TRANSITION METAL OXIDES BASED SUPERCAPACITOR

A

Thesis Submitted To
Odisha University of Agriculture and Technology, Bhubaneswar
In Partial Fulfilment of The Requirement of The Degree of
MASTER OF SCIENCE IN CHEMISTRY

By

RUDRA RATIKANTA POTHAL

Admission No.: 06CHEM/19

DEPARTMENT OF CHEMISTRY

COLLEGE OF BASIC SCIENCE AND HUMANITIES
ODISHA UNIVERSITY OF AGRICULTURE & TECHNOLOGY
BHUBANESWAR- 751003
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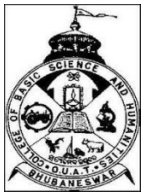

Dr. (Mrs.) Swarnabala Jena
Assistant Professor
Department of Chemistry

CERTIFICATE – I

This is to certify that the thesis entitled, "**TRANSITION METAL-OXIDES BASED SUPERCAPACITORS"** submitted in partial fulfillment of the requirements for the award of the degree of Master of Science in **CHEMISTRY** to the Orissa University of Agriculture and Technology, Bhubaneswar, is a faithful record of bonafide research work carried out byRUDRA RATIKANTA POTHAL **, Adm No: 06- CHEM/19**under my guidance and supervision and that no part of thesis has been submitted for any degree or diploma or published in any form.

It is further certified that the help and sources of information availed of during the course of study have been duly acknowledged.

Place:Bhubaneswar
Date:

Dr. Swarnabala Jena
AssistantProfessor,
Department of Chemistry
CHAIRMAN
ADVISORY COMMITTEE

CERTIFICATE-II

This is to certify that the thesis entitled**"TRANSITION METAL-OXIDES BASED SUPERCAPACITOR"** submitted by RUDRA RATIKANTA POTHAL to Orissa University of Agriculture and Technology , Bhubaneswar in partial fulfilment of the requirements for the award of the degree of MASTER OF SCIENCE IN CHEMISTRY has been approved by the students' Advisory Committee .

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EXAMINER _____

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Finally I pay my obeisance at lotus feet of lord JAGANNATH for his blessings to be an asset to do my research work.

Place: Bhubaneswar (Rudra RatikantaPothal)

Date:

CONTENT

LIST OF FIGURES

ABBREVIATIONS AND SYMBOLS USED

SS:	-	Stainless steel
SHE:	-	Standard hydrogen electrode.
AC:	-	Activated Carbon
SC:	-	Specific Capacitance
CV:	-	Cyclic-Voltametry
et al.,	-	et alebi (and others)
etc	-	et cetra
Fig	-	Figure
g	-	Gram
ml	-	Millilitre
XRD	-	X-ray diffraction

TRANSITION METAL – OXIDE BASED SUPERCAPACITOR

ABSTRACT

Today's world is in greater threat due to global warming and increasing energy demand due to extensive use of fossil fuel. In order to fulfil the hunt for increasing energy demand researchers triggered for search of generation of sufficient amount of energy in a greener method. Hence, development of various high performance energy storage devices,such as fuel cells, batteries, and supercapacitors has gained much attention in recent years. In order to meet the future energy demand , amongst the previously mentioned energy storage devices, much attention has been given towards the development of high-performance supercapacitorsas they have several advantages, such as fast charging and discharging ability, longer cyclic lifespans, and wide operating temperature ranges over the fuel cell and battery. In supercapacitors charge storage occurs either by ion adsorption or redox reaction. This classifies the super capacitors into electrical double layer (EDLC) and pseudo capacitors. The synthesis of metal oxide has drawn much attention due to their distinguished physical and chemical properties. Metal oxides with unique porous structure, high surface area and easy access of the electrolyte ions into the electrode surface through the pores of active materials make them superior material for supercapacitor applications. Along with this distinguished properties metal oxides have attractive performances for fabricating various supercapacitor devices in a broad voltage window. The transition metal oxide materials, due to their abundance reserves, environmental benignity, easy approachability has earned greater attention along with other fascinating characters such as their diverse constituents, large surface area and high theoretical specific capacitance. They play a central part of the electrodes of the electrochemical supercapactors and improves capacitance by adjusting their defects at surface / interfaces under nano scale range and increases energy density. However, low electrical conductivity, uncontrollable volume expansion, and slow ion diffusion in the bulk phase hinders their practical application. Hence, bimetallic oxide materials are highly useful in order to overcome the poor electric conductivity of single metal oxide materials to achieve high capacitance and raises the energy density at capacitor level. In this review some metal oxide both metallic and bimetallic have been discussed along with their energy storage mechanism, the influence on chemical composition, structural features, electro conductivity ,morphologies, and various electrolyes in the electrochemical behaviour are discussed so that in near future researchers find a new direction on the future of metal oxide based supercapacitors.

INTRODUCTION

In the recent decades, environmental pollution accompanied with energy crises is the great issues for researchers. Now days the consumption limit of fossil fuel is too high that the earth accelerates towards the path of darkness in the near future. The environmental pollution also increases owing to the depletion level of fossil fuel reservoir. The increasing combustion offossil fuel results in the production of gases like CO_2, NO_2, and CH_4 etc., which absorbs the solar radiation from the atmosphere and makes the earth hotter. According to NASA`s survey at GODDARD institute , the average temperature of earth increases by 0.8°c due to rapid industrialisations and this small change in temperature causes melting of polar ice caps and glaciers which in turn causes flooding and rising of sea level at the coastal regions[1-3]. This ultimately threatens the survival of life on earth. Hence, in order to maintain the sustainability of life on earth and their life standards, there is a need of energy sources like solar wind etc.that gives sufficient energy for survival. However, these natural energy sourcesface various climatic issues and cannotfulfil sufficiently our demands for energy. This stimulates the scientific community for the search of alternative energy storage systems that can reduce the use of fossilfuels.

many energy storage devices such as battery, capacitors,fuel cells and super capacitors are used today to store energy. Amongst,super capacitor or electrochemical capacitor is considered as an excellent energy storage device due their high power densities, long life span and short charging time .The more energy density and life line of the super capacitors mainly depends upon the electrode materials used and the stability of electrolytes [1]**.**In 1978, a super capacitor introduced by NCE, which is used to provide the power back up for the computes [4]**.** Generally, the electrode materials used for super capacitor should possess various physio chemical properties such as high conductivity, high surface area,amorphous,good corrosion resistance, high temperature stability and relatively low cost. Several materials such as transition metal oxides, carbon aerogels, and graphene composites etc. Areused as electrode materials for super capacitors. Among them, transition metal oxides are considered as promising candidate as electrode material for super capacitor due to their easy abundance, environmental benignity, easy approachability , low cost , high surface area, chemically non-hazardous and high theoretical specific capacitance[5-7] . RuO_2 is the best

transition metal oxides for this purpose, but the technical huddles associated with it is high expensive [8]. Various TMO $NiFe_2O_4$, and BiFeO3are useful for super capacitive electrode materials [4, 9-14]. The design of metal oxides depends in terms of their composition. The fabrication of the nanostructure mainly based on the electrical conductivity and oxygen vacancies of the metal oxides.. For better electrical conductivity binary metal oxides shows efficient electrical conductance than single metal oxide. For example, electrodes of NiCo2O4 show more electrical conductivity than the individual one NiO and Co3O4. By experiment,It is seen that the addition Ni with Co3O4 increases the electrical conductivity from 3.1×10^{-5} s cm^{-1} to 0.1 s cm^{-1} [15-17].Again, the metal oxides having porous structure can easily transport the metal ions so that electrical conductivity increases. The oxygen vacancies in the metal oxides makes the electrodes porous and increases the surface area due to which electrical conductivity along with storage capacity increases which can be given by the formula C α A/ D [18 – 21] . It is proved that MoO_{3-x} has two times larger electrical conductivity than MoO_3[22].

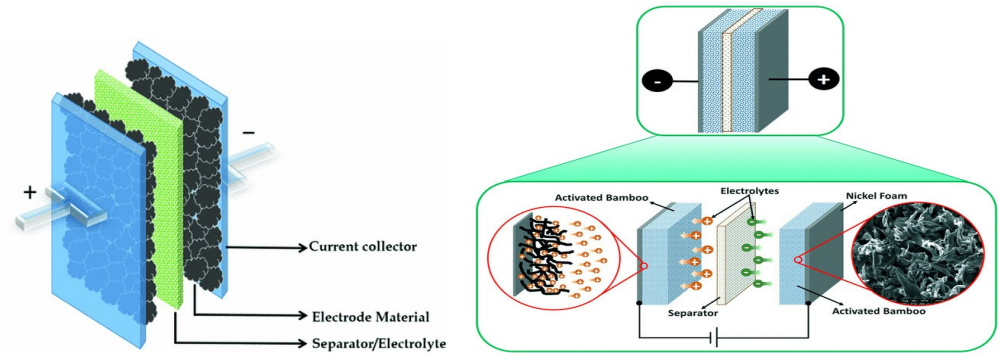


Fig 1- diagram of supercapacitor and its components.

Supercapacitorsare also known as ultra-capacitors, double layer capacitors or electrochemical capacitors. They utilize large surface area and thinner dielectrics to achieve greater power density than that of batteries and greater capacitances with higher energy density than that of conventional capacitors[23-29]**.**Super capacitor reaches 20 times P.D (>10 KILOWAAT PER KG) and good life cycle (>105 cycles) than that of batteries, also it can be charged/discharged rapidly[30, 31]. It is used in variety energy storage device. Fig. 2 indicates the comparison of specific energy and specific power.. [32-33]

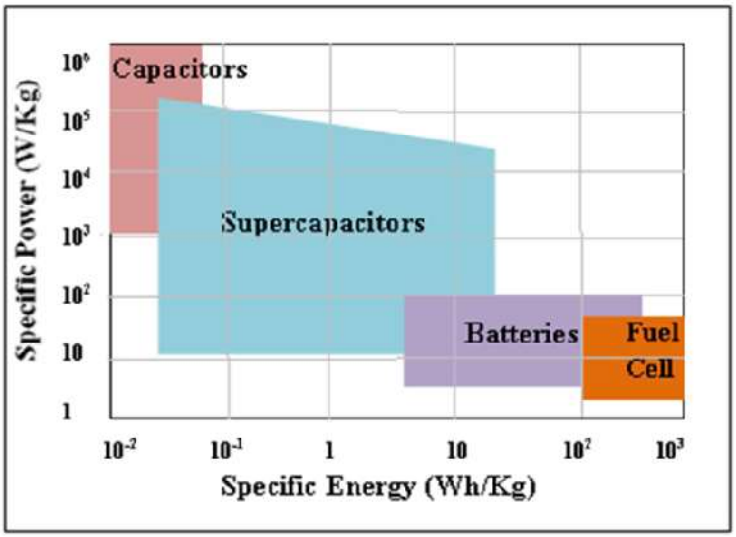


Fig 2 Ragone plot: Specific Energy Vs Specific Power Plot

In this review article, we have presented the Basic idea about capacitor, super capacitorworking of supercapacitor, types of supercapacitor,electrodematerial, electrolytes used and transition metals used as electrode materials like RuO2 , MnO2,Mn3O4,Fe2O3,Fe3O4,NiOetc

Capacitor:

Capacitor is an electric component, whichis used to store charge in the form of electric potential. Capacitor consists of two parallel plates separated by small distance in few milimeter. Here the Amount of charge store in the capacitoris known as capacitance, it depends upon the dimensions of the capacitor. The increase and decreasing of capacitance depends upon dimension of the capacitor and materials used in it. When the capacitor is attached across the battery an electric field develops across the dielectric causing +ve charge on one plate and –ve charge on another plate.[wikipedia]

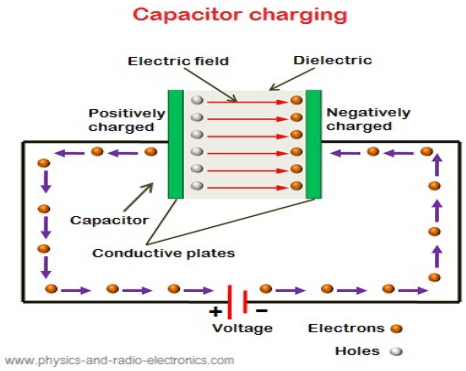


Fig 3- picture of capacitor

Super capacitor

Supercapacitors are capacitors that have a higher capacitance and energy density than ordinary capacitors. By delivering great power performance in a small design, super capacitors can bridge the gap between ordinary capacitors and batteries. It is made up of two electrodes, an electrolyte in the middle, and a membrane that separates them.[Wikipedia]

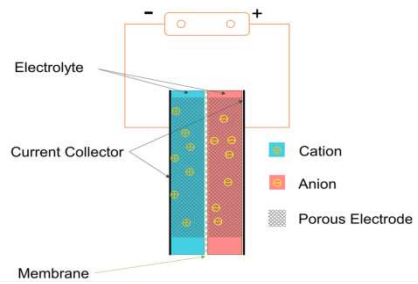


fig 4 – picture of super capacitor

-

Working of supercapacitors:

A supercapacitor consists of one porous membrane, which separates the +ve and –ve plate is called separators. The two electrodes are electrically connected with ionic liquid called electrolyte. When the voltage is applied to the +ve electrode it attracts the –ve ions from the electrolyte. Similarly when the voltage is applied to the –ve electrode it attracts the +ve ions from the electrolyte. These ions are stored near the surface of the electrodes due to which the distance between the electrodes decreases. Due to decrease in distance, the capacitance becomes very large which can be shown by the formula C α A⁄D. [wikipedia]

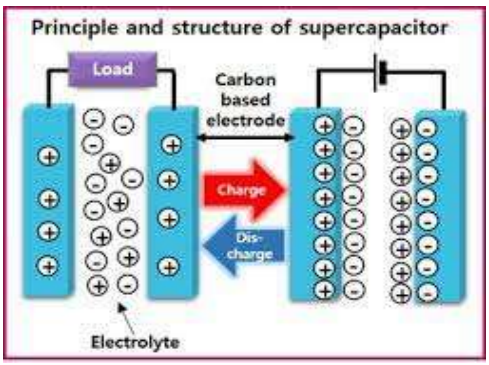


Fig 5 – Picture of working of supercapacitor

Types of super capacitors :

Normally based on mechanism of energy storage and cell configuration the supercapacitorsare divided into 3 types such as: (i) ElectricDouble- Layer Capacitors (EDLC's), (ii) Pseudocapacitors and (iii) Hybridcapacitors.

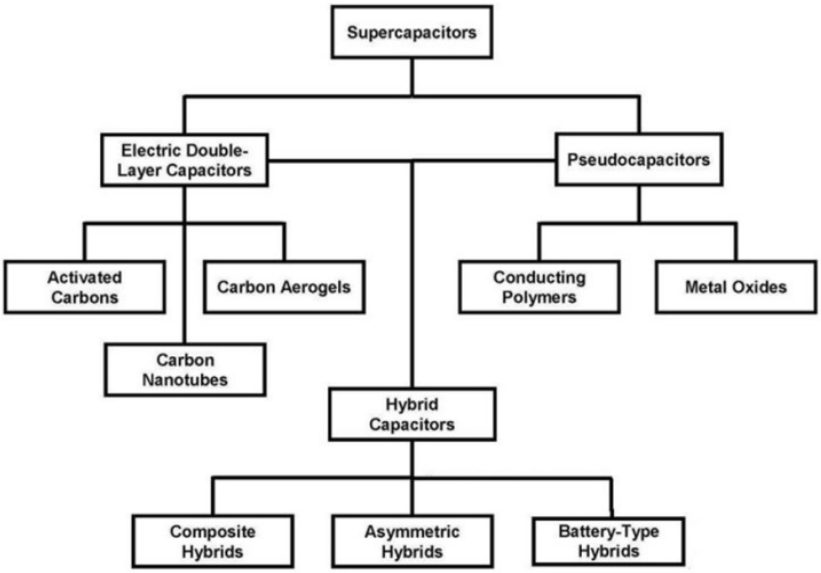


Fig -6 variety types of super capacitor

Electric double layer capacitor (EDLC) :

EDLCs are made up of two porous carbon-based electrode materials separated by an insulator. The energy charge is stored in a non-faradaic way here, with the charge storage process relying on the buildup of electrostatic charge at the electrode-electrolyte interface.Because carbon nanomaterials have distinctive structures with large surface areas, higher electrical conductivity, and excellent chemical and mechanical durability, activated carbon is the most popular electrode material[34, 35]. The construction of EDLCs is identical to that of ordinary capacitors, with the exception that the dielectric is replaced with electrolyte. The positive and negative ions of the battery are charged during the charging process.Negative and positive electrodes separate and adsorbe electrolyte, respectively[36]. EDLC can store much more charge than traditional capacitors. [37]

Pseudocapacitor:

Pseudo capacitor that stores energy through a reversible redox process or a Faradic reaction[38]. In comparison to EDLCs, pseudo-capacitors store charge electrostatically. In Pseudocapacitors, faradaic charge transfer occurs at the electrode-electrolyte interface. Due to Faradic process, it has moreeng.den.and capacitance than EDLC.Transition metal oxides and conducting polymers are primarily utilised as pseudocapacitor electrodes in pseudo capacitors[39-46].

Hybrid supercapacitor:

Hybrid supercapacitors combine the properties of both EDLCs and pseudocapacitors to create a third type of supercapacitor. The electrodes of hybrid supercapacitors are made up of a mix of EDLC (CARBON, carbon nanotubes, etc.)

and pseudocapacitive (transition metal oxides and conducting polymers) materials).Because hybrid supercapacitors combine EDLC and pseudo capacitors, they provide a high energy density and quick charging rate in a single cell. Due to the larger operating voltage of an organic electrolyte and the excellent specific capacity of the battery type electrode, combining two distinct electrodes results in more energy storage.
There are three types of hybrid capacitors based on configurations of electrodes (a) compositehybrid capacitors, (b) asymmetrichybrid capacitors and (c) battery-types hybrid capacitors [47-54**]**.

Electrolytes:

Aside from electrodes, the electrolyte is another essential component that can have a significant impact on the electrochemical performance of a supercapacitor device. Electrolyte can be found both inside the separator and within the active material layers. High ionic concentration, low resistivity, low viscosity, and other key parameters for an electrolyte might impact the power deposition.Aqueous electrolytes, organic electrolytes, and ionic electrolytes are the three types of electrolytes often utilised in supercapacitors. H2SO4, KOH, Na2SO4, HCl, NaCl, and NH4Cl aqueous solution,. Aqueous electrolyte supercapacitors may have a greater charge storage capacity.. Acetonitrile and propylene carbonate (PC) are two popular solvents for organic electrolytes. Aqueous electrolyte is utilised as a supercapacitor in some situations when cost is more essential than performance.(55-58)

Electrode materials supercapacitor(sc):

Carbon, metal oxide, and conductive polymer are some of the electrode materials that may be utilised in supercapacitors. Carbon materials with capacitive behaviour, including as carbon, carbon nanotubes), multi-walled (MWCNTs), single-walled (SWCNTs), and graphene, are commonly used as electrodes for EDLC. Metal oxide, on the other hand, especiallysupercapacitor.There are now a large range of materials available for super- capacitors that were produced using various techniques, particularly to obtain varied morphologies and porous architectures. Transition metal oxides such as ruthenium, manganese, nickel, cobalt, tungsten, and vanadium are among the materials. Meanwhile, conducting polymers of polyaniline (PANI), polypyrrole (PPy), and poly(3,4-ethylene dioxytetrafluoroethane . Although many synthesis methods have been developed to prepare the above materials, they can be grouped into the following categories: sol–gel synthesis, chemical precipitation, hydrothermal/ solvothermal synthesis, thermal decomposition, and electrochemical preparation, all of which can be combined with various nanotechnologies to achieve unique microstructures and advanced performances[59].

.

Here We must concentrate on transition metal oxides in this casedue to their high performances.

CV – Curve:

Cyclic voltammetry is an electrochemical technique for measuring the current response of a redox active solution with potential sweep between two or more set values. The cyclic voltammetry (CV) curve of EDLC supposed to be rectangular, but in pseudo-capacitance, the shape of the curve will become non-rectangular due to faradaic process. Hence, overall shape of the CV curve in hybrid type capacitors is a nonrectangular as it is combination of both EDLC and Pseudocapacitors.

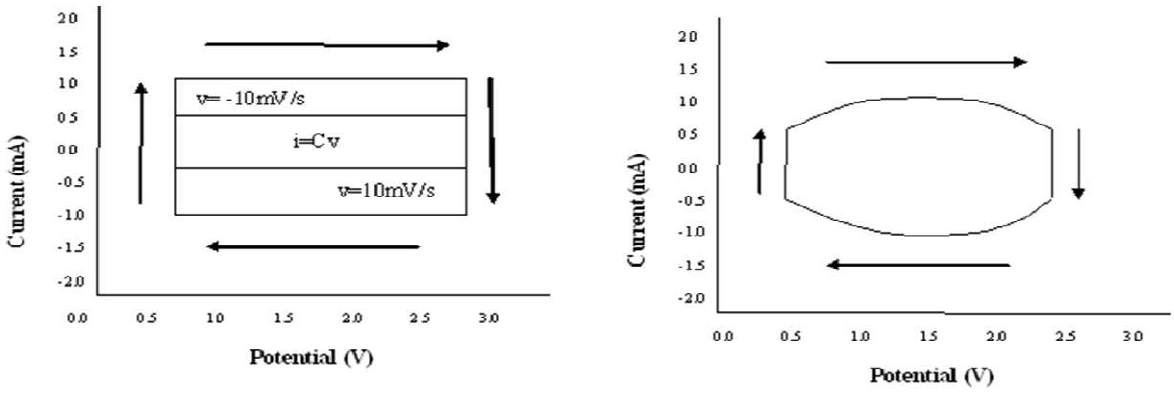


Fig 7 - Typical CV curve of EDLC and Pseudocapacitors

There are two major components of supercapacitor having some properties due to which it can store high capacitance energy, one is electrode and another is electrolyte.

Transition metal oxides used as electrode materials :

Ruthenium oxides :

There are two different phases of Crystalline ruthenium oxides i.erutile phase RuO2 and hydrated RuO2·*x*H2O.Ruthenium oxide is electrochemically stable in both crystalline and hydrous states. Buzzanca et al. in 1971 [60] showed hydrous RuO2 as a pseudocapacitive electrode material in an acidic supercapacitor electrolyte for the first timeRuthenium is a rare earth metal that is 100 times more costly than manganese and nickel. We chose Ruthenium oxides as an electrode material for SCs because of its high conductivity, strong thermal stability, superior electrical conductivity, higher rate capability, and high specific capacitance of 750–2000 F g[61,62].In an aqueous electrolyte, this capacitance is sufficient for the transition from Ru(ii) to Ru(vi). [63-64].

As Ruthenium is expensive and less available in earth crust, to overcome this problem researchers directs some alternative methods by which we can get more productive and high yielding of RuO2**.**

Table- 1 (preparation methods and specific capacitances)

No.	Prep. method	Film prop.	Sp.capacitance (F g-1)	Ref.
1	Hydrothermal	Hydrous RuO2 with multi-walled carbon nanotubes (MWCNT)	1585	(Chaitra et al., 2016)
2	Facile template method	Hydrous RuO2 nanotubes	746	(X. Wu et al., 2015)
3	- hydrothermal	1D RuO2□1.84 H2O	511	(Kim et al., 2015)
4	Laser scribing method	Graphene/RuO2 nanocomposite	1139	(Hwang et al., 2015)
5	Hydrothermal	RuO2/graphene	29	(p.Leng et al., 2015)
6	Solution phase	RuO2/graphene	480	(S.Deng et al., 2014a)
7	ionic layer adsorption and reaction	PANI-RuO2	664	(Deshmukh et al., 2014)
8	Hydrothermal	RuO2-reduced graphene oxide (RGO)	521	(Shen et al., 2013)
9	Electropolymerisation and redox deposition	Nanoscopic RuO2/ es	532	(D.Q. Zhao et al., 2012)
10	Chemical bath deposition (CBD)	RuO2 thin film	73	(Patil et al., 2011)
11	Laser printing	SWCNT/RuO2 nanowire	138	(P. Chen et al., 2010)
12	Sol-gel and low temperature annealing	Hydrous RuO2/graphene with particle-attached layered structure	570	(Z. ZHANG.-S. Wu et al., 2010)

. Several studies shows that by combining Ruthenium with other materials to form composite electrodes so that we can make the variety of ruthenium oxides composites and solve the cost excessive problem of ruthenium.

Ruthenium oxide-based composites:

For example, a Ru–V–O composite containing RuO2 and other oxides such as VOx, TiO2, MoO3, NiO/RuO2, SnO2 and CaO, RuO2/PANi, PPy, carbon/hydrous RuO2, and others has a maximum capacitance of 290 F/g. Electrochemically generated RuO2 is deposited on Ni, Ti, Pt, and Si foils through cathodicgalvanostatic deposition Literature reports that CVs of RuO2/TiO2 electrodes are pseudocapacitive in behaviour. The RuO2 based composite electrodes exhibit mixed capacitive behaviour in 1 M KOH, with a broad potential window of 0 to 1.4 V and an excellent SC of 120 F/g. The RuO2/TiO2 composite electrodes produced have a low internal resistance of 1.5.Ω[65-68].

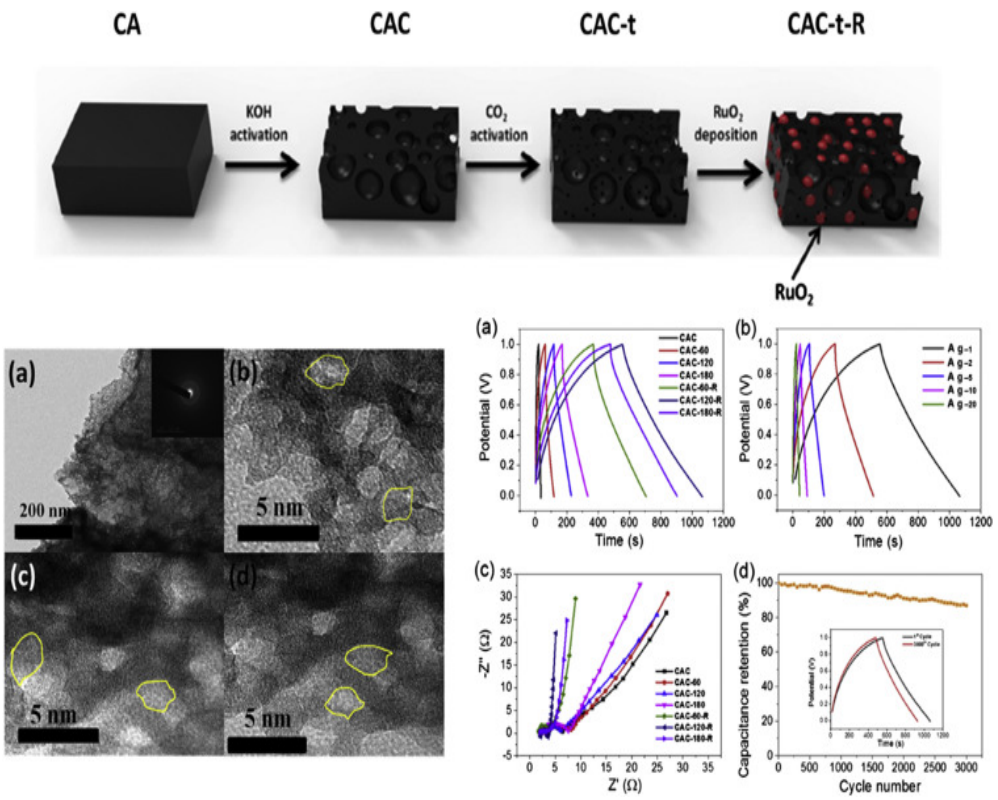


Fig 8 - schematic diagram and cv curve of RuO2-carbon composites

The energy storage mechanism of RuO2 can be describedin the equation as givenbelow

$RuO_2 + xH^+ + xe^- \rightarrow RuO_{2-x}(OH)_x \ (0 < x < 2)$

or

$RuO_2 + H^+ + e^- \rightarrow RuOOH$

The specific capacitance of anhydrous RuO2 is 24 Fg-1 over a large rangeOFvoltage (2.0 V), but hydrous RuO2.6H2O has a higher sp.Cap.of 343 F g-1, as seen by the CV curve. As a result, hydrated RuO2 has a greater specific

capacitance than anhydrous Ruthenium Oxides Amorphous Ruthenium Oxides has a greater specific capacitance of 1581 Farad per gram when compared to crystalline Ruthenium Oxides. because the amorphous structure's flexibility allows for solid structure depending on ion intraction, resulting in more active redox reaction sites [69-76]

Four variables have been postulated to determine the capacitance performance of RuO2.xH2O:

(i) Electron hopping within RuO2 .xH2O NPs;

(ii) Electron hopping among RuO2. xH2O NPs and carbon particulates;

(iii) Electron hopping between electrode materials and current collectors;and

(iv) Proton diffusion with in RuO2 .xH2O NPs

The capacitive properties of RuO2.xH2O are unaffected by NaAcO concentration or plating temperature, although the rate of deposition is affected by electrode shape and deposit adherence. The specific capacitance of RuO2. xH2O is linearly lowered from approx. Based on adhesion properties, capacitive performances, and deposition rate, RuO2.xH2O/Ti electrodes with RuO2.xH2O mass loading of 0.6mgcm 2 and annealing in air at 200 °c for 2h, plated from the 10mM RuCl3.xH2O solution with 10mM NaAcO around 50 °c should be the best choices for high-power applications.

,Ruthenium oxide-based super- capacitors are commercially available in Taiwanas shown in the picture below

Fig9-Commercial SCmade up of RuO2- electrodes

Manganese oxides:

Manganese (Mn) is a mineral found in nature in enormous amounts. Two types are ore and metal nodules. The cathodes used for the aqueous asymmetrical super capacitor devices were extensively investigated with manganese oxide materials. The transition metal oxide of manganese oxide is seven-stage oxidation: Mn(0), to Mn (VII). The discussion will take place on two of them. (MnO2 and Mn3O4) are ecologically friendly and abundant on the globe and have a great operating potential window, a high special capacitance. Manganese oxide (MnO2) is cheaper and less harmful than ruthenium oxide-based supercapacitors. [77,78]Thepseudocapacitive behaviour of Lee and Goodenough was suggested in 1999. With the following eqn may be defined the charging store in the supercapacitor:

$MnO2 + M+ + e- \leftrightarrow MnOOM$

WhereM+ presents the alkali cations (Li+, Na+, K+).

Manganese oxide minerals are available in a variety of crystalline form, including as, ß, g, and β, as depicted in Figure 10. These crystal forms can influence the pseudo capacitance of MnO2 electrodes. They include 1 Dimentional structures in a tunnel, 2 Dimentional layer and 3 Dimentional spinel. Due to its porous structure, electrolyte ions may be moved more rapidly, which results in a higher specific capacitance. K+,ÚI -Manganese oxide with a channel diameter of 4.61, and interlayer spacing of 7.1 is easily accommodated with an ionic diameter of 3.0 But manganese oxides and µ are unable for transportation of K+ through a narrow channel (3.2).

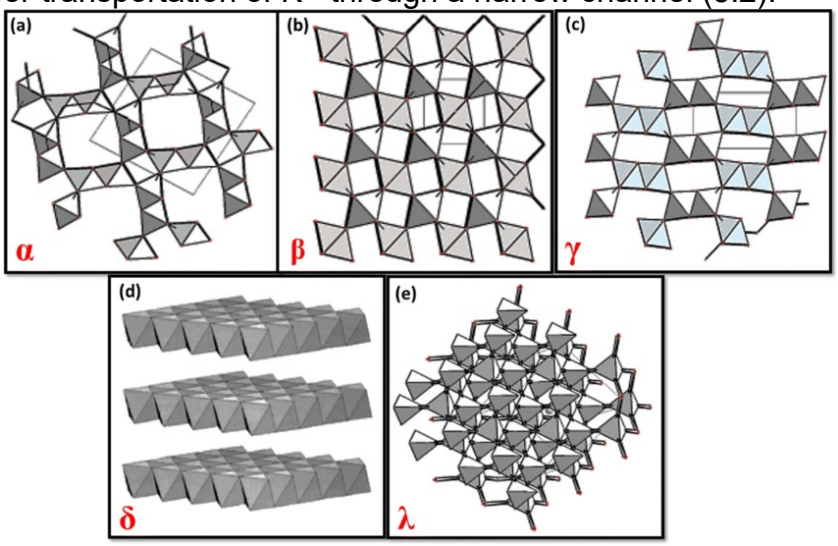


Figure 10 Alpha, beta.gamma, delta,lamda. Oxides of manganese

Some of the inconvenience of MnO2-based electrode materials, which can restrict electron transportation, cycle-life and a particular surface area, include low electroconductivity and high dissolubility of basic and neutral electrolytes. We must dop MnO2 materials to improve their electrical conductivity. For example, li-mn1-xRuxO2, has a pseudo-capacitative property at 361 Farad per gramme.In order to increase the conductivity of MnO2 products, we use carbon materials such as active carbon, CNT, and graphite as well as polymers. Leading polymers are used as protective shells to avoid evaporation throughout the cycle of MnO2 compounds. The form of the MnO2 material plays a significant role in the achievement of high capacity and the surface area in terms of supercapacitor capacitance. Depending on their morphologies, Mno2 – specific areas of materials may cover from 20 to 306.9 m2 g-1. The manganese oxides are therefore categorised as (0D), (1D), (2D) &(3D). [82-86]

SCs containing nanoparticles based on MnO2 0D were discovered.. MnO2 painting techniques on 3-dimestic graphite-style capsules, as provided in Figure-11, were proposed by Jian et al. Jian. [87] MnO2 0D hollow structures have been literature extensively.. The special area of the MnO2 nanospheresreached by 253 m2 g-1. This hollow structure also has a capacitance of 300 Farad per gramme at 6 mV s-1. [88]
The core-shaft zero-dimensional nanostructures form a strong, hollow and thin shell. The nanostructures Core Shell 0D have a wide range of advantages such as huge specific surface areas, superior conductivity, high scatterability and chemical and

mechanical stability. Nanostructures constructed from C-MnO2 have been produced from core shell. [89,90]
The many structures in 1D-MnO2 nanostructures include nanorod, nanotubes and nanotubes. As demonstrated in Figure11b, the hydrogenation approach for the production of oxygen-deficit MnO2 nanorods providing 449F g-1 high speed capacity at 0.75 mA cm-2. MnO2 performs extensively due to the concentration of oxygen vacancy (Figure 11c,d). This may cause electrochemical activity through changes in oxygen vacancy concentrations. Yao et al. were able to manufacture extremely long, 105 length-diameter MnO2 nanowires by use of hydrothermal techniques.. MnO2 nanotub arrays were produced in 10 minutes using anodic aluminium oxide (AAO) model, whereas MnO2 nanotube arrays required 60 minutes. The MnO2 Micro Tubes arrays have 320 F g-1 capacity, whereas the MnO2 nano Tubes have just 101 F g-1 capacity. [91-93].

Due to the enormous specific surface surfaces and numerous active sites, were widely investigated. 2D nanostructuring may be utilised to produce electrodes that are stand-by and not require a substratum, in contrast to 0D and 1D nanostructures. A nanofilm with a high speed of 640.8 F g-1 at 10 A g-1 was produced on the active paper using the electrodeposition technique. MnO2 nanofilms are often synthesised by the method of redox deposition. Hydrothermal 2D MnO2 nanofilms have less mass burden than electrodeposition or redox repositioning films when it is a question of mass loading. A high specific conversion of 1035 F g-1 at 2mV S-1 may be achieved with a loading of 0.09 mg cm-2 on 2D MnO2 nanofilms (Mn paper-80) (Figure 11f)..Wang et al. have devised a sacrificial template approach for the production of MnO2 nanosheets. [94.95].

.3Dimentional MnO2gives pathways to the electrolyte and provide a high S.A and stability of mechanical for SC electrodes. Bag et al. created the self-branche 3D-MnO2@-MnO2, a template-free approach (Figure 11g,h). With a wide specific area of 238 m2g-1, and a pore area of 3.6 nm, this 3D self-connected -MnO2@-MnO2, allows quicker transfer of loads. Zhu etcoll have produced a novel 3D MnO2 nanostructure consisting of nanoflocks -MnO2 and -MnO2.[96.97].

Another Manganese oxide that is used as an electrode material is the Mn3O4, a Manganese oxide with an electrodestructure that provides a strong crystalline architecture with 3D diffusion channels. In comparison with MnO2, and Mn3O4 has less electronic conductivity, with less capacities. Unknown is the process of Mn3O4 energy storage. Recent investigations have been performed in situ X-ray absorption near-edge spectrum (XANES). [98,99]

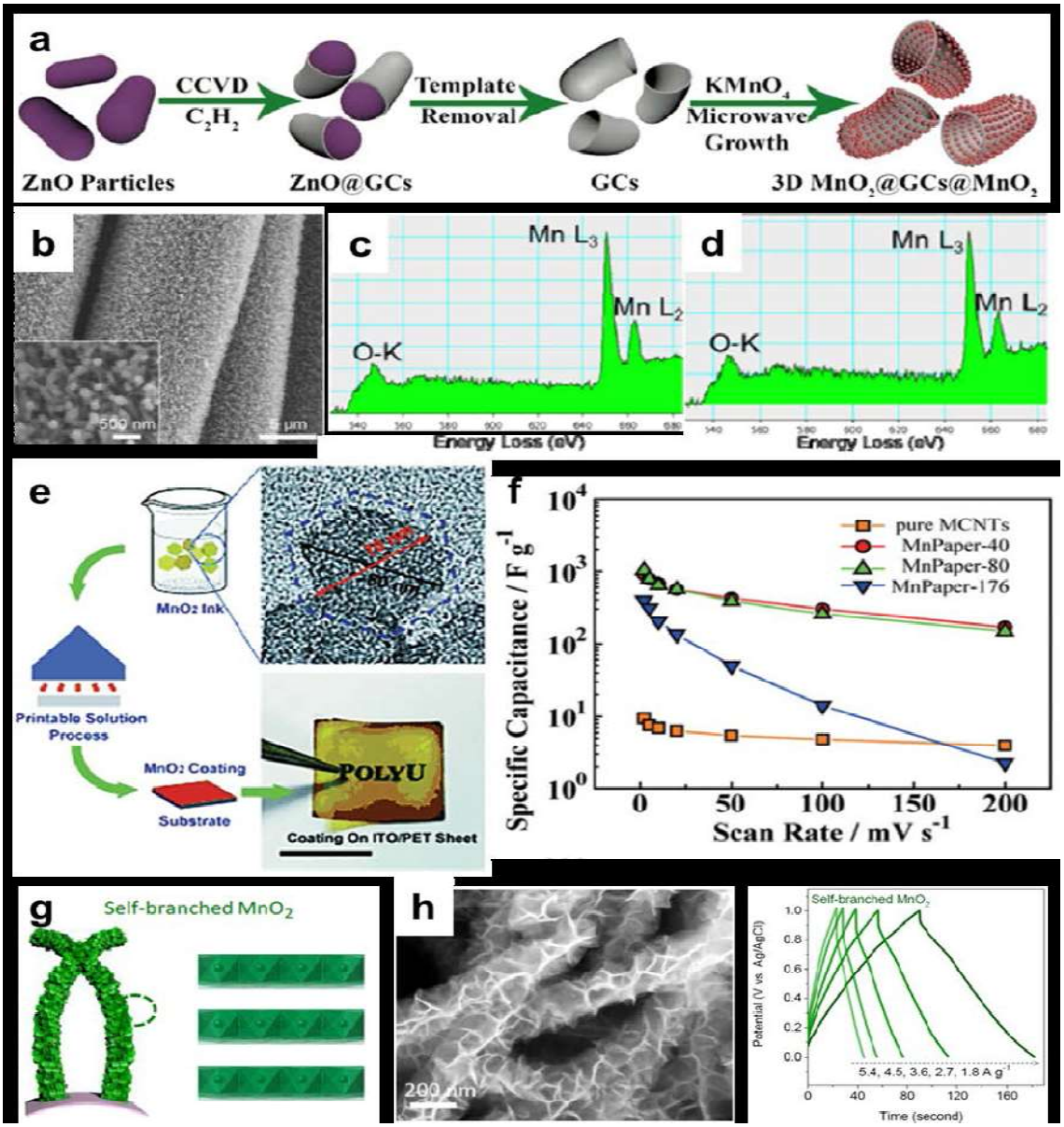


Figure 11.(a) synthesis of MnO2@GCs@MnO2.. (b) FE-SEM image OF MnO2(c) edged part and (d) MNO2 NANOwires (e) TEM image of MnO2 (f) specific capacitance with scan rate for 2D MnO2 (g) branched MnO2 electrode (h) FE-SEM image, and (i) GCD curves .

The Porous Nanoparticles MN3O4 (NPs)with the synthesis of tube (F127) asadispersantasis in fig. 12. Porous nanoparticulates (NPs). Theamorphous manganese precursors should beuniformlydispersedontothe polymer Duetotheaffinity of theMn(II)ionof the hydrophilicpartofF127. [100]

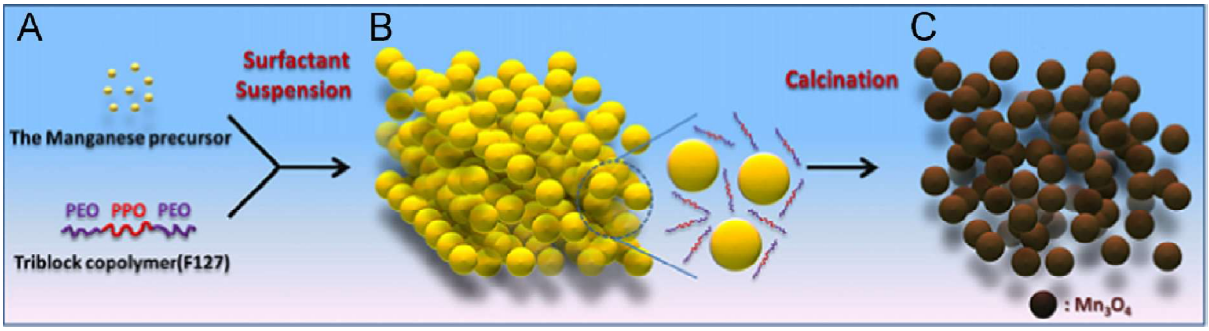


Fig.12.The thermaldecomposition strategy of nanocrystals Mn3O4;Step(A):manganeseacetate and copolymer triblock was dissolved into the methanol;Step(B):suspension of copolymer triblock and phase-transformation manganeseacetate;Step(C):Mn3O4 nanoparticles formed under calcination.

Zhou et al. also established a straight forward synthesising technique, as shown in Fig. 13, for freestanding MnO2-nanophlakes/Porous Carbon Fibres (PCNFs) (MnO2/PCNFs). The MnO2 nanoplates are vertical on the outside surface of the PCNF, which contribute to a considerable area between the PCNFs, as seen by electron microscopy (SEM) scanning pictures. A significant degree of mesoporosity and a big area (1814 m2/g) were present in the MnO2/PCNF produced and 92,3 percent of the initial capacitance was preserved after 4,000 cycles.
However, compared to MnO2/PCNF it was found that the results of Electrochemical Spectroscopy (EIS), which was attributed in great part to the very high conductivity of the el [101-103], showed that PCNF had a lower impedance to charge transmission.

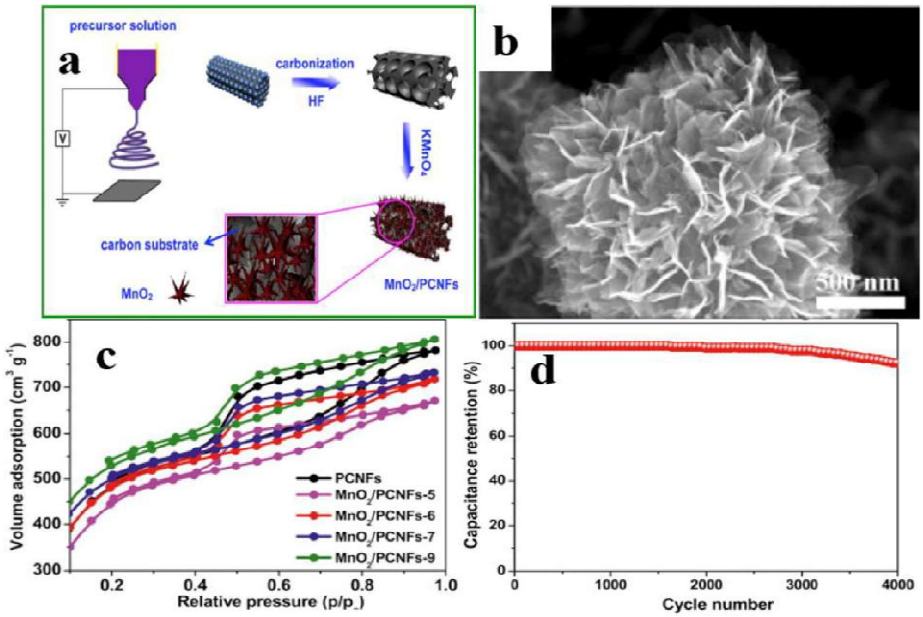


Fig. 13(a) MnO2/PCNF synthesis schematic depiction.

(b) MnO2/PCNFs-6 SEM picture.

(c) PCNF and MnO2/PCNFs with differing weight ratios of KMnO4 and PCNFs adsorption/desorption isotherms in nitrogen.

(d) MnO2/PCNFs-6 electrode long-term stability with a current density of over 4000 cycles of 0,5 A/g.

Table 2 **(**The film properties with specific capacitance ofMnO2)

No.	Prep. method	Film prop.	Sp.Cap.(Farad per gram)	Reference
1	Anode depo.	MnO2 nanostructure on gold film	432	(Shi et al., 2017)
2	Electrodeposition	Co3O4□MnO2□NiO nanotubes	2526	(A.Singh et al., 2016)
3	pyrolysis	Mn3O4 thin film	395	(BB.Yadav et al., 2016)
4	Hydrolysis of Urea	NiMnO2 layered double hydroxide	1512	(Guo et al., 2016)
5	Electrodeposition	CoMnO2 layered double hydroxide	1063	(Jagadale et al., 2017)
6	reaction of Sacrificial	Manganese oxide decorated graphenenanosheets	280	(Unnikrishnan et al., 2016)
7	Anodic deposition	Mn-Ni oxide	251	(Tahi et al., 2016)
8	S-gel method	Manganese oxide (MWCNT)	335	(S.-H. Cheen et al., 2016)
9	S-gel method	MnO2 oxide film	361	(Sark.et al., 2015)
10	Hydrothermal	Mn3O4/graphene	367	(H.-M. Lee et al., 2015)
11	Hydrothermal	Ni(OH)2/MnO2/RGO	1985	(H. Chen et al., 2014)
12	Electrospinning	/MnO2 core-shell tubular structure	237	(Hon.g et al., 2014)
13	Electrospinning	Carbon nanofiber/MnO2	311	(Zhi et al., 2012)
14	Hydrothermal	NiMnO2	284	(C.-H. Wuu et al., 2012)
15	Cat. deposition	Manganese oxide thin	365	(Liuu et al., 2010)

It is important to note that in thin films, MnOx works better. Since on the ground only there is a light coating of snow. In addition, during cycling, thick layer greatly reduces electrochemical performance. In contrast to patla film, the thin film offers a superior layer on the substratum that lowers the ion transportation barrier. The substrate used impacts the electrochemical performance significantly. By employing a conduction network, the capacity may be enhanced. The carbon substance is the most common fault in the conduction network. The proper usage of carbon material like MWCNT contributes to the construction and maintenance of porous structures and network relationships.
MnOx can also be mixed with an excellent carbon compound called graphene. MnOx particles attached to the graphene sheets do not stack graphene sheets, whereas graphene sheets do not cluster MnOx particles. There are a lot of additional things to consider in addition to carbon monoxide. Nickel was included and the particle size was changed from rod-like to plate-like.. The ternary composite is also widely investigated.Ternary hybrid nanotubes have exhibited excellent electrical performance via Co3O4-MnO2-NiO (2525 F g-1). It is because of the sophisticated arrays of nanotubes, which can readily permeate the electrolytes. The hydrothermal Ni(OH)2/MnO2/RGO generated on the other hand has a particular 1985 F-1 capacitance. The development of a porous floral structure has helped to store the load. 104-114]

Iron oxides:

The, broad working fencing with -ve potential, non-toxic, earth-abundant, less costhigh theoretical capacity, environmental friendly, low ESR material, Amorphous and monochristalline material with pseudo-Capacitors and other benefits are commonly used as an electrodes for Supercapacitors such as Fe2O3 and Fe3O4. Ma has studied iron oxides' energy storage methods to understand better how they store energy [115-118].
The oxidation processes of Fe3O4 may be described as below

Fe + 2OH- + 2e- (E0 = –1.076 Vs. SCE) Fe(OH)2
3Fe[OH]2 +2OH- + 2e- (E0= -0.859V vs. SCE) Fe3O4 + 4H2O + 2oh)
One putative feed storage method of FeOxis appears in the neutral aqueous electrolytes in the equation as FeOx+ zM++ ye- or MzFeOx
Where M is Li, Na, or K.. [119]

A potential anode material between two iron oxides is porous Fe2O3. Fe2O3 has a structural, optical, electrical and physical effect on its concentration. The characteristics of semi-conducting may be shown with iron oxide. Fe (III) is a semiconductor of n-type, while Fe (II) is a highly-doped, narrow band divider of the p-type semiconductor and so on. On t, the largest transitions in Fe redox Iron oxide is an effective oxidising agent to improve SC and conductivity while reducing ESR for Polymer Composites, inorganic, non-metallic composites and supercapacitor electrodes.
SC findings for an iron oxide-based electrode are good with a moderated potential window. The resistance of the electrode build up in the electrochemical series is low.

Fe2O3 materials' crystal morphologies are essential to electrochemical performance modifications.
Figure 14 sums together four distinct crystal structures, including (Hexagonal structure centred in the Rhinos), (CBC), (CUBS), and -Fe2O3 Figure 14 (orthorhombic structure). When compared with other crystal structures, -Fe2O3 has a unique form, which makes it a good electrode material for long lasting SCs and has a greater thermodynamic stability. Other intermediate phases, including -Fe2O3, can be produced by heat treatment to -Fe2O3. [120,121]

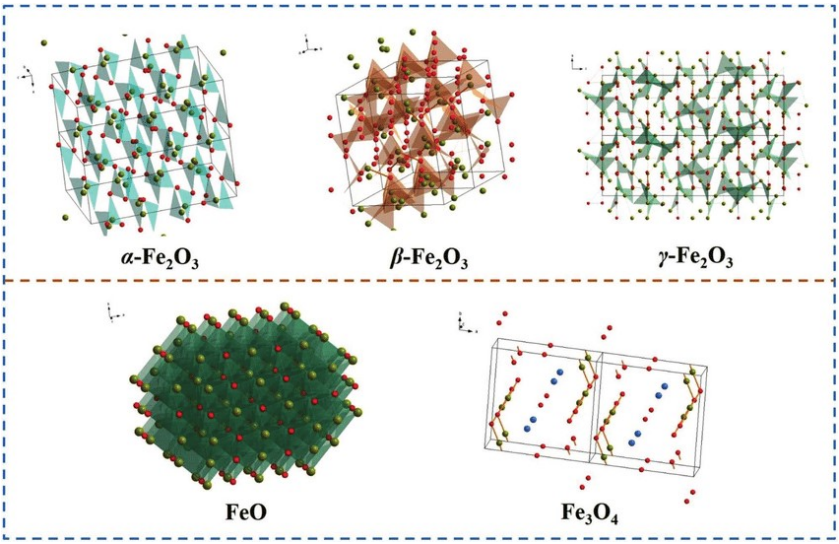


Figure 14. α, β, ć, τ-Fe2O3, and Fe3O4 crystallines. Figure 14. Reproduced by licence (Xia et al. 2016). 2016, Wiley, Copyright.

A range of variables, including crystal structures, morphology and compositions, impact the electrochemical properties of iron oxides. Many approaches were presented to enhance the specific capacity, cycle stability and specified iron oxide rate capacity in light of the factors, including the nanostructure engineering and the hybridisation components. The application of methods for nanostructural engineering can enhance survival.
Various approaches have recently been developed for the manufacture of Fe2O3 nanostructures from 0D to 3D,..[122-124].
In general, 0D nanostructures are spherical nanoparticles. For example, Shivakumara et al. utilised sol-gel to produce -Fe2O3 solid nanoparticles with an enormous specific area of 386 m2 g-1 (Figure 15a,b). The generated nanoparticles – Fe2O3 (Nano Fe2O3) had a specific capacitor of 300 F-g-1 in 1 A g-1 on an electrolyte 0.5 M Na2SO3. [125]

The 1D nanostructures of Fe2O3, such as nanodes, nanowires and nanotubes, are used as electrode materials because they are extremely special surfaces, have a great 1D electron transport pathway and have a lot of flexibility in ion intercalation. Lu et al. employed techniques of thermal and solvothermal disintegration to create 1D-Fe2O3 nanorods in a flexible carbon fabric (Figure 15d) which are oxygen deficient (N-Fe2O3).Superior capacitance of the oxygen-deficient nanorods -Fe2O3 (N-Fe2O3) was 382.7 mF cm-2 comparedwith oxygen-rich -Fe2O3 nanorods., at 0.5 mA cm-2 in a watery electrolyte of 3 M LiCl as contrasted with the -Fe2O3 vacancy free of oxygen (A-Fe2O3) (Figure 15e). A combination solvothermal

decomposition technique has been employed for the manufacture of Fe2O3 nanowires. Fe2O3 has a high conductivity of nanowires .[126]
2D nanostructures enhance the electrolyte contact surface while minimising the ion diffusion pathways and enhancing capacitive performance. As demonstrated in Figure 15g, Liu et al employed an electrochemical induced technological method to produce ultrathine α-Fe2O3 nanoflakes of α-Fe2O3 nanorods. A higher areal capacitance at 1 mA cm2 (Figure 15h) than the α-Fe2O3 Nanorods-based Electrode (NR), due to its enhanced surface surface and reduced resistance, generated the obtained nanofloke electrode (NF) of α-Fe2O3 (Figure 15i). [127,128].
Zheng et al. employed a hydrothermal method for producing 3D -Fe2O3 hollow, 30 nm wall thick holes and 100 nm length nanoshuttles (Figure 15j). The nanoshuttle hollow -Fe2O3 has a high capacity as Figure 15k shows. s demonstrated in Figure 15l, the special capacitance of hollow nanoshuttles -Fe2O3 has changing from 20° C (203 F g-1) to 60° C, little (234 F g-1). [129]

For SCs with various morphologies another common iron oxide, Fe3O4, was generated and studied. For the formation of Fe3O4 nanoparticles, the Fe2+/Fe3+ molar ratio should be 0.5. But the Fe3O4 nanoparticles are easily combined, leading to large particles with a little surface area. Wang et al. utilised an ultrasonic aided technique for producing Fe3O4 2 m diameter nanoparticles. [130-133]

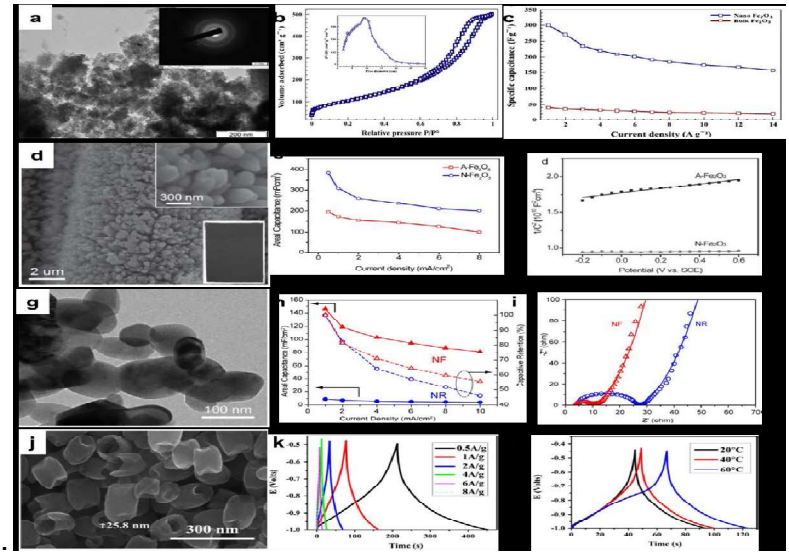


Illustration 15.(a) SEM IMAG (b) N2 adsorption-desorption isotherm and (c) Fe2O3 nanoparticle rate capability. (d) picture-FE-SEMs, (e) capacity rates, and (f) pplots of α-Fe2O3 (g) TEM plots, (h) capacity rates (I) curves of GCD (j) FE-SEM picture, (k) GCD curves of various current densities,

Nickel oxides:

Because of their huge surface area, its high pseudo-capacity and its low cost, Ni(OH)2 has been widely studied in transition metal oxides. Nickel and nickel oxide are commonly employed in rechargeable batteries and supercapacitors because of their low toxicity and comparable electrochemical conduct. This electrode is essential in the manufacture of supercapacitors because of its ionic characteristics. The greatest value of SC 703 F/g was obtained for the flower-species with a wide surface area in 6-M KOH electrolytes at potential windows of 0 to 0.5 V at a 2 mV/s scan rate. The high surface porosity structure significantly improves the transfer of charge and capacity of an electrode. The two dimensional (2D) and three-dimensional (3D) nano arrays display outstanding electrical capabilities due to their large volume surface, good structure and open form. NiO was generated in many morphologies including nanoparticles, nanoparticles, nanoparticles and nanosheet-based NiO-sphere-sphere, nanoparticles, nanofibers, nanosheets, nanotubes, architectures of flowers and hollow spheres.The CV curve shape shows a SC value and a restricted window for redox pinnacles. The resistance of the built electrode to electrical chemicals is low. The Co (OH) 2/Ni composite electrode works effectively with a large potential window of 0.1 V to 0.6 V and high SCs of 1017 F/g in 2 M KOH. [134-149]

Table -3 (synthesis settings for nickel oxide/hydroxide deposition details and thin films of their composition using electrodeposition method) (Ref.-S.G.Sayyed, et.al 2019)

Slno.	Chemical /Bath Composition & conditions	Substrate Electrode		Details						Remarks/Properties	SC
		A	K	R	APP. VOLT.	DEPO. TIME	TEM.	SCAN RATE	ELECTROLYTE		
1	0.08 M Ni(NO3)2, After deposition film was thermal treated at in air at 250°C (temp rate: 5 °C/min)	Ni	Pt	SCE	-0.90	-		40	1M KOH	Formation of α-nickel hydroxides with the grain size of 3.48 nm. The capacitance maintained up to 87% of maximum capacity after	1478

	in muffle stove for 2 h.									500 cycles	
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	0.5 mA/cm	60MlN	Room tempr	25	1M KOH	Film exhibits highly porous morphologywithnanoflakes like structure of thickness 12–16 nm. XRD pattern indicates that theformation of NiO with poor crystallinity.87.5%retention of capacitance after 5000 cycles.	167.3
3	Three solution: NiCl2.6H2O (NiO-C), Ni(NO3)2.6H2O (NiO-N) and NiSO4.6H2O (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 NiO–N: -0.7 to -0.55 V NiO–S: -0 .8 to -0.65	30MlN	Room tempr	5	1M 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	893

										with better stability (85.6%).	
4	0.1 M Ni(NO3)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	30cycles		100	1M KOH	Formed NiOnanoflakes 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
5	0.08 M Ni(NO3)2·6H2O	Ni	Pt	Ag-AgCl	-0.90 V	-	Room tempr	-	1M KOH	α-Ni(OH)2 showed particle like morphology with a loosely packed structure.	2595
6	3 mM Ni(NO3)2.6H2O + 3 mM Fe(NO3)3.9H2O	NF	Pt	Ag-AgCl	-1.0 V	300s	10°c	5	1M KOH	The formation of interconnected mesoporous structures with the pore size of 50 nm.	

NiO redox reaction may be characterised as follows in an alkaline electrolyte:

$$NiO + OH^- \leftrightarrow NiOOH^- + e^-$$

The electrochemical performance of NiO is entirely caused by the crystallinity which is altered by heat treatment. Wu et al. found that nickel hydroxide was transformed to nickel oxide with a high SC of 1478 by nickel hydroxide placed on Nickel substrate at 250 degrees Celsius. The sulphate solution NiO Electrode has good electrochemical characteristics in all areas.

However, two significant drawbacks are the use of NiO for supercapacitor electrode I which has low cycle stability. (ii) poor conductivity electricity. In order to avoid these inconveniences, it is recommended to compose NiO with other substances and produce nanostructured NiOs
In addition, the binary oxide of NiCo2O4 has shown its outstanding electrochemical efficiency that has international attention. This can be done in a straightforward way, such as co-precipitation or hydrolysis. The co-precipitation technology resulted in a 1211 F g-1 compound of NiCo2O4/graphene oxide.

Sodium dodecyl Sulphate Morphology for NiCo2O was investigated (SDS)..
NiCo2O4/SWCNT, on the other hand, has a specific capacity of 1642 F g-1 that uses a controlled hydrolysis method. The water:ethanol ratio has been adjusted to identify the optimal solvent composition of NiCo2O4/SWCNT electrode. Different ratios of water and ethanol result in different morphologies. A 1:4 ratio of water to ethanol was discovered to be the optimal condition for electrode production. 150-154].

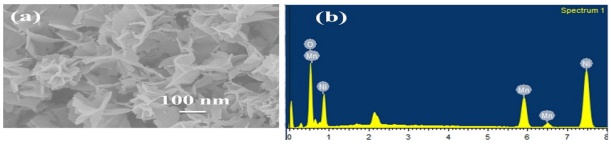
NiMn2O4 as supercapacitor applications

Because of their excellent electrical performance, NiMn2O4, a single phase spinel-structured product, has just become more prominent than many other metal oxides. For electrically powered materials and excellent electrochemical performance, high energy density and high energy densities are necessary when used as electrodes, as already mentioned. Due to its outstanding electrochemical performance, a single-phase spinel-structured NiMn2O4, is attracted much attention recently.
As has previously been said, high density and high density electrodes demand high conductivity materials and good electrochemical performance.

Morphological characterisation

This FESEM image contains densely packaged NiMn2O4 agglomerated nanoparticles 6 to 10 nm (8 nm mean size). The excess contact area of the material with the electrolyte efficiently generates a porous surface with a highly special surface area, thereby increasing electrochemical performance of electrodes, via the creation of densely packed small NiMn2O4 nanoparticles. Surface area measurements using Brunauer-Emmett-Teller (BET) reveal NiMn2O4 nanostructures' porous nature.

The typical type IV NiMn 2O4 isothermal, according to its mesoporous structure, appears in Figure 16. Figure 16. The material has a specified area of 43.6 and an average pore size of 13.3 nm, which implies that there are a lot of electrochemical locations involved..



Nanoparticles SEM picture NiMn2O4

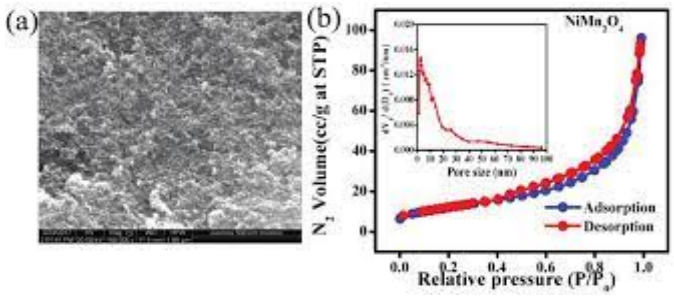


Figure 16:N2 adsorption-desorption and pore size of NiMn2O4.

Electrochemical characterization:

TheCV curves of the NiMn2O4 Electrode demonstrate Faradiccharge transfer comportamiento owing to functional group or poresize dispersion. The CV curves shows the redox nature of the electrode material and informs the electrode about its pseudocapacitative conduct. Several peaks in CV (Mn3+, Mn4+ and Ni2+ and Ni3+) may also be readily recognised because of the Eq-related faradic redox processes.
NiMn2O4 + Na^+ + e^- = NaNiMn2O4
A scan rate of 2 mV s 1 was obtained by measuring the specific capacitance (Cm) of the electrode for each scan rate using the CV curves. The greatest specific capacitance was reached at 875 g 1. The diagrams demonstrate clearly a decrease in the loading/unload time of the increased density of the current, which may be explained by ion diffusion.
Na+ ions from the electrolyte solution occupies a broad electrode surface at lower current densities as they have more time to approach the maximum active sites of the electrode and result in increased specific capacity.
[155,156]

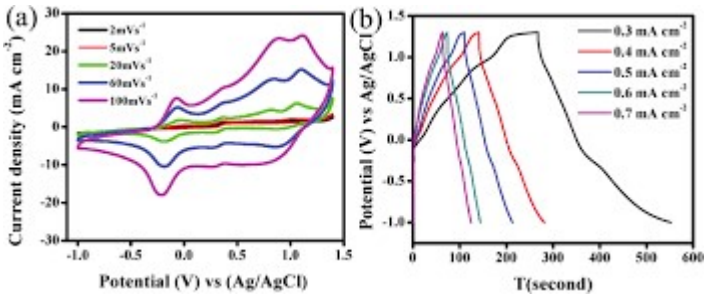


Fig -17(a) CV curves at various scans, and (b) GCD curves for the NiMn2O4 composite at differing current densities.

Other metal oxides :

All the materials used as supercapacitor, in addition to RuO, MnO, NiO and CoO, FeO electrodes were explored as copper oxide (CuO), Vanadium oxide (VO), Molybdenum oxide (MoO), Titanium oxide (TiO), Tin oxide (SnO), BiO, and Indium oxide (inol) The electrical deposition on several substrates of thin copper oxide

amorphous films such as copper oxide produced with copper foam was utilised to make copper oxide amorphous thin films.According to Ghadgeet al, the copper hydroxide thin film electrode generated by anodizing method has a special capacitance of up to 6000 F/g. TiO has been coated using an electro-chemical anodization technique on titanium metal foil which results in 1300 F/cm2 of specific capacity. The amorphous VO has a maximal specific capacity of 350 F per g, according to Lee et al. The amorphous, electrodepositionally manufactured MoOx sheet has a capacity of 507 F/g in a 1-M H2sO4 solution. The thin layer on a copper substratum is 98 F/g for the particular capability of electrodepositing Bi2O3. Amorphous SnO generated by electrochemical deposition has the greatest specific capacity of 285 F/g. Prasad et al. developed Infilm with a specific capacitance of 190 fg [157-166], using the electrochemical deposition method. Due to their high theoretical capabilities from the faradaic load transfer mechanism, several TMOs are often used in supercapacitors including ruthenium oxide (RuO2), manganese oxide (MnO2), nickel oxide (NIO), cobalt oxide (CO3O4) and vanadium oxide (V2O5). [167-172]

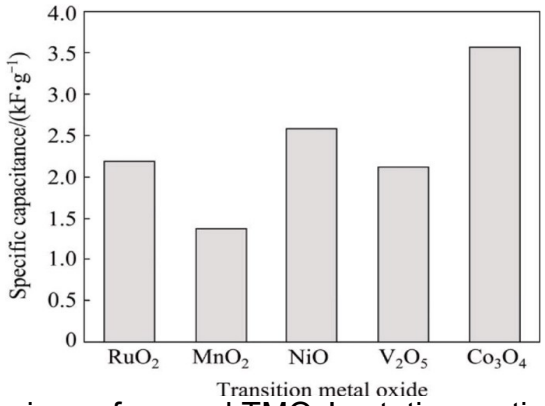


Fig-18 Comparison of several TMOs' putative particular capabilities

CONCLUSION

Metal oxide appears like a viable electrode material for supercapacitor applications. Metal oxide based electrode electrodes have a variety of structures, created by distinct production methods, diverse material combinations and a number of experimental conditions that impact their electrochemical performance. Charge storage processes in different additives. With more knowledge of charge storage mechanism in different material combinations, the electrochemical performance of the supercapacitor electrode may be enhanced.Supercapacitors are a new form of energy storage device with higher energy density, excellent electrical properties and cyclical stability. In a broad rank, the smaller dielectric and higher thermal and electrochemical conductivity may be used in a range of applications including emergency energy sources, specialised power systems, ackup and pulse power. In addition, the creation of supercapacitors for electric car hybrid systems has proven quite interesting. Different transition metal oxides/hydroxides may be easily produced into supercapacitors due to their high conductivity, larger areas and improved stability. Metal oxide and hydroxide electrode supercapacitors and composite materials may achieve outstanding performance. The focus of research should be on generating new high capacity, high energy, high power and a greater variety of uses for electrodes.

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