Nano-Metal Oxide Based Supercapacitor via Electrochemical Deposition

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In this rapid growing world, the demand of alternate or non-conventional energy sources with high density and power has been tremendously increased. Supercapacitor is one of the promising energy storage devices which possess high specific capacitance, high power density and long life cycle. The performance of supercapacitors is evaluated by its electrode materials. Among the various supercapacitor electrode materials, recent research focused on synthesis of transition metal oxides/ hydroxides, carbon metals and polymers. Transition metal oxides such as manganese oxide (MnO₂), ruthenium oxide (RuO₂), cobalt oxide (Co₃O₄), nickel oxides (NiO) etc. have been widely used as supercapacitor electrode materials for storing the potential energy. In this paper, we explored the details of metal oxide material based supercapacitor electrodes and their composition via electrochemical deposition technique. We also discussed the basic parameters involved in supercapacitor studies and advantages of electrochemical deposition technique through analysis of the literature.

Keywords: Supercapacitors; Metal Oxide; Electrodeposition technique

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1. Introduction

Owing to the environmental issues like global warming, pollution, fuel problems, etc, it has become necessary to develop clean, efficient and sustainable energy sources for storing energy.^{1,2} Also many applications such as stand-by power systems, cell phones and electric hybrid vehicles require energy storage.³ In 1978 a device called supercapacitor was introduced by NCE which was used to provide the power backup for computers.⁴ Further it was found that these supercapacitors could be used to boost the fuel cell or battery in an electric hybrid vehicle to provide the necessary power.⁵⁻¹⁰ Recent developments have made supercapacitor as a complement of fuel cells or batteries to store the energy.¹¹ Also it can be used in laptops, mobile phones, digital cameras, etc.³ Hence tremendous theoretical and practical research work is going on for development of supercapacitor as it can be an environmental friendly and low cost storage device.¹²⁻¹⁹

Supercapacitor consists of two identical electrodes with a separator immersed in an electrolyte.²⁰ Electrode material plays an important role in supercapacitor.^{21,22} There should be an effective contact between the electrode materials and the electrolyte to achieve excellent supercapacitive properties. Transition metal oxides (2 to 50 nm) such as RuO₂, NiO, Co₃O₄, MnO₂, In₂O₃, Fe₃O₄, V₂O₅, IrO₂, Bi₂O₃, NiFe₂O₄, BiFeO₃ etc are promising materials for the fabrication of supercapacitor

with high energy density due to their exceptional physic-chemical properties, suitable pore size and high specific surface area.²³⁻²⁸

One of the most promising techniques for fabrication of transition metal oxide is electrochemical deposition. Because of its versatility it leads to increase the specific capacitance of the supercapacitors.³⁰ This technique is widely used as it is cheap, easy and one step technique to synthesis metal oxides, polymers and its composite. The morphology and the chemical composition of the deposited film can be easily controlled by optimizing electrochemical parameters to achieve adherent film.

There are many published review article on the supercapacitors. In literature [1, 34, 37, and 97] metal oxides-based materials, conducting polymers and carbon based materials for supercapacitor electrodes are reviewed in detail. According to authors in article,¹²¹ supercapacitive performance can be enhanced by developing the nanostructure and composite materials. R.C. Ambare *et al.*, has presented a brief review on electrode materials, also discussed their charge transport and configurations of supercapacitors.⁶⁴ Evaluation of charge capacity for both negative as well as positive electrode materials was demonstrated in Ref. [66].

In this review article, we have presented synthesis of different metal oxides via electrochemical deposition used by various research groups as supercapacitor electrode material. We focused on fabrication of transition metal oxide by electrochemical deposition technique only. The main aim of this review is to give detailed information on metal oxide based supercapacitors, parameters and performance of supercapacitors.

1.1 Fundamentals of Supercapacitors

Supercapacitors are also known as ultracapacitors, double layer capacitors or electrochemical capacitors. They utilize large surface area and thinner dielectrics to achieve greater power density than that of

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batteries and greater capacitances with higher energy density than that of conventional capacitors.³¹⁻³⁷ Supercapacitor reaches 20 times higher power density (>10 kW/kg) and better life cycle (>10⁵ cycles) than that of batteries, also it can be charged/discharged rapidly.^{29, 38, 39} It can be used in various energy storage devices, either in combination with batteries or stand-alone. Fig. 1 shows the comparison between specific energy and specific power for different electrical energy storage devices.^{40, 41}

This Ragone plot indicates that supercapacitors occupy a region between batteries and conventional capacitors. Supercapacitors are driven by the basic principle of conventional capacitors but the difference is that they have electrode material with higher surface area and have thinner dielectrics which decrease the distance between the electrodes. The capacitance 'C' is directly proportional to the surface area 'A' and inversely proportional to the distance 'D' between the electrodes:

$$C = \epsilon_0 \epsilon_r \frac{A}{D} \quad (1)$$

where, ϵ_r is the electrolyte dielectric constant, ϵ_0 is the permittivity of a vacuum.⁹ The stored energy E in a supercapacitor depends upon specific capacitance (C) and the operating voltage (V):⁴²

$$E = \frac{1}{2} CV^2 \quad (2)$$

The maximum power (Pmax) depends upon operating voltage (V) and the internal resistance (R) as follows:

$$P_{max} = \frac{V^2}{4R} \quad (3)$$

Generally, the mechanism of the supercapacitors categorizes into three types based on energy storage and cell configuration: (i) Electric Double-Layer Capacitors (EDLC's), (ii) Pseudocapacitors and (iii) Hybrid capacitors⁴³ as shown in Fig. 2.

Electric double-layer capacitors (EDLC's):

EDLCs are made up of two carbon based porous electrode material which are separated by an insulator. A basic configuration of EDLC is shown in Fig. 3. The energy charge is stored in a non-faradaic manner; the charge storage mechanism is based on the electrostatic charge accumulation at the electrode-electrolyte interface.^{44, 45} The most common electrode material is activated carbon. Carbon nano materials

are having unique structures with large surface area, better electrical conductivity and high chemical & mechanical stability. They require wide potential window, high conductivity, fast charge/discharge rate and large surface area.^{46, 47} The specific capacitance in carbon-based electrode materials is less and hence achieving a high energy density has become a difficult task in EDLC's.

Pseudocapacitors:

Pseudo-capacitors electrostatically store the charge as compared to EDLC's. The faradaic charge transfer in Pseudocapacitors takes place at electrode-electrolyte interface.⁴⁸⁻⁵² It exhibits high energy density and high specific capacitance than that of electrical double layer capacitance due to Faradic process.⁵³ Transition metal oxides⁵⁴ and conducting polymers⁵⁵ are mainly used as pseudocapacitor electrodes. It requires high surface area, large potential window, doping of the conducting polymer and fast charge/discharge rate.^{56, 57} The main disadvantage of the pseudocapacitors is low power density.⁵⁸

Hybrid capacitors:

EDLC's offers large power performance and good cyclic stability while pseudocapacitors possess greater specific capacitance and energy densities. Hybrid supercapacitors are combination of both EDLC and Pseudocapacitors which offer a high energy density and fast charging

Fig. 1 Ragone plot: Specific Energy Vs Specific Power Plot.

Fig. 2 Classification of Supercapacitors.

Fig. 3 Schematic diagram of EDLC.

rate in the same cell.^{54,62} The combination of two different electrodes typically results in more energy storage due to the wider operating voltage of an organic electrolyte and the good specific capacity of the battery type electrode. Hybrid capacitors have been tested with both negative and positive electrodes in aqueous electrolytes solution to improve the performance.⁶³ There are three types of hybrid capacitors based on configurations of electrodes (a) composite, (b) asymmetric and (c) battery-types.

The cyclic voltammetry (CV) curve of EDLC supposed to be

Fig. 4 Typical CV curve of EDLC and Pseudocapacitors.

Table 1 Significant parameters of Supercapacitor.

Sr. No.	Parameters	Relation	Specification
1	Capacitance of material	$C = \frac{dQ}{dV}$	dQ/dV = rate of change of surface charge density with electrode potential
2	Double layer capacitance	$C_{dl} = \frac{\epsilon A}{4\pi t}$	ϵ = dielectric constant of EDLC material A = surface area of the electrode t = thickness of electric double layer
3	Voltage scan rate	$S = \frac{dV}{dt}$	dV/dt = rate of change of electrode potential
4	Interfacial capacitance	$C_i = \frac{C}{A}$	C = capacitance A = area of deposited electrode
5	Specific capacitance	$SC = \frac{C}{W}$	C = capacitance W = mass of deposited electrode
6	Average capacitance (i) From CV curve	$C = \frac{I}{dv/dt}$ $C = \frac{1}{2mv} [Q_a + Q_c]$	I = average current dV/dt = voltage scanning rate m = weight of deposited electrode v = applied potential window
	(ii) From galvanostatic charge -discharge curve	$C = \frac{I * \Delta t}{m * \Delta V}$	Q_a = anodic charge in one cycle of potential sweep Q_c = cathodic charge in one cycle of potential sweep
6	Energy density and Power density	$E = \frac{CV^2}{2}$ $P = \frac{E}{t}$	C = Capacitance in farad, V = Cell voltage in volt t = Discharge time in second
7	Efficiency	$\eta = \frac{t_d}{t_c} * 100$	t_d = discharging time t_c = charging time

rectangular in shape, but in pseudo-capacitance the shape of the curve will become non-rectangular due to faradaic process as shown in Fig. 4. Hence overall shape of the CV curve in hybrid type capacitors is a non-rectangular as it is combination of both EDLC and Pseudocapacitors.

1.2 Supercapacitive parameters

There are various significant parameters to evaluate the performance of as prepared electrode materials for supercapacitive application as shown in Table 1.⁶⁴⁻⁶⁶

1.3 Background of Electrodeposition technique for synthesis of Nanostructure electrode materials

Thin films play an important role in the electrochemical studies and applications. The behavior of the thin film typically $< 1 \mu\text{m}$ depends upon the properties of the electrode surface. There are many synthesis technique used to produce electrodes for supercapacitors such as chemical bath deposition,^{67, 68} Chemical vapor deposition (CVD),^{69, 70} spray pyrolysis,⁷¹ SILLAR method,⁷² sol-gel method,^{73, 74} hydrothermal technique⁷⁵ and electrochemical deposition etc. Among various methods, electrochemical deposition is an attractive and well known technique due to its inexpensive, simple and effective process of fabrication of the metallic coatings under ambient temperature. It is a versatile technique used for deposition of the metals,^{76, 77} metal alloys,^{78, 79} metal oxides⁸⁰ and hybrid materials.⁸¹ The technique involves the movement of metallic ions towards a cathode in the solution driven by an electric field. The ions either accept the electron and get deposited on the cathode or lose electron and get deposited on anode in the form of atom or molecule. The general setup of electrochemical deposition is shown in Fig. 5.⁸² It involves the following "electrical" terms.

a. Electrolyte- The electrolyte is a conducting medium through which the flow of electric current takes place by movement of ions. It can be aqueous, non-aqueous or molten, in presence of suitable metal and chalcogenide salts.

b. Electrode- An electrode is a conductor through which an electric current enters or leaves an electrolyte. When electrode is connected to positive terminal, it is referred as an anode and when it is connected to negative terminal it is referred as cathode. At anode, positive ions are formed or negative ions are discharged or oxidizing reactions occur. At cathode, positive ions are discharged or negative ions are formed or reducing reactions occur.

c. Electrode potential- An electrode potential is the difference in potential between an electrode and the electrolyte, measured against or referred to, an arbitrary zero of potential.

d. Equilibrium electrode potential- It is a static electrode potential when the electrode and electrolyte are in equilibrium with respect to a specified electrochemical reaction.

e. Standard electrode potential- A standard electrode potential is the equilibrium potential, for an electrode in contact with an electrolyte, in

which all the components of a specified electrochemical reaction are in their standard state.

f. Reference electrode- A reference electrode is defined as an electrode on which the state of equilibrium of a given reversible electrochemical reaction is permanently secured under constant physicochemical conditions. Equilibrium potential of standard hydrogen electrode is 0 V, whereas, it is $+ 0.2415 \text{ V}$ for saturated calomel electrode (SCE).

Electrodeposition method is an isothermal process in which, the thickness, crystallographic orientation,⁸³ morphology,^{83, 84} and dopant density⁸⁵ of the films can be easily controlled by electrochemical parameters such as electrode potential or current (charge),⁸⁶ time, deposition temperature, electrolyte composition,⁸⁷ concentration,⁸⁹ pH of the bath,⁹⁰ etc. Thus, electrodeposition allows obtaining uniform films grown on substrate of complex shapes and areas which is not possible by other methods. One disadvantage of electrodeposition is that, it requires a conducting substrate such as glassy carbon, metals (Au, Pt, Ti, Ni, and Cu), oxides (ITO, FTO) or alloys (stainless steel).

2. Electrochemical deposition of metal oxides

To deposit metal oxides mostly alkaline solutions with metal complex are used as an aqueous solution. Electrochemical deposition of metal oxides can be carried out under both oxidizing and reducing conditions from alkaline solutions. In both conditions, the metal ions are directly deposited on the electrode as an oxide. Deposition under oxidation condition includes the deposition of MnOx from Mn(II) ammine complex,⁹¹ CuO from Cu(II)-tartrate ,⁸⁶ CeO_2 from Ce(III)-acetate ,⁹² NiOx from Ni(II) ammine complex⁹³ and Co_3O_4 from Co(II) glycine in alkaline solutions.⁹⁴ Deposition of metal oxides under reduction conditions includes deposition of ZnO ,^{88, 95} CdO ⁹⁶ and Cu_2O from alkaline Cu(II) solution etc.

For supercapacitor application, metal oxide required some properties includes: (i) It should be electronically conductive. (ii) It must exist in two or more oxidation states which coexist in the continuous range without changing the phase. (iii) The protons should be freely intercalated into the oxide lattice and out of the lattice for reduction and oxidation states respectively. Till date above mentioned properties are explore for metal oxide such as manganese oxide, ruthenium oxide, nickel oxide and cobalt oxide.

2.1 Ruthenium oxide/hydroxide and their composition

Among the various metal oxides, both crystalline and amorphous RuO_2 are promising electrode material because of excellent electrochemical capacitance ($\sim 2000 \text{ F/g}$), high electrical conductivity, good thermal & chemical stability, large potential window, long life cycle and good electrochemical reversibility.^{97, 98} It has various forms for example nanoporous film⁶⁷ nanoneedles,⁹⁹ and nanoparticles.¹⁰⁰ Ruthenium Oxide formed by various techniques including CBD,⁶⁷ CVD,⁶⁹ Sol-gel method,¹⁰¹ Polyolmethod¹⁰³ Hydrothermal,⁷⁵ electrodeposition method etc. Also lots of research carried out on the combination of RuO_2 with other oxides or polymers such as NiO , TiO_2 , VOx , SnO_2 , RuO_2/CNT , RuO_2/PPy , PANi etc. Table 2 represents the synthesis conditions with details of deposition used by various researchers to obtain the electrodeposited ruthenium oxide/hydroxide and their composition thin films.

Amorphous ruthenium oxide electrode shows different reaction in alkaline and acidic electrolyte solution for example in KOH electrolyte the electrode exhibited specific capacitance of 710 F/g when calcinated at 200°C while in H_2SO_4 aqueous electrolyte it showed capacitance of 720 F/g when heated at 150°C .¹⁰¹ In acidic electrolyte solution, RuO_2 obeys following rapid faradaic reaction:^{118, 119}

Fig. 5 Electrochemical deposition setup.

Table 2 Electrochemical deposition of Ruthenium oxide/hydroxide and their composition.

Sr. No	Chemical/Bath Composition & conditions	Substrate Electrode			Details					Remarks/Properties	SC (F/g)	Ref.
		A	K	R	Applied Current/Voltage	Depo. time	Temp.	Scan Rate mV/s	Electrolyte			
1	50 mM Ruthenium nytril of complexed by ammonia	ITO	Pt	Ag/AgCl	0 to -1 V/Ag	-	Room temp	5	0.5 M H ₂ SO ₄	Formation of nanograins of RuO ₂ with tetragonal crystal structure.	498	104
2	0.04M (RuCl ₃ ·xH ₂ O) After deposition the RuO ₂ films were dried in a furnace at 100°C.	Ti	-	-	5.0mA/cm ²	180 Min	50°C	10	0.5 M H ₂ SO ₄	Surface morphology shows cracked-mud and grains size of RuO ₂ is in nanometer. Thickness: 0.0014 g/ cm ² . The specific capacitance and energy efficiency decreases with increasing the film thickness. Capacitance obtained from charge –discharge curve is smaller due to increased ESR through the presence of a separator.	788	105
3	0.04M (RuCl ₃ ·xH ₂ O), pH: 2.0 to 2.5 After deposition RuO ₂ films were dried in a furnace at 373 K.	Pt	Ti	-	5.0 mA/cm ²	30 Min	50°C	10	0.5 M H ₂ SO ₄	The RuO ₂ films are nanocrystalline and porous. The charging-discharging behavior showed that the RuO ₂ electrodes were stable in the H ₂ SO ₄ electrolyte.	788	106
4	RuCl ₃ ·xH ₂ O After deposition, the films were dried in air	SS	Gh	SCE	-0.45 V/SCE	2Hr	333°K	20	0.5 M H ₂ SO ₄	The values of capacitance and contact angle decreased because of surface treatments (i.e. anodization, air	650	107
5	0.05 M (RuCl ₃ ·nH ₂ O), Continuously stirred, After deposition electrodes were heated at 175°C	TiO ₂	Pt	Ag/AgCl	0.25 to 1.45 V	-	50°C.	50	0.5 M H ₂ SO ₄	The area ratio of O 1s to Ru 3d increased from 0.19 to 0.45 when the deposition range changes from 0.2 – 1.2 V to 0.25 –1.45V. After 300 cycles, the capacitance of RuO ₂ on TiO ₂ nanorods was maintained at about 93% of its initial value.	534	108
6	0.02 M RuCl ₃ + 0.005 M HCl, After deposition heating treatment at 150°C for 2 h	TiO ₂ /Ti	Pt	-	-1.0 mA/cm ²	30 min	298°K	10	1.0 M H ₂ SO ₄	Energy dispersive peaks at 2.25, 2.61 and 3.18 keV has been observed for RuO ₂ electrodes. After 400 cycles the specific capacitance retained about 80% of its initial value. Nyquist plot showed much lower impedance values in low frequency region.	640	109
7	10 mMRu(III)Cl ₃	SS	Gh	SCE	0 to +1 V	45 min	333°K	20	0.5 M H ₂ SO ₄	Film was porous without any cracks and pinholes. Film thickness: 0.376 mg/cm ² . RuO ₂ electrode was almost stable for thousands of cycles.	1190	110
8	5 mM RuCl ₃ ·3H ₂ O + 0.01M HCl + 0.1M KCl, pH: 2.0 After deposition film was dried in a furnace at 150 °C for 2 h.	Ti	Pt	-	25mA/cm ²	8 Min	Room temp	2	0.5 M H ₂ SO ₄	The formation of uniform spherical grains with nanometer in sizes and porous network structure of the RuO ₂ ·nH ₂ O. Highest energy efficiency reaches 99.58% obtain by charge discharge curve.	786	111

Table 2 Electrochemical deposition of Ruthenium oxide/hydroxide and their composition.

9	10mM $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ + 0.1M NaAcO, After deposition films were annealed in air at 150°C for 2 h.	Ti	-	-	1.0V	-	50°C	25	0.5 M H_2SO_4	The formation of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ indicates that the deposition rate of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ from the negative shift in the onset potential. It was observed that film has low resistance (i.e. high electronic conductivity and low contact resistance between Ti and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$).	552	112
10	5 mM $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ + 0.01 M HCl + 0.1 M KCl After deposition films were dried by a cool air flow.	Ti	Pt	Ag/AgCl	-200 and 1000 mV	-	50°C	50	0.5 M H_2SO_4	Formed film was porous with amorphous structure. XPS indicates material consist of mixed oxyruthenium with various oxidation states. CV and charge-discharge curve showed that the redox transitions of various oxidation states on $\text{RuO}_x \cdot n\text{H}_2\text{O}$ were electrochemically reversible. The capacitance value was constant up to 120 cycles.	100	113
11	10 mM RuCl_3 + 0.1 M NaAcO After deposition electrode was annealed in air at 200 °C for 2 h	AAO coated Gh or Ti	-	-	1.0V	10-30 Min	-	4000	1.0 M H_2SO_4	Nanotubular structure with thickness $\sim 40 \pm 5$ nm and Onset-overfilled morphology was found. The specific power and energy is equal to 4320 kW/kg and 7.5 W h /kg, respectively.	550	114
12	5mM $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ + 0.1 M NH_4Cl + 0.01 M HCl, pH: 2 by adding NaOH After deposition films were annealed at 200°C for 10 h	CNT	Pt	SCE	-200 and 1000 mV	-	-	10	0.5 M H_2SO_4	The annealed film was of hydrous form with an amorphous structure.	1170	115
13	5mM $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ + 0.1 M NH_4Cl + 0.01 M HCl, pH: 2 by adding NaOH After deposition films were annealed at 200°C for 10 h	Pt/Ca /CNT	Pt	SCE	-200 and 1000 mV at scan rate 50 mV/s	-	-	10	0.5 M H_2SO_4	The annealed sample showed crystalline amorphous structure. As-prepared film was uniformly deposited on the CNT substrate and heterogeneously nucleated with ~ 3 nm thickness and 3D nanoporous structure. RuO_2/CNT electrode showed overall good performance compare to other electrodes.	1170	116
14	0.01 M $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, After deposition film was calcinated at 250°C for 2 h	Co(OH) ₂	Pt	SCE	-1 V	20 min	333°K	20	30wt % KOH	XRD data showed presence of the elements Co, O and Ru with tetragonal structure of both RuO_2 and Co_3O_4 . Formation of mesoporous morphology with particle size 0-15 nm. Film was stable about 96% after 5000 charge discharge cycles.	905	117
15	10 mMRuCl ₃ .xH ₂ O + 0.1 M NaAcO After deposition dried at	AAO-coated Gh	SH E	Ah/Ag/AgCl	1.0V	10-30 min	-	1000	1M H_2SO_4	Structure of formed film reduces the diffusion resistance and increases the facility of ion transportation also	1300	102

Where $0 \leq n \leq 2$, according to above eq (16) in acidic solution, oxidation states of Ru can change from Ru(II) to Ru(IV). But in an alkaline solution, changes of oxidation states for RuO_2 are different. It has been reported that RuO_2 composite with carbon electrode will be oxidized to RuO_4^{2-} , RuO_4^- and RuO_4 and reduced to RuO_2 .^{120, 121}

The performance of RuO_2 depends upon crystallinity, surface area, combination of water, temperature and size of particle. The crystallinity depends on the synthesis technique which affects the supercapacitive performance of RuO_2 . Amorphous RuO_2 thin films formed by anodic deposition showed maximum capacitance of 1190 F/g in H_2SO_4 electrolyte for 10 cycles, as number of cycles increases capacitance decrease upto ~ 800 F/g for 1000 cycles.¹⁰⁰ To increase capacitance value one of the most effective way is to increase the surface area.¹⁰¹ The unique electrochemical features result in CV curve as shown in Fig. 6. The figure indicates an ideal capacitive behavior.¹⁰⁴ As reported in ref [105] the specific capacitance and energy efficiency decreases with increasing the film thickness. Combination of water with RuO_2 is used to enrich the diffusion of cations inside the electrode layer. As reported in Ref [111] hydrous ruthenium oxide ($\text{RuO}_2 \cdot n\text{H}_2\text{O}$) formed by cathodic electrodeposition showed a capacitance of 786 F/g. Whereas $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ formed by anodic deposition showed specific capacitance of 552 F/g when heated at 150°C for 2 hr.¹¹² The $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ nanotubular array electrode formed by using anodic deposition exhibits SC as high as 1300 F/g along with an energy density of 7.5 Wh/kg.¹⁰² Annealing Temperature is another most important factor for electrochemical performance, RuO_2 electrode was prepared by cathodic electrodeposition on Ti substrate exhibits maximum capacitance of 788 F/g when calcinated at 100°C .¹⁰⁵ Kim *et al.*, has reported that the electrochemically prepared composition of RuO_2 with carbon nanotube film exhibits much higher capacitance of 1170 F/g.¹¹⁵

In summary, the composition of RuO_2 with carbon nanotube based electrode improves the supercapacitive performance. Even though RuO_2 showed extremely high specific capacitance but it is not suitable for commercial application due to its relatively high cost and environmental harmfulness. There are two ways to reduce the cost: (i) by composing

RuO_2 with other metal oxide. (ii) depositing RuO_2 on low cost substrate.

2.2 Manganese oxide/hydroxide and their composition

Manganese oxide (MnO_2) shows all over good electrochemical performance that why it has been widely used as an electrode materials for supercapacitor applications. Manganese oxide is an alternative to replace RuO_2 because of their low toxicity, low cost, and high theoretical capacitances value between 1100 to 1300F/g and long cycle life $\sim 10,000$ cycles.¹²²⁻¹³¹ Many efforts have been made to obtain mesoporous MnO_2 by using different synthesis techniques includes CBD, SILAR method, template method, hydrothermal, ultrasound irradiation and electrodeposition method.¹³²⁻¹³⁴ Table 3 presents the summary of synthesis condition with deposition details electrodeposited manganese oxide /hydroxide and their composition thin films.

MnO_2 has various oxidation states, such as Mn(0), Mn(II), Mn(III), Mn(IV), Mn(V), Mn(VI), and Mn(VII)¹⁷¹ with several crystal structures like α , β , γ , δ .¹⁷² Following two mechanisms show the charge behavior of MnO_2 which involve a redox reaction of oxidation states between the III and IV of Mn.

Equ (17) indicates the insertion of electrolyte cations like $\text{H}^+ = \text{C}^+$, Na^+ , Li^+ , and K^+ in the bulk material and equ (18) implies that the surface adsorption of electrolyte cations on the MnO_2 electrode.^{173, 174}

Electrochemical performance of MnO_2 depends upon some important factors includes Morphology, Crystallinity, Crystal Structure, Thickness of the electrode and Surface area.

a. Morphology: The Morphology of film depends upon synthesis process and conditions. Dubal *et al.*,¹³⁸ has prepared the MnO_2 thin film by different modes of electrochemical deposition, it was found that significant change in the surface morphologies due to different modes. Four different morphologies i.e. nanonods, nanospheres, nanosheets and nanoflowers of MnO_2 were demonstrated by varying current density and concentration of H_2SO_4 . It was found that highest capacitance of 362.5 F/g for nanonode electrode at 0.5 A/g.¹⁴⁷

Fig. 6 The CV curves of RuO_2 electrode at different scanning rates in 0.5 M H_2SO_4 electrolyte. Reproduce from Ref [104].

Fig. 7 XRD patterns of (a) g- MnO_x and (b) p- MnO_x . Reproduced from Ref. [141].

b. Crystallinity: Alike to RuO_2 crystallinity depends upon synthesis process. High crystallinity gives increase in conductivity but decrease in surface area. To achieve greater conductivity annealing temperature plays an important role. Chang *et al.*,¹³⁵ has investigated effect of heat treatment on material. Amorphous oxide film converted into fibrous shape with nanocrystalline when calcinated at 200°C for 2 h. However at high temp (400°C) formed films indexed to Mn_3O_4 and Mn_2O_3 .

c. Crystal structure: The performance of electrode also depends upon crystal structure. It is observed that the various synthesis conditions can results in the different structures of MnO_x . Three types of crystal structures for MnO_2 were demonstrated, ε - MnO_2 prepared without any complex agent, defective rock salt MnO_2 from EDTA containing solutions, and defective antiferroite MnO_2 from citrate containing solutions. It was found that the defective rock salt and antiferroite structures of MnO_2 exhibit better capacitive properties than that off ε - MnO_2 . Whereas in Ref [141] GS deposition mode indexed to tetragonal phase of Mn_3O_4 while pulse current mode indexed to two structures i.e. tetragonal Mn_3O_4 and orthorhombic MnOOH as shown in Fig. 7 (XRD patterns). It was observed that the pulse current deposition mode showed better capacitive properties.

d. Thickness and surface area: As thickness increases the specific capacitance decreases. Qiu *et al.*,¹⁴⁰ has reported that the formation of MnO_2 film with thickness of $0.58 \sim 1.25 \mu\text{m}$ and the specific surface area of as-prepared sample was $7.7 \text{ m}^2/\text{g}$. Wanchaem *et al.*, has prepared MnO_x by two precursors i.e. MnSO_4 and KMnO_4 . The highest specific capacitance was found by using MnSO_4 as a precursor due to its nanosheet structure with a large surface area.¹⁴²

In literature¹⁴⁶ amorphous $\text{MnO}_x \cdot n\text{H}_2\text{O}$ is fabricated by three different modes i.e. potentiostatic, galvanostatic, and potentiodynamics. It was observed that all deposits showed similar capacitive properties because of similar oxidation states.¹⁵⁴ Rusi *et al.*, has fabricated composition of MnO_2 with NiO by three different modes of electrochemical deposition. The best electrochemical performance of CV mode was found in mixed $\text{KOH}/\text{K}_3\text{Fe}(\text{CN})_6$ electrolyte in comparison with Na_2SO_4 electrolyte. The maximum specific capacitance of 3509 F/g was found.¹⁵⁸ Whereas in same electrolyte (mixed $\text{KOH}/\text{K}_3\text{Fe}(\text{CN})_6$) electrodeposited rGO/MnO_2 nanocomposite electrode exhibits specific capacitance as high as $13,333 \text{ F/g}$ with power density of 68.35 kW/kg and energy density of 1851 Wh/kg .¹⁵⁹ Fig. 8 and 9 represent a typical charge discharge, CV curve and cyclic stability of

Fig. 8 (A) CV curve and (B) Charge-discharge curve of MnO_2 - NiO Composite electrode. Reproduced from ref. [158].

Fig. 9 Charge-discharge curve and (b) Cyclability of rGO/MnO_2 nanocomposites electrode in three different electrolytes. Reproduced from ref. [159].

MnO₂-NiO composite and rGO/MnO₂ nanocomposites respectively.^{158,159}

In conclusion, one can increase the specific capacitance, energy and power densities by depositing MnO₂ onto carbon material with large surface area and high conductivity. The composition of NiO with MnO₂ is versatile, cost efficient and scalable for supercapacitor applications. Addition of glucose with MnO₂ can give rise in specific capacitance, energy and power densities.

2.3 Nickel oxide/hydroxide and their composition

Nickel oxide/hydroxide electrode plays an important role in fabrication of supercapacitors because of its high specific capacitance (theoretically ~3750 F/g), easy synthesis, high chemical and thermal stabilities, environment friendliness and low cost.¹⁷⁵⁻¹⁷⁹ NiO has several nanostructures such as nanorods, nanowires, nanobelts, and nanoflowers. Literature analysis for synthesis conditions with deposition details of Nickel oxide/hydroxide and their composition thin films via electrodeposition technique is shown in Table 4.

The redox reaction of NiO in an alkaline electrolyte can be described as follows:¹⁸⁶⁻¹⁸⁸

The electrochemical performance of NiO totally depends upon Crystallinity which affects by heating treatment. Wu *et al.*, has reported that the nickel hydroxide electrodeposited on nickel substrate was transformed into the nickel oxide when calcinating at 250°C, which exhibits high SC of 1478.¹⁸⁰ In literature¹⁸² NiO electrode obtained from three precursors i.e. nitrate, chloride and sulphate. It was observed that the NiO electrode prepared from sulphate solution showed all over good electrochemical performance. Particle-like nickel hydroxide prepared by electrodeposition technique exhibits the maximum specific capacitance of 2595 F/g.¹⁸⁴

Because of high specific capacitance and low cost of Ni/ Ni(OH)₂, it should be promising electrode materials for supercapacitor applications. But there are two main disadvantages of using NiO for supercapacitor electrode (i) it has poor cyclic stability. (ii) low electric conductivity. To overcome these drawbacks, composing NiO with other materials and fabricating nanostructured NiO are advisable.

2.4 Cobalt oxide/hydroxide and their composition

Cobalt oxide (Co₃O₄) has a cubic structure and most studied material due to their high electrical conductivity, large surface area, excellent reversible redox behavior and long-term stability with high theoretical capacitances value (~3560 F/g).¹⁸⁹⁻¹⁹⁶ Table 5 presents the summary of synthesis conditions with deposition details used by various researchers for obtaining electrodeposited Cobalt oxide /hydroxide and their composition thin films.

The redox reaction of Co₃O₄ in alkaline electrolyte can be expressed as follows:^{202, 203}

Nanocrystalline Co₃O₄ film was formed by electrodeposition method exhibits specific power and energy of 1.33kW/kg and 4.0Wh/kg respectively.¹⁹⁷ Jagadale *et al.*, has prepared cobalt oxide by three different modes of electrodeposition technique. Film deposited by PS mode showed maximum values of specific capacitance, specific energy and specific power as compare to PD and GS modes.¹⁹⁹ Aghazadeh *et al.*, has prepared β- cobalt hydroxide with flake-like morphology by green electrochemical synthesis as shown in Fig. 10 (TEM image)

exhibits the specific capacitance of 1288.1 F/g.²⁰⁰ Rajeswari *et al.*, has prepared cobalt hydroxide nanoplates on cadmium oxide (CdO) as conducting base electrode exhibits high capacitance value of 1119 F/g.²⁰¹

In conclusion, Co(OH)₂ electrodes showed good performance as compare to Co₃O₄. However, both NiO/Ni(OH)₂ and Co₃O₄/Co(OH)₂ have same drawbacks, which limits their practical use.

2.5 Other metal oxides

Other than RuO₂, MnO, NiO and Co₃O₄ electrodes, copper oxide (CuO),²⁰⁴⁻²⁰⁷ Vanadium oxide (V₂O₅),^{208, 209} Molybdenum oxide (MoO₃),²¹⁰ Titanium oxide (TiO₂),^{212, 213} Tin oxide (SnO₂),²¹⁴ Bi₂O₃,²¹⁵ Iron oxides (Fe₂O₃ / Fe₃O₄)²¹⁶ and Indium Oxide (In₂O₃) have been studied for supercapacitor electrode materials.

Amorphous copper oxide thin films have been synthesized by electrodeposition on different substrate for example copper oxide grown on copper foam exhibits maximum capacitance of 212 F/g²⁰⁶ while on stainless steel substrates showed specific capacitance of 36 and 179 F/g in 1 M Na₂SO₄ electrolyte.^{204, 205} Ghadge *et al.*, has reported the copper hydroxide thin film electrode formed by anodization method exhibits maximum specific capacitance of 6000 F/g.²⁰⁷ TiO₂ has been deposited via electrochemical anodization technique on Titanium metal foil showed specific capacitance of 1300 μF/cm².²¹⁷ Lee *et al.*, has reported that the amorphous V₂O₅ exhibits a maximum specific capacitance of 350 F/g.²¹⁸ Amorphous MoOx film formed by electrodeposition technique showed capacitance as high as 507 F/g in 1 M H₂SO₄ electrolyte.²¹⁹ Electrodeposited Bi₂O₃ thin film on copper substrate exhibits specific capacitance of 98 F/g.²²⁰ Amorphous SnO₂ exhibits the maximum specific capacitance of 285 F/g synthesized by electrochemical deposition method.²²¹ Prasad *et al.*, has prepared In₂O₃ film via electrochemical deposition method which exhibited a specific capacitance of 190 F/g.²²²

3. Conclusion

Supercapacitors have emerged as an alternative solution to energy technology with higher energy density, excellent electrochemical properties and good cyclic stability. Due to its large surface area thinner dielectric and higher thermal & electrochemical conductivity, it can be used in many application such as emergency power supplies, specific power systems, back-up and pulse power applications. Also there has been great interest in developing supercapacitors for electric hybrid vehicles power systems. Supercapacitor can be easily fabricated using various transition metal oxides/hydroxides due to their high

Fig. 10 TEM image of β- cobalt hydroxide with flake-like morphology. Reproduced from ref. [200].

conductivity, larger surface area, and better stability. We have reviewed the various transition metal oxides/hydroxides used for supercapacitor via electrochemical deposition. The high performance of supercapacitors could be achieved by metal oxide/hydroxides electrodes with composite materials. Key challenges for supercapacitor are their limited energy and power densities. To overcome this problem, researchers should

focus to develop new electrode materials with high capacitance, energy and power densities and wider potential range. For these electrode materials should have low internal resistance, suitable pore size, high surface area and better electrochemical & mechanical stability. Hence this area requires further research and development for supercapacitors to become a realistic power solution.

Table 3 Electrochemical deposition of Manganese oxide/hydroxide and their composition.

Sr. No	Chemical/Bath Composition & conditions	Substrate Electrode			Details					Remarks/Properties	SC (F/g)	Ref.
		A	K	R	Applied Current/Voltage	Depo. time	Temp.	Scan Rate mV/s	Electrolyte			
1	0.5 M $\text{Mn}(\text{CH}_3\text{COO})_2$, After deposition film was annealed up to 600°C for 2 h.	Gh	Pt	SCE	0.5 V	-	25°C	-	2 M KCl	Amorphous film transformed into a fibrous structure with dispersive nanocrystals after annealing at 200°C for 2 h. When the temperature increased to 400°C, partial crystallization of Mn_2O_3 and nanocrystalline Mn_2O_3 was found. It was observed that the growth of oxide particles, without crystalline structure changed as the annealing temperature was increased to 600°C. Electrode annealed at 200°C was stable up to 500 cycles.	202	135
2	20 mM KMnO_4	SS	Pt	Ag/AgCl	0.5 to 1 mA/cm^2	0.5 hour	-	10	0.5M Na_2SO_4	XRD showed that, the formation of amorphous MnO_2 film. Capacitive performance of the films was increased with the increase in deposition current density. Specific capacitance slightly decreases after 300 cycles.	174	136
3	0.02 – 0.1 M KMnO_4	Ni, meshes,	Pt	-	2 mA/cm^2	10 min	-	2	0.5M Na_2SO_4 and 0.5M K_2SO_4	Films were amorphous, nearly spherical with the size ~ 30 nm, while some particles of ~ 100 nm were also seen.	240	137
4	0.1M manganese sulphate + 0.1M citric acid, pH ~10.5 by adding 1M NaOH.	SS	Gh	SCE	PD mode: +1.3 and -1.2 V PS mode: +1.1 V GS mode: 5 mA/cm^2	-	-	20	1 M Na_2SO_4	All electrodes revealed that the formation of amorphous phase. Different modes significantly affect the surface morphology of MnO_2 films. TEM showed that, the growth of the film was cluster by cluster with nanocrystals. The film for PD mode shows overall good performance.	237	138
5	0.1 mol/dm^3 TBAClO_4 + 0.002 mol/dm^3 monomeric LMnCl_2 , After deposition the film was dried at room temperature.	ITO	Pt	Ag/AgCl	-1.2 and 1.5 V	-	Room temp	2	1 mol/dm^3 KCl	Film was homogeneously deposited with 12 μm thick. The binding energy for the film lies within the range of 1-2 eV. Increase in conductivity may be because of addition of ca. 19 wt% carbon.	144	139
6	0.1 M manganese acetate After deposition the film was annealed at 150°C for 2 h.	AC	-	Ag/AgCl	0.90 V	120 sec	25°C	-	-	The formation of MnO_2 with thickness of the film was about 0.58 ~ 1.25 μm . The specific surface area of as -prepared sample was 7.7 m^2/g . Film was stable up to 2000 charge discharge cycles.	485.4	140

7	0.25 mol/L Mn(CH ₃ COO) ₂ After deposition the electrodes were dried at 50°C in vacuum for 12 h.	Gh	Pt	SCE	PC mode (p-MnOx): 25 mA/cm ²	ON-ti me: 0.25s OFF-ti me: 0.5 s	25°C	10	3mol/L KCl	g-MnO _x indicates the tetragonal phase of Mn ₃ O ₄ while p-MnO _x indicates two structures i.e. tetragonal Mn ₃ O ₄ and orthorhombic MnOOH. Surface morphology of g-MnO _x found to be rough with many cracks while for	252	141
8	Two solution: 0.1 M KMnO ₄ (MnOx-K) and 0.1 M MnSO ₄ (MnOx-S)	SS	Pt	Ag/ AgCl	1 mA/cm ²	10 min	60°C	5	1M Na ₂ SO ₄	The morphology of MnOx-K found to be thin film with a thickness of ~ 850 nm while MnOx-S has nanosheets with a sheet thickness of ~40 nm. The improvement in specific capacitance of MnOx-K may be due to nanosheet structure which increases the surface area.	233.5 5	142
9	0.5M MnAc ₂ + 0.51M KAc, After deposition the film was immersed in 2-propanol for 24 then annealed at 200°C for 2 h.	Pt/Si	Pt	SCE	1.0V	-	Room temp	10	0.5M Na ₂ SO ₄	Nanostructure and mesoporous MnO ₂ films were obtained.	449	143
10	0.25 M Mn(CH ₃ COO) ₂	Gh	Pt	SCE	0.3 V to 0.6 V	-	25°C	400	-	The results showed that the higher potential sweep rate produced compact oxide film with a higher density. As potential sweep rate increased (100mV/s to 400mV/s) thickness of film decreased (~3 µm to ~2 µm).	337	144
11	0.1 M KMnO ₄ + 0.1 M KNO ₃ + 200 ml DDW + Stirring for 1 hr After deposition the film was dried at 353 K for 5 h.	SS	Gh	SCE	+ 0.5 to + 1.5 V	-	Room temp	5	1 M Na ₂ SO ₄	Thin film has microporous structure with very fine nanosheets ~15 nm thick. All peaks of XRD pattern indicate the formation of γ-phase of MnO ₂ . Retention of film was about 94% after	333	145
12	Three solution: 0.3 M MnSO ₄ , 0.3 M MnSO ₄ + 0.2 M EDTA disodium salt and 0.3 M MnSO ₄ + 0.3 M sodium citrate, pH:7.0	Pt	-	-	100 mA/cm ²	-	70 °C	5	0.5M Na ₂ SO ₄	Three types of nanocrystal structures were found, ε-MnO ₂ prepared without any complex agent, defective rock salt MnO ₂ from EDTA containing solutions, and defective antiferroite MnO ₂ from citrate-containing solutions.	C	146
13	0.2 M MnSO ₄ + x.H ₂ SO ₄ After deposition the electrode was dried in a vacuum oven at 60°C for 5 h.	CFP	-	-	3 mA/cm ² and 35 mA/cm ²	-	95 °C	50	0.5M Na ₂ SO ₄	Four different morphologies i.e. nanospheres, nanosheets, nanoflowers and nanonods of MnO ₂ were obtained by varying the current densities of 3mA/cm ² , 3mA/cm ² , 3mA/cm ² , 35 mA/cm ² and concentration of H ₂ SO ₄ i.e. 0 mol/L, 0.5 mol/L, 1.1 mol/L and 1.1 mol/L respectively. After 5000 cycle electrodes retained high capacitance.	362.5	147
14	0.1 M manganous Acetate + 0.1 M sodium sulfate After deposition film was heated in air at 300°C.	Ni	-	SCE	0.4 V	5 or 10 hr	Room temp	50	0.1M Na ₂ SO ₄	The surface morphology showed MnO ₂ film has highly porous in nature. The specific capacitance of the film was maintained up to 1500 cycles.	389	122

15	0.1 M manganous Acetate + 0.1 M sodium sulfate After deposition film was heated in air at 300°C for	Ni	-	SCE	+0.4 V	5 or 10 hr	Room temp	50	0.1M Na ₂ SO ₄	Particle diameter of MnO ₂ film was found to be ~200 nm. SEM results showed film has porous microstructure with grain sizes between 10 to 20 nm in	389	148
16	Mn films: BMP-NTf ₂ + 0.05 M Mn block After deposition Mn film was cleaned with CH ₂ Cl ₂ solution and dried in air.	Ni	Mn block	Pt	-1.8V	-	50°C	50	0.1M Na ₂ SO ₄	The SEM results revealed that the formed film has fibrous (porous) microstructure. Mn Oxide formed by potentiostatic method showed good results even after 500 CV cycles.	332 & 180	149
	Mn Oxide: 0.1M Na ₂ SO ₄	Mn film	Pt	SCE	PS mode: 0.9V CV mode: 0-0.9 V & sweep rate 25 mV/s	10 min 10 cycles						
17	5mM MnCl ₂ + 0.4-0.8 g/l PEI in the ethanol-water After deposition film were dried at room temperature for 24 h.	Pt	Nickel foils	Pt	2 mA/cm ²	5 min	-	10	-	It was observed that the presence of polymer content in the deposit can be varied by the varying concentration of polymer. X-ray pattern showed that the formation of crystallization of Mn ₂ O ₃ at 300°C and Mn ₂ O ₃ at 500°C. Increase in number of cycle results in increasing porosity of the film. Resistance of the prepared film increases with increase in the amount of deposited material.	425	150
18	Mn film: BMP-NTf ₂ + 0.05 M Mn block After deposition Mn film was cleaned with CH ₂ Cl ₂ solution and dried in air.	Ni	SH E	Pt	-1.8V, -2.0V, and -2.2V	-	50-110°C	5	0.1M Na ₂ SO ₄	Mn film was found to be spherical particles, with numbers of sub-grains of few nano-meters in size. The capacitance of the Mn oxide film retained 94% after 500 CV cycles.	402	151
	Mn oxide: 0.1M Na ₂ SO ₄	Mn film	Pt	SCE	5-500 mV/s	500 cycles	25°C					
19	0.15 M H ₂ SO ₄ + 2M MnSO ₄ ·5H ₂ O After deposition films were annealed at 400, 500 & 600°C.	SS	Pt	SCE	1.25-5mA	-	-	-	0.1M Na ₂ SO ₄	Film annealed at 500°C assigned to Mn ₂ O ₃ . Morphology of the prepared film showed mesoporosity, nano structure with 10µm thickness. Specific energy and power was found to be 86Wh/kg and 54kW/kg respectively. Capacitance remains constant up to 10,000 cycles.	410	152

20	MnO ₂ Nanowire Array: 100 mM manganese acetate, After deposition film was soaked in 3M NaOH for 30 min.	AA O	Pt	Ag/ AgCl	0.60 V Total charge: 750mC/cm ² for 4.5 μm long wires or 250 mC/cm ² for 1.5 μm long nanowires.	-	-	50	1 M LiClO ₄	MnO ₂ nanofibrils distributed on the MnO ₂ nanowire surface. Simple conversion of the MnO ₂ nanowires into Mn ₂ O ₃ resulted in the formation of hierarchical MnO ₂ nanofibril/ nanowire. Capacitance retention was about 85.2% after 1000 cycles.	298	153
	Synthesis of MnO ₂ Nanofibril/Nanowire Arrays: 100 mM manganese acetate	Mn O ₂	Pt	Ag/ AgCl	-0.85 V & Sweeping potential: 1.0V							
21	0.16 M MnSO ₄ .5H ₂ O, pH: 5.6. After deposition film was dried in vacuum oven at room temperature for overnight.	Gh	Pt	Ag/ AgCl	PS mode: 0.8 V & 3.7 mA/cm ²	-	-	10	0.1M Na ₂ SO ₄	Surface morphology of CV mode for 10 cycles showed the film was uniformly deposited and highly porous nanostructure in a 3D network. All deposits showed similar oxidation state.	230	154
					CV mode: 0.4 and 1.0 V at Scan rate 10mV/s	30 cycles						
					GS mode: 3.7 mA/cm ²	-						
22	0.25 M Mn(CH ₃ COO) ₂ After deposition the film	CA	Pt	SCE	0.5 to 0.95 V	-	25°C	5	2 M KCL	Both trivalent and tetravalent manganese oxides formed at deposition potential of	240	155
23	0.25 M MnSO ₄ .5H ₂ O, pH: 6.4	Gh	Pt	Ag/ AgCl	0.75 V	-	-	5	0.1M Na ₂ SO ₄	Amorphous hydrous manganese oxide (a-MnO ₂ .nH ₂ O) was formed.	285	156
24	0.25 M MnSO ₄ .5H ₂ O, Different pH values adjusted by adding 0.1 M H ₂ SO ₄ and 0.15 M Na ₂ SO ₄ . After deposition film was annealed in air for 2 h.	Gh	Pt	Ag/ AgCl	0.92 and 1.3 V	-	-	5	0.1M Na ₂ SO ₄ & 0.3M KCL	Amorphous hydrous manganese oxide (a-MnO ₂ .nH ₂ O) was formed. The stability of the electrode was improved by annealing treatment but the value of capacitance was decreased with increase in temperature. The surface morphology became smoother at 350°C annealing temperature.	0.038 7	157
25	0.01M Mn(CH ₃ COO) ₂ .4H ₂ O + 0.25 M Ni(CH ₃ COO) ₂ .4H ₂ O + 0.8 M H ₂ SO ₄	SS	CA	Ag/ AgCl	CP Mode: 8 mA	10 min	-	-	Na ₂ SO ₄ & KOH/ K ₃ Fe (CN) ₆	XRD peaks indexed to α-MnO ₂ and NiO. The electrode formed with CV mode exhibited a highly amorphous nature, high homogeneity and good capacitance compared to other mode. The specific capacitance of 3509 F/g was found in mixed KOH/K ₃ Fe (CN) ₆ electrolyte for CV mode electrode. The electrode showed the higher energy and power densities of 1322 Wh/ kg and 110.5 kW/kg, respectively.	3509	158
					CA Mode: 1.5 V	-						
					CV Mode: 0 to 1 V at a scan rate 20 mV/s	7 cycle						

26	GO (10 mL)+ 0.01 M manganese acetate After deposition film was dried at 300°C for 6 h.	SS	CA	Ag/ AgCl	0 to 2 V at scan rate of 50 mV/s	-	-	10	0.5 M KOH/ 0.04 M K ₃ Fe(CN) ₆	Uniform nanoflake morphology was obtained when 0.03 M glucose was added into solution. Electrode showed high specific power and energy density of 68.35 kW/kg & 1851 Wh/kg respectively. After 2000 cycles capacitance retention was about 46%.	13,33 3	159
27	0.1 M Mn(CH ₃ COO) ₂ ·4H ₂ O + 0.2 M NiCl ₂ ·6H ₂ O, After deposition the film was dried with nitrogen gas, and annealed in an oven at 250°C for 3 h.	Gh	Gh	Ag/ AgCl	1.2 V	60 s	Room temp	20	0.5 M Na ₂ SO ₄	Film was numerous nanofibers in a 3D network. The film contained γ-MnO ₂ and NiO. Mn -Ni oxide electrode retention of about 86% was found over 2000 charge -discharge cycles.	424	160
28	0.1 M N ₂ SO ₄ + 0.1 M Mn(CH ₃ COO) ₂ , pH: 5.5	SW CN T	Pt	Ag/A gCl	-	5 min	-	10	1 M KCl	γ-MnO ₂ nanostructure with poor crystallinity was formed. Surface morphology showed that the film has two types of microstructures i.e. nanowire and nanocactus.	187.7 5	161
29	Two solution: 0.1 M MnSO ₄ (CNTK) and 0.1 M KMnO ₄ (CNTS)	MW CN T	-	-	1 mA/cm ²	5 , 10 and 15 min	60°C	5	1M Na ₂ SO ₄	Both electrode showed different morphology i.e. clusters morphology in CNTK solution while nanosheets with thickness of ~40 nm were formed in CNTS solution. The CNTS for 10 min deposition showed the highest specific	267.0 3 ± 31.75	162
30	0.2 M KMnO ₄ + 1mg/mL CNTs + 0.1M phosphate buffer solution, pH:7.0 After deposition film was dried at 60°C for 1 hr.	rGO -PV DF	Pt	Ag/A gl	-2 to 2 V at scan rate of 200 mV/s	200 Cycle	-	-	6 M NaOH	1D structure with diameters of about 100 nm and rough surface was formed. The CNTs-MnO ₂ /rGO-PVDF film indicates that the material was highly flexible. Loss in the specific capacitance was about 17% after 1000 cycles with 22.2 Ω resistance.	276.3	163
31	0.25 M MnSO ₄ , pH:6.5, After deposition electrode was dried at 150°C for 30 min.	PED OT	-	-	0.75V	-	-	100	0.1M Na ₂ SO ₄	Morphology of composite film formed a rod-of-beads structure. The presence of Mn 3p with binding energy of 653.5 eV and Mn 2p with binding energy of 641.5 eV was found. The capacitance retention of ~68% was found after 500 cycles.	61.5	164
32	0.2M MnSO ₄ ·5H ₂ O, After deposition electrode was dried at 80°C for 5hr.	CN T	-	SCE	1V	Pulse-on time: 0.3 s Pulse off time: 2.1 s for 50 cycles	-	10	1.0M KCl & 1.0M LiClO ₄ /PC (organic)	Thin MnO ₂ layers with a thickness of about 3–5nm showed 3D nanoporous structure. Electrochemical properties of thin film in organic electrolyte showed better results.	576	165

33	0.16 M $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$, pH: 5.6 After deposition film was dried in vacuum at room temperature for 24 hr.	CN Ts/ Ni	Pt	SCE	0.4 V	3 min	25°C	5	0.1 M Na_2SO_4	10-25 nm amorphous MnO_x nanoparticles formed on the CNTs/Ni substrate. The surface area of $6.0 \text{ m}^2/\text{g}$ for MnO_x/Ni and $20.2 \text{ m}^2/\text{g}$ for $\text{MnO}_x/\text{CNTs}/\text{Ni}$ substrate was found. The capacitance retention was about ~79% over 1000 cycles.	415	166
34	0.01 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ + 0.02 M $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ + 0.01 M KCl, After deposition film was annealing at 500°C for 6 h.	ITO	Pt	Ag/A gCl	-1.1 V	60 s, 120 s and 180 s	70 °C.	1	2 M KOH	The MCO nanosheets were compact with homogeneous shape and uniformly grown with 3D structures of thicknesses in the range of 10–40 nm & length ~1–2 μm . Formation of MnCo_2O_4 with an atomic ratio of ~1:2 for Mn and Co. electrode showed good cyclic stability after 1000 CV cycles.	290	167
35	MnO_2 : 0.1 M $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 0.1 M citric acid, pH ~10.5 by adding NaOH. Fe: MnO_2 : 0.5, 1, 2 and 4 at% of ferric sulfate.	SS	Gh	SCE	5mA/cm ²	-	Room temp	5	1 M Na_2SO_4	The value of capacitance decreases with increase in scan rate. Maximum specific capacitance achieved for 2 at% Fe: MnO_2 . Due to the Fe addition specific energy and specific power increased from 1.2 to 1.6Wh/kg and 0.4-103 to 0.5 -103 W/kg respectively. Supercapacitive performance of MnO_2 thin films improved due to addition of Fe.	218	168
36	Mn oxide deposition: 0.01 M $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ + 0.02 M $\text{NH}_4(\text{C}_2\text{H}_3\text{O}_2)_2$ + 10 % $\text{C}_2\text{H}_6\text{OS}$, After deposition the samples were dried in air at 100°C for 60 min.	Ni foa m	Pt	-	5–25 mA/cm ²	2.5-10 min	60 °C	5	0.5M Na_2SO_4	The film was poorly crystalline with grain size ~5nm, it could be indexed to either a hexagonal structure (MnO_2) or cubic spinel structure (Mn_3O_4). Addition of PEDOT cause to increased the specific capacitance from 120 to 159F/g. The capacitance value slightly decreased after 2000 cycles.	159 & 120	169
	PEDOT deposition: 0.08 M EDOT + 0.2 M LiF_4B + 0.14 M sodium dodecyl sulfate	Mn Oxi de film	Pt	SCE	1 V	45 s	25 °C					
37	0.1 M $\text{Mn}(\text{CH}_3\text{COO})_2$ + 0.1 M Na_2SO_4 . After deposition films were dried and annealed in air at 300°C for 2 h.	Ni foa m	Pt	SCE	PD mode: +0.3 to +0.6 V at scan rate: 25 mV/s	1500 cycles	Room temp	5	9 M LiNO_3	All electrodes indexed to pyrolusite MnO_2 . PS + PD mode showed higher pore volume, pore size & higher specific capacitance (325F/g), than those of PD (200F/g) and PS mode (175 F/g). The energy and power density of PS + PD mode electrode was found to be 7.66 Wh/kg & 600 W/kg respectively. The retention of capacitance was 98% over 10,000 cycles.	325	170
					PS mode: +0.6 V	1800 s						
					PS+PD mode: +0.6 V & (+0.3 and +0.6 V) at a scan rate 25 mV/s	900 s & 800 cycles						

Table 4 Electrochemical deposition of Nickel oxide/hydroxide and their composition.

Sr. No	Chemical/Bath Composition & conditions	Substrate Electrode			Details					Remarks/Properties	SC (F/g)	Ref.
		A	K	R	Applied Current/Voltage	Depo. time	Temp.	Scan Rate (mV/s)	Electrolyte			
1	0.08 M Ni(NO ₃) ₂ , After deposition film was thermal treated at in air at 250°C (temp rate: 5 °C/min) in muffle stove for 2 h.	Ni	Pt	SCE	-0.90 V	-		40	1 M KOH	Formation of α - nickel hydroxides with the grain size of 3.48 nm. The capacitance maintained up to 87% of maximum capacity after 500 cycles	1478	180
2	0.13M sodium acetate + 0.13M nickel sulfate + 0.1M sodium sulfate. After deposition film was dried at 300°C in air for 1 h.	SS	Pt	Ag/AgCl	0.5mA/cm ²	60 min	Room temp	25	1 M KOH	Film exhibits highly porous morphology with nanoflakes like structure of thickness 12–16 nm. XRD pattern indicates that the formation of NiO with poor crystallinity. 87.5% retention of capacitance after 5000 cycles.	167.3	181
3	Three solution: NiCl ₂ ·6H ₂ O (NiO-C), Ni(NO ₃) ₂ ·6H ₂ O (NiO-N) and NiSO ₄ ·6H ₂ O (NiO-S), After deposition films were annealed in air at 500°C for 2 h.	SS	Gh	SCE	NiO–C: -0.75 to -0.6 V	30 min	Room temp	5	1 M KOH	All electrodes showed the cubic phase of NiO. It was observed that the growth of nanoflakes uniformly distributed on the surface. NiO–S electrodes showed all over good performance i.e. high capacitance, low impedance 1.27Ω/cm ² and high surface area 91.5 m ² /g with better stability (85.6%).	893	182
					NiO–N: -0.7 to -0.55 V							
					NiO–S: -0.8 to -0.65							
4	0.1 M Ni(NO ₃) ₂ , After deposition film were annealed at 573 K for 90 min.	SS	Gh	SCE	0 to -1.2 V at scan rate:50mV/s	30 cycles	-	100	1 M KOH	Formed NiO nanoflakes thin film showed specific power of 1.0 kW/kg and energy 14.6Wh/kg. Impedance of prepared film was 1.34Ω and cyclic stability up to 94% over 1000 cycles	222	183
5	0.08 M Ni(NO ₃) ₂ ·6H ₂ O	Ni	Pt	Ag/AgCl	-0.90 V	-	Room temp	-	1 M KOH	α-Ni(OH) ₂ showed particle like morphology with a loosely packed structure.	2595	184
6	3 mM Ni(NO ₃) ₂ ·6H ₂ O + 3 mM Fe(NO ₃) ₃ ·9H ₂ O	NF	Pt	Ag/AgCl	-1.0V	300 s	10° C	5	1M KOH	The formation of interconnected mesoporous structures with the pore size of 50 nm.	-	185

List of Abbreviates:

Pt: Platinum
 Gh: Graphite
 SS: Stainless steel
 ITO: Indium doped tin oxide
 SHE: Standard hydrogen electrode.
 SCE: Saturated calomel electrode
 Ti: Titanium
 TiO₂: Titanium oxide
 AAO: Anodic Aluminum oxide
 Ni: Nickel
 AC: Activated Carbon
 Si: Silicon
 Mn: Manganese
 Cu: Copper
 CFP: Carbon fiber paper
 CNT: Carbon nanotube

SWCNT: Single walled Carbon nanotube
 MWCNT: multiwalled Carbon nanotube
 CdO: Cadmium oxide
 NF: Nickel Foam
 rGO: Reduced graphene oxide
 PVDF: Polyvinylidene fluoride
 ED: Electrodeposition
 SC: Specific Capacitance
 PD mode: Potentiodynamic mode
 PS mode: Potentiostatic mode
 PC mode: Pulse Current deposition mode
 GS mode: Galvanostatic mode
 CP mode: Galvanostatic (chronopotentiometry) mode
 CV mode: Cyclic voltammetry mode
 CA mode: Potentiostatic (chronoamperometry) mode
 CV: Cyclic-Voltammetry.

Table 5 Electrochemical deposition of Cobalt oxide/hydroxide and their composition.

Sr. No	Chemical/Bath Composition & condition	Substrate Electrode			Details					Remarks/Properties	SC (F/g)	Ref.
		A	K	R	Applied Current/Voltage	Depo. time	Temp.	Scan Rate mV/s	Electrolyte			
1	0.05 M cobalt chloride, pH: ~10 by adding 30% ammonia.	Cu	Pt coated Ti	Ag/AgCl	-1.2 V	15 min	-	20	2M KOH	Formation of Co ₃ O ₄ film with nanocrystalline structure. Film was highly porous with thickness of 0.60 mg/cm ² . The specific power and energy of the electrode were 1.33 kW/kg and 4.0 Wh/kg respectively.	235	197
2	0.1 M Co(NO ₃) ₂ ·6H ₂ O After deposition film was dried in vacuum oven at 200°C for 2h	CA foam	Pt	Ag/AgCl	-0.8V	20 min	70°C	500	1 M NaOH	All peaks were indexed to cubic lattice of Co ₃ O ₄ . SEM & TEM showed that the formation multilayers with sheet like structure of Co ₃ O ₄ .	106	198
3	0.05 M Co(NO ₃) ₂ After deposition film was air annealed at 623 K for 180 min	SS	Gh	SCE	PD mode: 0 to -1.2 V at scan rate: 50 mV/s	-		100	1M KOH	Formation of cubic crystal structure of Co ₃ O ₄ . Morphology of the film shows the porous with nanoflakes-like structure. PS electrode showed energy and power density of 19 Wh/kg and 3.8kW/kg respectively.	248	199
					PS mode: -0.9 V	5 min						
					GS mode: 3 mA/cm ²	-						
4	1.189 gr CoCl ₂ ·6H ₂ O + 1 gr C ₁₂ H ₂₂ O ₁₁ were dissolved in 1 liter water.	SS	Gh	Gh	10 mA/cm ²	30 min	40°C	5	1M KOH	The formation of hexagonal brucite-like structure of β-Co(OH) ₂ phase. SEM and TEM showed that the	1288.1	200
5	0.1 M Co(NO ₃) ₂ ·6H ₂ O + Na ₂ SO ₃ in 1:1 volumetric ratio	CdO	Pt	Ag/AgCl	4 mA	300 sec	Room temp	10	1M KOH	All XRD peaks were matched with Co(OH) ₂ . The capacitance retention was about 54% after 1000 cycles. Electrode showed high energy and power density of 98.83Wh/kg and 0.75kW/kg respectively.	1119	201

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