors which offer a high energy density and fast charging rate [22-30]. The cyclic voltammetry (CV) curve gives information about charge storage mechanism in Supercapacitors. Shape of the CV curve in hybrid type capacitors is a non-rectangular as it is combination of both EDLC and Pseudocapacitors.

Electrodes For Supercapacitors

The electrode material plays a vital role in determining the performance of the device. Electrode materials can be divided into three categories: carbon materials, conductive polymers, and transition metal oxides (TMOs). Carbon materials are usually used as electrode materials for EDLCs. TMOs have higher specific capacitance (100–2000 F g 1), higher energy density than carbon materials, and better chemical stability than conductive polymers [31–33]. Metal oxides, particularly transition metal oxides (TMOs), exhibit faradaic pseudocapacitive behavior arising from rapid and reversible redox reactions. Their high theoretical capacitance, cost-effectiveness, and tunable physical properties make them attractive for supercapacitor electrodes. The main performance indicator of supercapacitors are the specific capacitance (normalized by electrodes mass, volume, or area), density of energy, capacity for power, rates efficiency (retained capacitance at a high current loading), and cycle stability [34]. The energy density and power density of a supercapacitor may be improved by increasing its specific capacitance (C),

expanding its working voltage window (V), and decreasing its equivalent series resistance (R).

II. METAL OXIDE

The metal oxide have high conductivity, therefore they have been explored as a possible electrode material for pseudocapacitors [34-38]. The electrochemical performance of oxides is strongly dependent on their morphology, surface area, crystallinity, and porosity—all of which are influenced by the synthesis technique. There are many review articles on metal oxide based supercapacitors. The literature shows that ruthenium oxide is mostly used as stable electrode for supercapacitors [39-43]. However as considering cost effectiveness, now a days various transition metal oxides are employed as an electrode for supercapacitors. These includes MnO_2, NiO, In_2O_3, Co_3O_4, V_2O_5, Fe_3O_4, Bi_2O_3, IrO_2, etc.

The electrochemical performance of transition metal oxide (TMO) electrodes is highly sensitive to synthesis method, as it governs particle size, crystallinity, phase purity, morphology, defect structure, and specific surface area. The electrochemical performance of oxides is strongly dependent on their morphology, surface area, crystallinity, and porosity—all of which are influenced by the synthesis technique. Following are some of the methods and their advantages as considering their applications as a supercapacitors.

i) The sol–gel method is widely used due to its excellent control over stoichiometry and homogeneity at the molecular level. Typically, metal precursors (e.g., metal alkoxides or nitrates) are hydrolyzed in a solvent system (often alcohol-water mixtures), followed by poly-condensation to form a colloidal network (gel). The gel is then dried and calcinated to yield oxide powders. For example, NiO nanoparticles synthesized via sol–gel method showed specific capacitances exceeding 1000 F/g, attributed to the uniform grain size and porous structure facilitating ion transport [44].

ii) Hydrothermal synthesis involves the crystallization of materials from aqueous solutions under high pressure and temperature (typically 120–220 °C) in a sealed autoclave. This method promotes slow nucleation and crystal growth, leading to highly crystalline, well-faceted nanostructures such as nanorods, nanowires, nanotubes, and hierarchical microspheres. Hydrothermally synthesized MnO_2 nanosheets, for instance, have demonstrated superior pseudocapacitance (~700–1000 F/g), due to their ultrathin morphology and enhanced redox kinetics [45].

iii) Solvothermal synthesis is conceptually similar but uses non-aqueous solvents such as ethylene glycol, N,N-dimethylformamide (DMF), or alcohols. These solvents modulate solubility and dielectric constant, facilitating unique morphologies and phase control. For example, Co_3O_4 nanosheets synthesized in ethanol medium showed increased porosity and charge transport properties compared to aqueous systems [46].

iv) Thermal decomposition involves the breakdown of solid precursors—such as metal acetates, oxalates, or citrates—upon heating in air or inert atmospheres. This route is particularly suitable for producing phase-pure oxides with high crystallinity. For example, pyrolysis of Co-based MOFs produced Co_3O_4 nanocages with hierarchical porosity and high surface area (>100 m^2/g), yielding specific capacitance values >900 F/g [47].

v) Electrochemical deposition is used to fabricate thin-film oxide electrodes directly on conductive substrates such as Ni foam or carbon cloth. A typical setup involves applying a constant voltage/current in a metal salt solution, leading to the nucleation and growth of oxides or hydroxide intermediates, which can later be thermally converted. Electrodeposited RuO_2 films have demonstrated areal capacitance up to 1500 mF/cm^2 and long cycle stability [48].

Now we will focus on some the oxide materials already reported as an electrodes for supercapacitors.

i) Ruthenium oxide (RuO_2) based supercapacitors

RuO_2 has high theoretical capacitance, it has good electrical conductivity, high chemical and thermal stability, as well as a big voltage window. Therefore in it is in either a crystalline or amorphous hydrous form a promising electrode material for supercapacitor. The C-V curve for the ruthenium oxide is nearly rectangular. The redox reactions taking place throughout the potential window have an impact on the curve. RuO_2 has a high capacitance of about 150-260

F cm^2 [49]. Some of the representative synthesis condition already reported by different researchers to produce ruthenium oxide, their composition, properties and value of supercapacitanance are shown in the table 1.

Sr. No.	Deposition method and conditions	Properties	SC (F/g)	Reference
1	Electrodeposition: Substrate: CNT, 0.005 M $RuCl_3$ 0.1 M NH_4Cl 0.01 M HCl, Potentiodynamic: -0.2 -1 V/s, scanning rate 50 mV/s, annealing at 473 K for 10 h	RuO_2 is heterogeneously nucleated, opening in the CNT are not blocked by RuO_2 deposit. RuO_2 layer on CNT with 3-D nano-porous structure	965 (400 mV/s)	50
2	Electrodeposition Substrate: Ti, 0.005 M $RuCl_3.3H_2O$ - 0.01 M HCl - 0.1 M KCl, Room temperature, 25 mA/cm^2, 8 min, Heated at 423K.	Highly porous, 3-D structure, 60 nm particle size, Rough	788 (2 mV/s), 627 (50 mV/s)	51
3	Electrophoretic deposition Sole-gel prepared from0.1 M $RuCl_3$ 0.3 M NaOH, Substrate: Ti, DC voltage: 50 200 Vfor10- 600s, Annealed 100 673Kfor1h	Heat treated (473K)developed a network of nanoparticles (10nm)with porous structure	734(1mV/s),608(50mV/s), 25Wh/Kg: Sp Energy 21KW/kg: Sp. power	52
4	Chemical bath deposition Glass and Ti substrates, 0.01 M $RuCl_3$ sintering at 573K in air for 10 min	Amorphous, closely packed sphericalnanograins,100e125nm diameter,260nmthickness	416(5mV/s), 325(100mV/s)	53
5	Chemical deposition (SILAR) Substrate: glass, ITO, and Ti, 0.01 M $RuCl_3$-H_2O, Room temperature 50 cycles	Smooth, well covered, amorphous, porous, 3D view. 30-40 nm particle size, Band gap: 2.2 eV, p-type electrical conductivity	50 on Ti (20 mV/s) 25 on ITO (20 mV/s)	54
6	Spray deposition Substrate: Ta foils, $Ru(OC_2H_5)_3$ in ethanol, Substrate temperature:373-573K	At 523K,crystallinefilmformation, Below473Kamorphous,porous particles,Flakes,Particlesize:10micron	593	55

ii) Manganese oxide based supercapacitor

There are several oxidation states, including Mn(0), Mn(II), Mn (III), Mn(IV), Mn(V), Mn(VI), and Mn(VII), for manganese oxides [56]. Owing to its rich natural content, no environmental pollution, and high theoretical specific capacitance (1380 Fg^{-1}), MnO_2 has been widely studied as the most competitive transition metal oxide [57–59].

Manganese oxide (MnO) shows good electrochemical performance therefore it has been used as an electrode materials for supercapacitor applications. Manganese oxide is an substitute to RuO because of their low toxicity and cost, and high theoretical capacitances value between 1100 to 1300 Fg^{-1} and long cycle 122–131 life ~10,000 cycles [60-69].

For some of MnO_2 preparation and their supercapacitive performance are listed in Table 2.

Sr. No.	Deposition method and conditions	Properties	SC (F/g)	Reference
1	Electrodeposition methods Graphite substrate, 0.16 M $MnSO_45:H_2O$ Galvanostatic: 3.7 mA cm^2, Potentiostatic: 0.8 V/SCE, Potentiodynamic: +0.4-+1.0 V (10 mV/S, 30 cycles).	Amorphous by XRD, Different morphologies for different methods, Nanostructured hydrous MnO_2, Non-stoichiometric by XPS	230 (25 mV/s), potential window: 1 V (for galvanostatic methods)	70
2	Electrochemical anodization Graphite substrate, 0.5 M Mn acetate, Room temperature, Applied potential: +0.5 V/SCE	Amorphous by TEM (as deposited), Annealing from 473 to 873 K showed nanocrystaliine nature, surface with different morphologies	202 (as deposited, charge-discharge method)	71
3	Solegel dip coating Nickel substrate, Colloidal MnO_2 by reducing Mn (VII) with Mn(II)in alkaline aqueous medium, calcinationsat573K.	Nanocrystalline, highly porous	698(50mV/s),charge-discharge capacity decreased to26.4% after1500 cycles	72
4	Hydrothermal route 0.608g $KMnO_4$ and 1.27ml HCl (37wt%) were added to70ml distilled water kept at140^0Cfor12h	Single-crystala-MnO_2nanotubes, one-dimensional nanostructure has a tetragonal open end with an edge length of about 80nm and longitudinal length of several nm	220	73
5	Chemical bath deposition 0.2 M $MnSO_4$ and 0.2 M $(NH_4)_2SO_4$,	Tetragonal hausmannite Mn_3O_4, spherical beads-like architecture	284	74

Nickel oxide (NiO) based supercapacitors

Nickel oxide is beneficial as an electrode for supercapacitor due to its high theoretical specific capacitance value of 2584 Fg^{-1}. Nickel oxide films have been prepared by various methods such as thermal treatment of electrodeposited Ni(OH)2 [75-77], solegel [78-81] and electrostatic spray deposition [82].

The cubic NiO films with different morphologies were prepared by hydrothermal and electrodeposition methods on ITO-coated glass and Ti-foil [83]. The Supercapacitor value of about 148$Fg^{-1}$was obtained for the electrodeposited film. Using SILAR method, ITO assisted mesoporous and amorphous nickel hydroxide electrodes of 120 m^2 g^{-1} surface area (pore-size distribution centered.12 nm) were synthesized [84].

NiO has several nanostructures such as nano-rods, nanowires, nano-belts, and nano-flowers. Because of high specific capacitance and low cost of Ni/ $Ni(OH)_2$, it should be promising electrode materials for supercapacitor applications.

The details of some of Nickel Oxide based electrodes for supercapacitor application are shown in Table 3.

Sr. No.	Deposition method and conditions	Properties	SC (F/g)	Reference
1	Carbon cloth using CBD process. 2 M KOH Three electrode system. Platinum as counter and Hg/HGO as reference	The nano-flakes are thin (10 nm)	765 Fg^{-1} at 1 Ag^{-1}	85
2	Hydrothermal process 6 M KOH, Three electrode system. Platinum as counter and Ag/AgCl as reference.	The NiO spheres of uniform size 300 nm were dispersed in rGO.	1016.6 Fg^{-1} at mVs^{-1}	86
3	Electrochemical oxidation. 2 M KOH, Three electrode system. Platinum as counter and /HgO (1 M NaOH as reference.	The porous Ni foam houses 3D micro branched Cu-NiO composite.	416 Fg^{-1} at 10 mVs^{-1}	87
4	Electrochemical Deposition 0.13M sodium acetate + 0.13M nickel sulphate + 0.1M sodium sulphate. After deposition film was dried at 300◦C in air for 1 h.	Film exhibits highly porous morphology with nano-flakes like structure of thickness 12–16 nm.	167.3	88
5	Electrochemical Deposition 0.08 M $Ni(NO3)_2 \cdot 6H_2O$	α-$Ni(OH)_2$ showed particle like morphology with a loosely packed structure.	2595	89

Cobalt oxide (Co_3O_4) based supercapacitors

Spinel Co_3O_4 can be considered as one of the better substitute material to hydrous RuO_2 due to its high theoretical capacitance (3560 Fg^{-1}), controllable size and shape, good electrochemical performance and structural properties. It has high electrical conductivity.

A variety of Co_3O_4 nanomaterial have been synthesized, such as nanowires [90], nano-fibers [91], nanoparticles [92,93], and nano-sheets [94]. Yue and co-workers [95] used a simple and environmentally friendly one-step hydrothermal and calcination method to prepare Co_3O_4/reduced graphene oxide (rGO) composites. The prepared electrode has more active sites than Co_3O_4 nanowires [96] to achieve better electrochemical performance. Nanocrystalline CoO film was formed by electrodeposition method exhibits specific power and energy of 1.33kW/kg and 4.0Wh/kg respectively.

The details of some of Cobalt Oxide based electrodes for supercapacitor application are shown in Table 4

Sr. No.	Deposition method and conditions	Properties	SC (F/g)	Reference
1	Epoxide addition method 1 M NaOH, Three electrode system. Platinum as counter and Ag/AgCl as reference.	The average particle size is 5 nm and pore size 3-4 nm	623 Fg^{-1} at 25 mVs^{-1}	97
2	Hydrothermal process 0.5 M KOH, Three electrode system. Ni Grid as counter and SCE as reference.	The desired structure grew in 220 planes. The Nano bundles shows excellent performance	590 Fg^{-1} at 15 mVs^{-1}	98
3	Solvothermal Method	The needle shaped Co_3O_4nicely incorporated.	157 Fg^{-1} at 0.1 Ag^{-1}	99

	2 M KOH, Three electrode system. Platinum as counter and SCE as reference			
4	Electrochemical Deposition 0.05 M cobalt chloride, pH: ~10 by adding 30% ammonia.	Formation of Co_3O_4 film with nanocrystalline structure. Film was highly porous with thickness of 0.60 mg/cm^2.	235	100
5	Electrochemical Deposition 0.05 M $Co(NO_3)_2$ After deposition film was air annealed at 623 K for 180 min	Formation of cubic crystal structure of Co_3O_4.Morphology of the film shows the porous with nano-flakes-like structure	248	101

Tungsten oxide (WO_3) based supercapacitors

Due to high electronic conductivity, high intrinsic density, small ion radius and appropriate phase structure for fast ion insertion tungsten oxide can be a good electrode material for supercapacitor application. Zhu et.al reported capacitance of up to 421 Fg^{-1} at current density 0f 0.5 Ag^{-1} for a pure tungsten electrode.

Jo et.al studied the electrochemical characteristics of mesoporous tungsten oxide which they prepared by template method [102]. The ordered structure of tungsten oxide exhibited capacitance of about 199 Fg^{-1}

The details of some of Tungsten Oxide based electrodes for supercapacitor application are shown in Table 5

Sr. No.	Deposition method and conditions	Properties	SC (F/g)	Reference
1	Hydrothermal process 1.0 M H_2SO_4 Three electrode system. Platinum as counter and Hg/HGO as reference	The GNS-W composite has a packed layer structure decorated with tungsten oxide.	143.6 Fg^{-1} at 0.1 Ag^{-1}	103
2	Microwave irradiation 30 wt % KOH, Three electrode system. Platinum as counter and SCE as reference	3D structure of carbon cloth acted as a support for the nanowire array of the WO3.	680 Fg^{-1} at 0.5 Ag^{-1}	104
3	Synthesis of mesoporous ordered tungsten oxide was done by using template KIT 6. 2.0 M H_2SO_4 Three electrode system. Platinum as counter and SCE as reference	The ordered mesoporous structure over the surface is observed which increases conductivity	199 Fg^{-1}	105

Other than Ruthenium oxide, Manganese oxide, Cobalt oxide, Nickel oxide and Tungsten oxide electrodes, copper oxide [106-109], Vanadium oxide [110-111], Molybdenum oxide [112], Titanium oxide [113-114], Tin oxide [115], Bismuth oxide [116], Iron oxides [117] and Indium Oxide have been studied for supercapacitor electrode materials.

Fig. (3) shows the reported SC values obtained for different metal oxide thin film based supercapicitors. The highest value (2104 F g^{-1}) is reported for Co-Ni hydroxide based supercapacitor. However, all other values range between 50 and 1100 F g^{-1}.

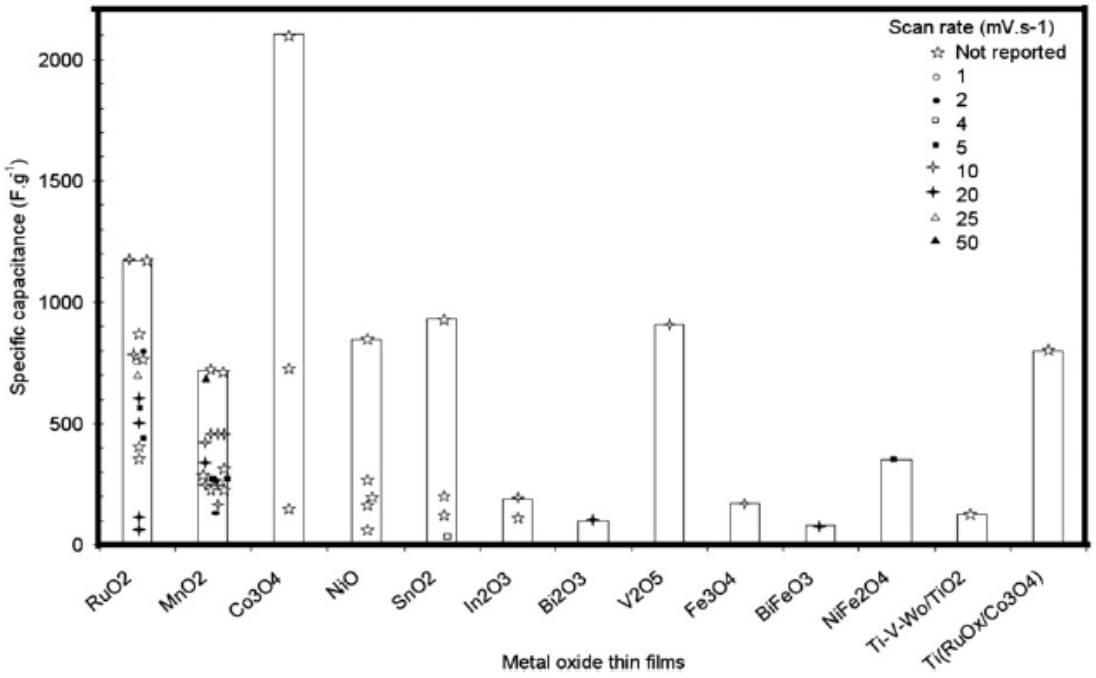

Fig. 3 The supercapacitive values obtained at different scan rates for different metal oxide thin films based supercapicitors.

III. CONCLUSION

This review focuses on synthesis of transition-metal-oxide electrodes from bio waste for their applications in supercapacitors. All the oxide materials have been prepared by various chemical methods such as electrodeposition, spray pyrolysis, chemical deposition, spin coating, dip dry etc. For many of the oxide materials only specific capacitance (Sc) values have been reported and specific energy and specific power are not studied. Among all oxide materials only RuO_2, MnO_2, NiO and Co_3O_4 thin films shows good value of capacitance as well as those materials are studied with more attention.

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