A Review on Recent Advancements in the Transition Metal Oxides and Their Compositesas an Electrode Material for Supercapacitor.

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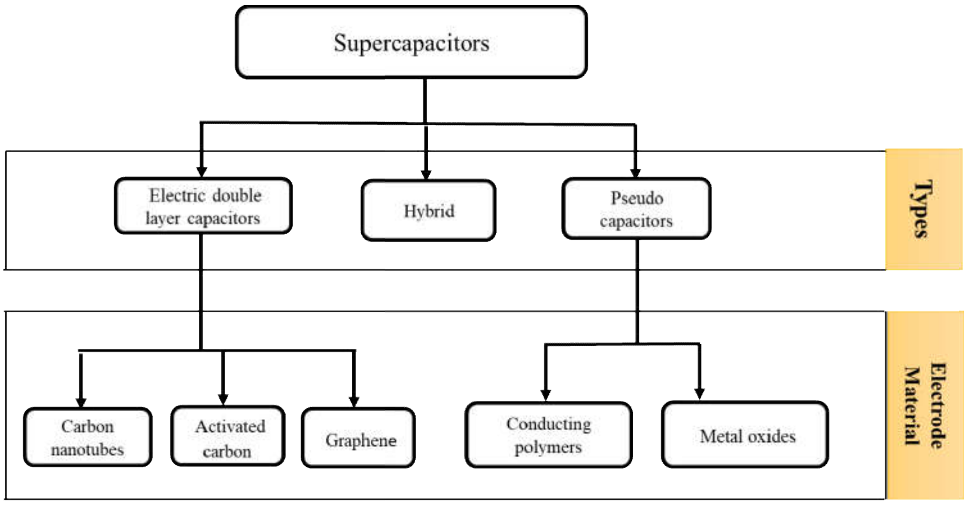
Abstract: -In future, use of electrochemical supercapacitor plays important role in energy & power storage devices.Currently research related to supercapacitor depends on their mode of energystorage, namely: (1) the pseudo capacitors and (2) the electrochemical double layercapacitor.The electrode material plays a crucial role on characteristics & performance of supercapacitors.TheRecent studies have shown that there are many new advancements in electrode materials for supercapacitors.Hence researchers have been focussed on development of novel electrode material such as high theoretical capacity, high power density, long life span, low production cost, natural abundance, light weight, eco-friendly. Transition metal oxides (ruthenium oxide, copper oxide, manganese oxide, cobalt oxide, nickel oxide, tinoxide, iron oxide, Ni $(OH)_2$, Co $(OH)_2$ and conducting polymers.) deposited by chemical methods have been tested for supercapacitor application. The main intention of this review article is focused on the recent advancements in the transition metal oxides and their composites as an electrode material for supercapacitor. Furthermore, the future prospects and current challenges on synthesis of transition metal oxides are proposed which will stimulates ongoing studies to expose potential of transition metal oxides and its composites in supercapacitor application.

Keywords: - Supercapacitor, Chemical synthesis, Transition metal oxides, Electrode material.

1. Introduction: -

With the increase in use of portableelectronic gadgets, automobiles, modern techniquesand industrialization the consumption of energy in variousforms has been extensively accelerated [1].Increasing the consumption of fossil fuels like coal, fuel, and natural gas, the problems of global climate change and environmental pollution are increasing day by day. Solar, wind, tidal, and other renewable clean energy is a way to solve current energy and environmental pollution problems [2-4]. However, practical use of renewable clean forms of energy having restrictions regarding environmental factors and energy supply continuity [5]. Therefore, it is necessity of develop effective and reliable devices for energy storage. Electrochemical energy storage devices such as lithium-ion batteries are major energy storage technologies, but their power density is low and their cycle stability is poor. Therefore, it is very important to develop an energy storage device with high performance [6]. Future research and innovation will build up the position of energy production and storage technologies. Supercapacitor is awidelyapproaching electrochemical energy storage device.Focus of the researchers attractedtowards supercapacitor worldwide. Supercapacitors exhibit high energy and power densities, long cyclic life and stability in a eco-friendly manner. The capacitive charge-storage performanceis superior than the present battery system, including long-term cycling stability, the ability to charge within seconds, and the capability to release energy ~10 times faster than the present battery systems. But at present, the low energy densityis still the drawback of supercapacitors.It is necessary to improve the energy density of supercapacitors so that they can be applied in large scale for energy storage.

Based on the energy storage mechanism, Supercapacitors are classified into three types as electrochemical double layer capacitor (EDLC's), Pseudo capacitors and Hybrid or Asymmetric capacitors [7]. For Electric double layer supercapacitors (EDLC), energy is stored byaccumulation of charge on the interface between the electrode and electrolyte. For pseudo capacitors, energy stored through the transfer of charges between the electrode and electrolyte. The process is known as reversible faradaic redox reaction [8,9].



I. Electric double layer supercapacitors (EDLC): -

Electric double layer supercapacitors (EDLC) are associated with accumulation of electrostatic charge at the electrode/electrolyte interface [10]. The process only involves the physical adsorption of ions without any chemical reaction [11]. When a voltage is applied across the electric double layer supercapacitors (EDLC), the electrons move from the negative electrode to the positive electrode through the external loop, leading to a collection of positive charge and negative charge on the two electrodes, independently. The cations from the electrolyte solution move toward the negative electrode and anions move towards the positive electrodes. During discharging the process will reverse. In this type of supercapacitors, due to reversible adsorption/ desorption of ions process electricdouble layers form at the interface of electrode and electrolyte.Hence energy is stored in the double-layer interface [12]. Electric double layer supercapacitors (EDLC)show energy density higher than conventional capacitors due to their maximum effective surface area and very small charge separation distances.Electric double layer supercapacitors (EDLC) contain an electrolyte (such as KOH, H_2SO_4, or Na_2CO_3) between the electrode systemwhere conventional capacitors contain dielectric medium in between electrode system.

The double electric layers contain two regions: an inner compact layer region and a diffusive layer [13]. The ions are adsorbed directly on the electrode surface in the inner compact layer to form “inner Helmholtz plane”. Followed by inner compact layer another layer formed of solvatedopposite charge ion to the electrode, that is a “outer Helmholtz plane”. The formation of diffusive layer region is assigned to the kinetic energy of the counter-ions [13]. The electric double layer supercapacitors (EDLC) exhibit usually a higher energy density than conventional capacitors owing to the potential drop largely confined to a small region (0.1–10 nm), and thus the capacitance of electric double layer supercapacitors (EDLC) is associated with the interfacial area of the electrodes. The electrodes mainly refer to extremely porous carbon-based electrode materials with high surface areas such as graphene, activated carbon, activated carbon fibre and carbon nanotubes (CNTs) [14-16]. Moreover, the biomass could also be transferred to carbon materials as one typical kind of electrode materials in the electric double layer supercapacitors (EDLC) [17]. These electrode materials have been widely studied for their high conductivity and excellent mechanical stability.

II. Pseudo capacitors: -

The pseudo capacitor is associated with a rapid and reversible Faraday reaction at or near the surface of the active material, which is similar to the charging and discharging process that occurs in batteries but do not result in phase transformation of the electrode material [18,19]. The electrode materials undergoing such redox reactions involve mainly transition metal compounds and conductive polymers [20]. The pseudo capacitor contains two major types of redox pseudo-capacitance and intercalation pseudo-capacitance [21]. When the ions in the electrolyte solution are adsorbed on or near the surface of the electrode, the electron transfer will take place during the redox pseudo-capacitance process. Transition metal oxides, typically ruthenium dioxide (RuO_2) has been found to possess redox pseudocapacitive characteristic. During the charging process, Ru oxidation states can change from (II) to (IV) along with rapid reversible electron transfer and electro-adsorption of protons on the surface of RuO_2 particles in the acidic solution. However, in an alkaline solution, especially for the carbon/Ru composite, the RuO_2 in the composite materials will be oxidized to higher valences (i.e. RuO_4^{2-}, RuO_4^{-} , and RuO_4) [22]. Higher valency state Ru oxide will reduce to lower oxidation states of Ru during discharging process.

III. **Hybrid capacitors: -**

Electric double layer supercapacitors (EDLC) exhibit relatively low specific capacitance which impacts further application in supercapacitor with low energy densities. Although, energy density of pseudo capacitors offers high energy density than electric double layer supercapacitors. However, pseudo capacitors have limitations for long life time, electrical conductivity and power densities because of faradaic reactions through it. To overcome limitations of electric double layer supercapacitors and pseudo capacitors third type of supercapacitor was developed which is known as hybrid capacitors. The hybrid capacitor is formed through the combination of electric double layer supercapacitors and pseudocapacitive materials; utilizing both faradaic and non-faradaic processes to store charge. In hybrid system faradaic pseudo capacitance electrode with higher capacitance provides high energy density, while the non-faradaic electric double layer supercapacitors electrode enables high power density. The hybrid capacitor electrodes can achieve higher capacitance, energy densities, power densities and chemical stability thanelectric double layer supercapacitorsor pseudo capacitor electrodes.

2. Transition metal oxides:

For fabrication of the electrode in energy storage devices transition metal oxides is one of the best and prominent active material due to its multiple physical and electrochemical characteristics. As transition metal oxides have multiple oxidation states , they can transfer multiple electrons which leads to extending discharge time. It will improve energy density in rapid Faraday redox reactions. Up till now a considerable number of transition metal materials (RuO_2, Co_3O_4, MnO_2, XCo_2O_4 (X = Mn, Cu, Ni), Fe_2O_4, V_2O_5) have been investigated for supercapacitor application including transition metal oxides, transition metal hydroxides their derivatives. Focus of researchers mainly concentrated on synthesis methods, construction of nanostructures, developing composite materials for effective electrodes.[23] Transition metal oxides having a relatively high specific capacitance [24] and superior specific energy [24], This makes them unique candidates for high-performance supercapacitors. But at the same time these materials have shown comparatively positive energy density and low conductivity. Due to this limitation of transition metal oxide many researches attraction have been made to fabricate hybrid supercapacitors which combine the advantages of the behaviours of both EDLCs and pseudo capacitors, enhancing the electrochemical performance.[25] Transition metal oxides have higher specific capacitance (100–2000 F g^{-1}), higher energy density than carbon materials and better chemical stability than conductive polymers [26].Among all transition metal oxides RuO_2 has high theoretical capacitance and rapid faraday redox reaction hence RuO_2 is thought to be an optimal pseudocapacitive electrode material [27]. However, its high price and toxicity to the environment serious obstacle to its application in supercapacitors [28]. Transition metal oxides such as Co_2O_4, MnO_2 have high capacitance, comparatively low cost as available in abundance, which makes them efficient substitute for RuO2 [29]. But major disadvantage of many transition metal oxides haspoor electrical conductivity [30]. As ternary metal oxides exhibit two metal ionsAB_2O_4 (A or B = Ni, Co, Mo, Mn, and so on)have more active reaction sites and high electrical conductivity than binary metal oxides will help in improvement of electrical conductivity. In addition, spinel cobaltite (XCo_2O_4, X = Ni, Cu, Zn, Mn, and so on) have received enormous research interest because of their low cost, enhanced electrochemical activity, and being a natural abundant resource [31,32]. In this review, transition metal oxide materials including RuO_2, Fe_2O_4, NiO, Co_3O_4, MnO_2, V_2O_5, XCo_2O_4 (X = Mn, Cu, Ni are firstly introduced and discussed. Particularly, we introduce the latest developments of transition metal oxides for supercapacitor electrode according to the strategies. Finally, the current scenario, challenges and future development in transition metal oxides as supercapacitor is discussed.

2.1. Rutheniumoxide(RuO_2) based supercapacitors: -

Ruthenium oxide(RuO_2) is one of the most prominent electrode materials due to its advantages over other metal oxides. Among all pseudocapacitive materials, RuO_2 material has the highest specific capacitance of 1000Fg $^{-1}$.[20]RuO_2exhibits a wide potential window, long cycle life, excellent reversible redox reactions, good thermal stability, metallic-type conductivity[34]. It also has three oxidation states accessible within 1.2V [33]. But RuO_2 has a very high cost [20], which reduces its applications towards energy storage . The double layer capacitance only contributes to about 10% of the stored charge in RuO_2 electrodes, working in parallel with pseudo capacitance [33]. Binder-free 3D-criss crossed, hollow hydrous RuO_2 nanotubes designed on a Ti metal substrate employing a facile low temperature metal oxide template method provided a high specific capacitance of 840 Fg-1 at a current density of 2 A g-1.[35]Chen and coworkers obtained exceptionally high gravimetric capacitance of ~1500 F g−1 which is close to the theoretical value of RuO_2 by employing nanoporous gold (NPG) to serve as both support as well as current collector for RuO_2-based supercapacitors. Nanoporous gold (NPG)contains large surface area, porosity, interconnected channels, with excellent electrical conductivity that promotes fast charge transfer process in electrochemical performance [36]. Pt@RuO_2 core-shell based arrays of nanotube obtained by RuO_2 electrodeposition on pre-designed Pt nanotubes for micro-supercapacitor applications indicated high utilization efficiency of the active electrode material that lead to remarkably high gravimetric capacitances (1585 Fg^{-1}) as well as areal capacitances (320 $mFcm^{-2}$) with little variation withvarying scan rates [37]. As RuO_2 costs higher, RuO_2 is often combined with less expensive transition metal oxides so that resultant pseudocapacitive effect from the two components is obtained with significant charging/ discharging cyclic performances. This is an effective approach to restore electrochemical performance.This will help to bypassing high cost problem up to some extent. Three-dimensional network of interconnected nanosheets of Co_3O_4 arrays decorated with well-dispersed RuO_2 nanoparticles were fabricated using electrodeposition technique that displayed balanced conductivity and electrolyte accessibility that led to improved gravimetric capacitance of ~ 905 Fg^{-1} at 1 Ag^{-1} current density[38].Porous PANI–RuO_2 composite has been prepared via simple, inexpensive successive ionic layer adsorption and reaction (SILAR) method obtained gravimetric capacitance 664 Fg^{-1} at potential scan rate of 5mVs^{-1} in 1 M H_2SO_4 with 89% capacitance retention efficacy for 5000 GCD cycles[39].3D-arrays of RuO_2 nanoparticles encaged polyaniline hollow nanospheres (RuO_2/H-PANI)assisted by polystyrene (PS) template synthesis were found to display specific capacitance value of 1570 Fg^{-1} at 10mVs^{-1} scan rate [40].

2.2. Manganese oxide (MnO_2) based supercapacitors: -

Manganese oxides is capable transition metal oxideto be an alternative for RuO_2 due to their relatively low cost, low toxicity , environmental safety and having theoretical high capacitances [1100–1300Fg^{-1}][41]. Pure MnO_2 and Composite electrodes based on MnO_2 containing carbon nanotubes,carbon blacks, polyaniline and other conducting materials areunder investigation for supercapacitor application.Manganese oxide thin films have been prepared using variouschemical synthesis methods such as hydrothermal, solgel, dip- or drop coating,electrochemical deposition, electrostatic spray deposition and physical vapor deposition followed by electrochemicaloxidation. Amade et al.reported the MnO_2 was electrodeposited lining the surface of the vertically aligned CNTs and recorded a high specific capacitance of 642 F g^{-1} was obtained at a scan rate of 10 mV s^{-1}[41]. Synthesis of

Carbon fabric (CF)-carbon nanotube array (CNTA)/MnO_2 composites with a 3D porous structure by the electrochemical deposition gives maximum specific capacitance 740 F g^{-1} with a mass loading of 0.34 mg cm^{-2} at the scan rate of 2 mV s^{-1}.[42] The MnO_2@CNT sponge nanocomposite shows a high specific capacitance of 600 F g^{-1} at 1 A g^{-1} with good retention capability.[43] Using the low-temperature hydrothermal method Multi-walled carbon nanotubes (CNTs)/manganese dioxide (MnO_2) nanocomposites were synthesized and reported specific capacitance of 30.3 F g^{-1} enhance to 405.15 F g^{-1} with a hydrothermal reaction time of 5 min using 1 M Na_2SO_4 electrolyte at a scan rate of 100 mVs^{-1} with better cycling stability after 1000 cycles .[44] Bio template derived N-dop3ed 3D graphene@MnO_2 (N-G@MnO_2) electrode exhibited a high specific capacitance of 411.5 F g^{-1} and a good cycling performance of 88.3% capacitance retention after 4000 charge/discharge cycles.[45] MnO_2 doped polyaniline (PANI) grafted on 3D CNTs/graphene was fabricated using basic in situ redox deposition showed maximum specific capacitance of 1360 Fg^{-1} at 5 mV s^{-1} scan rate with a good cycling stability of 82% after 5000 cycles.[46]

2.3. Iron oxide (Fe_3O_4) based supercapacitor :-

Ferrites show a good electrochemical performance due to variable oxidation states of the trivalent cation, Fe^{3+} which enhances the redox behaviour and improves the cyclic stability.Iron is the most important and easily available metal in earth having low cost. $ZnFe_2O_4$ has been identified as one of the best electrode materials due to its high theoretical capacity of 1000 $mAhg^{-1}$, cost-effective and eco-friendly. The Electrochemical performance of $ZnFe_2O_4$ is lagging behind due to its low electronic conductivity, relatively low mechanical stability during the charge discharge process due to self-aggregation. Electrochemical studies performed The $ZnFe_2O_4$ synthesized byYang et al.shows that using active carbon fiber electrochemical studies performed a specific capacitance of 192 Fg^{-1}. Due to use of activated carbon fibers capacitance of the material is enhanced with 92.7% of capacitance retention after 20000 cycles which is higher when compared to pure $ZnFe_2O_4$ which has a capacitance retention of 81.3 %and also prevents the self-accumulation..[47] Cai et al.recently investigated the electrochemical properties of NiFe2O4 synthesized via hydrothermal methodthe electrochemical performance was investigated using 1 M Na_2SO_4 electrolyte shows maximum specific capacitance of 210.9 Fg^{-1} at 0.5 Ag^{-1} and a good cyclic stability of no loss of capacitance over 5000 cycles.[48] $NiFe_2O_4$ shows a higher specific capacitance of 240.9 Fg^{-1} at a current density of 1 Ag^{-1} in this interestingly the specific capacitance increased up to128% after 2000 cycles at energy density of 10.15 $Whkg^{-1}$ at power density of 140 Wkg^{-1} .[49] Ferrites and its composites like carbon, polymer, etc. are also investigated.Gao et al.proposed the electrochemical properties of morphology controlled $NiFe_2O_4$ the specific capacitance of the electrode has been significantly improved up to 240.9 Fg^{-1} at a current density of 1 Ag^{-1} the specific capacitance improved to 128% after 2000 cycles.[50] Hybrid hydrogels with 3D networks of $CoFe_2O_4$ / rGO shows a specific capacitance of 356 F g^{-1} at 0.5 A g^{-1} with excellent cycling stability and 87% capacitance retention at 5 A g^{-1} after 4000 cycles.[51] Priyanka Makkar et al. synthesised the multifunctionality of the $CuFe_2O_4$-rGO nanocomposite by constructing a flexible asymmetric supercapacitor with a cathode of $CuFe_2O_4$-rGO nanocomposite and an anode of rGO. They reported 313 F/g at 2 A/g specific capacitance of a $CuFe_2O_4$-rGO nanocomposite with a high energy density of 26 Wh/kg and a power density of 2600 W/kg.[52] Bhawna Verma et al. proposed a completely novel ternary nanocomposite (PANI-acetylene black-$CuFe_2O_4$), the maximum specific capacitance was determined as 732.35 F/g at 0.5 A/g current density.[53]

2.4. Nickel oxide (NiO) based supercapacitors :-

Nickel (II) oxide (NiO) is a widely studied transition metal oxide for use in supercapacitors due to its availability, good theoretical capacitance and impressive reversible redox reactions.[53,54]Kim et al. studied flower-shaped NiO /a-Ni $(OH)_2$ hybrid structures by using a solvothermal process shows specific capacitance of 474 F g^{-1}at current density of 10 A/g. While enhance specific capacitance of 810 F g^{-1} at current density10 A/g when made composite with 20 wt. % addition of SWCNT.[55]. Liu et al.obtained Flakelet-like morphology onto the Ni substrate using hydrothermal technique for supercapacitor electrodes by facile way to prepare NiO. They got maximum SC of 760 F g^{-1} which is noticeably higher than 480 F g^{-1} for pure NiO using H2 as the reducing agent for the preparation of composite [56]. Zheng et al. introduced hydrothermal synthesis to fabricate NiO precursor at different temperatures, nanostructured NiO with a distinct flakelike morphology was obtained via heating at low temperature achieved specific capacitance approximate to 137.7 F g^{-1} at the current density 0.2 A g^{-1} [57]. Using monolayer polystyrene sphere template hierarchically porous NiO film has been successfully prepared by Xia et al. using chemical bath deposition. They reported specific pseudo capacitance of 309 F g^{-1} and due to high porosity and large surface area of the hierarchically porous NiO film, good capacity retention was observed [58]. Changzhou Yuan et al. reported a novel two-step strategy to synthesize self-supported hexagonal nickel oxide nanoplatelet arrays on Ni foam reported specific capacitance of 1124 F g^{-1} at 2 A g^{-1} and 864 F g^{-1} even at high current density of 16 A g^{-1} [59]. Cheng et al. prepared NiOx xerogels by using sol-gel method obtained excellent specific capacitance of

696 F g^{-1} at a current density of 2.0 $mAcm^{-2}$ for the NiOx xerogels heat-treated at 250 ^{0}C [60].

2.5. Cobalt oxide (Co_3O_4) based supercapacitors: -

By reviewing many TMOs, $Co3O_4$ has been attractedresearchers attention for supercapacitors due to its high theoretical capacitance (3560F g^{-1}), better electrochemical performance, environment friendly nature. This Co_3O_4 can be subjected to substitution by a transition metals, i.e., MCo_2O_4(Where M = Cu, Fe, Mg, Mn, Ni, and Zn). Such MCo_2O_4 shows active redox reactions compared to pure Co3O4 and provides good electrochemical performance from doped transition metal and its carbon based composites [61]. As transition oxide materials suffer from poor electronic conductivity; hence they need to be improved by trying to make composites with carbon and its derivatives [62]. Recently the graphene with MCo_2O_4 as a nanocomposite has drawn tremendous attention to its better physical and electrochemical properties than the bare MCo_2O_4 [63].

Table 1. The electrochemical performance of someMCo_2O_4(Where M = Zn, Cu, Ni, Mg, Mn and Fe). transition metal oxides (TMOs) and its composites electrode materials .

Sr. No.	Material	Preparation method	Electrolyte	Specific Capacitance	Cyclic Stability	Ref.
1.	1 mM Zn(CH3COO)2 + 2 mM Co(NO3)2 + 5 mM Co(NH2)2 + 2 mM NH4F + 40 mL DI water + 140 ◦C for 12 h (5 ◦C min^{-1}).	Hydrothermal	2 M KOH	694 (2 A g^{-1})	~85% even after 2000 cycles (10 A g^{-1})	63
2.	2 mM CoCl2 + 1 mM ZnCl2 + 5 mM NH4F + 6 mM HMT + 80 mL DI water + 100 mL polytetrafluoroethylene + 140 ◦C for 6 h.	Hydrothermal	2 M KOH	776.2 (1 A g^{-1})	Superior cyclic stability (84.3% at 3 A g^{-1})	64
3.	0.5 mM Zn(NO3)2 + 0.1 mM Co (NO3)2 + 2 mM NH4F + 5 mM urea + 1 mM SDS + 50 mL DI water + 120 ◦C for 6 h.	Hydrothermal	2 M KOH	832C g^{-1} (5 A g^{-1})	85.5% after 5000 cycles (50 A g-1)	65
4.	0.05 mM Zn(NO3)2 + 0.05 mM Co(NO3)2 + 40 mL DI water : Ethanol (50 :50) + 0.15 M Urea + 100 ◦C for 14 h.	Hydrothermal	2 M KOH	500 0.75 A g^{-1})	165% for 1000 cycles (5 A g^{-1})	66
5.	4 mM Zn(NO3)2 + 8 mM Co(NO3)2 + 6 mL ethanol + 60 mL isopropyl alcohol + 120 ◦C for 24 h.	Hydrothermal	3 M KOH	440 (1 A g^{-1})	155.6% after 3000 cycles (2 A g^{-1})	67
6.	**ZnCo2O4/rGO/sponge foam** 1 mM Zn(NO3)2 + 2 mM Co(NO3)2 + 60 mL DI water + 10 mM Urea + 8 mM + NH4F + GO/sponge + + 110 ◦C for 19 h.	Hydrothermal	2 M KOH	1116.6 (2 mV s^{-1})	93.4% after 5000 cycles	68
7.	**ZnCo2O4/rGO composite** 0.2 g (P123) + 0.04 g GO + 40 mL DI water + 2 mM Co(NO3)2 + 0.2 mM Zn(CH3COO)2 + 2 mM Urea + 120 ◦C for 5 h on NF.	Hydrothermal	2 M KOH	3222 (1 A g^{-1})	Good cyclic stability 5000 cycles	69
8.	**3D ZnCo2O4/N- doped rGO composite** 1 mM Zn(NO3)2 + 2 mM Co(NO3)2 + 5 mg mL^{-1} GO + 4 mM Urea + 2 mM hydrazine monohydrate + 180 ◦C for 6 h on NF.	Hydrothermal	1 M KOH	1613 (1 A g^{-1})	97.3% after 5000 cycles	70

9.	**ZnCo2O4 on NF@GO** [2 mgmL-1 GO + NF + 700 ◦C Ar-H2 (10:1) for 3 h = NF @GO] [1 mM Zn (NO3)2 + 2 mM Co(NO3)2 + CO(NH2)2 + 40 mL DI water + NF@GO + 120 ◦C for 6 h	Hydrothermal	2 M KOH	680 (1 A g^{-1})	95.6% after 3000 cycles	71
10.	0.4 mM CuCl2 + 0.8 mM CoCl2 + 16 mL Methanol + 4.8 mM Urea + 120 ◦C for 12 h.	Hydrothermal	3M KOH	405.36 (20 A g^{-1})	99.4% after 10,000 cycles (3 A g^{-1})	72
11.	0.17 g CuCl2 + 0.48 g CoCl2 + 60 mL DI water + 1.08 g Urea + 120 ◦C for 6 h.	Hydrothermal	2M KOH	1223.2 (1.08 A g^{-1})	88% after 2000 cycles	73
12.	0.01 M Cu(NO3)2 + 0.02 M Co(NO3)2 + 10 mL DDW + 2 g SBA- 15 + 80 mL n-Hexane + 60 ◦C for 5 h.	Hydrothermal	6 M KOH	1210 (2 A g^{-1})	Good cyclic stability	74
13.	10 mM CuCl2 + 20 mM CoCl2 + 50 mL DI water + NH4OH (pH = 14) + 180 ◦C for 24 h.	Hydrothermal	6 M KOH	1037C g^{-1} (5 mV s^{-1})	94% after 5000 cycles (10 A g^{-1})	75
14.	1mM Cu(NO3)2 + 2 mM Co(NO3)2 + 5 mM Urea + 35 mL DDW + 120 ◦C for 6 h on NF.	Hydrothermal	3 M KOH	1227.8 (5 mA cm^{-2})	95.4% after 1000 cycles	76
15.	4 mM Cu(CH3COOH)2 + 2 mM Co(CH3COOH)2 + DI water + Urea + 120 ◦C for 12 h on NF.	Hydrothermal	6M KOH	1595 (1 A g^{-1})	85.1% after 4600 cycles	77
16.	(2:1) ratio Cu (NO3)2.3H2O + 1 M KOH + 50 ml DDW + 90^0c for 5hrs in oil bath.	chemical-precipitation technique	2 M KOH	290 F g−1 (2 mA cm−2)	92% after 1000 cycles	77
17.	**Graphene wrapped CuCo2O4** [36.95 mg Cu(NO 3)2 + 72.75 mg Co(NO3)2 + 8 mL glycerol + 40 mL isopropanol + 180 ◦C for 6 h. = CuCo2O4] + [0.1 g CuCo2O4 + 10 mL isopropanol + 0.1 mL APTES + 20 mL DI water + 30 mL GO]	Hydrothermal	3 M KOH	1813 (2 A g^{-1})	95.2% after 6000 cycles	78
18.	2 mM Ni(NO3)2 + 4 mM Co(NO3)2 + 80 mL DI water + 12 mM NH4F + 24 mM Urea + 100 ◦C for 5 h	Hydrothermal	2 M KOH	2132 (10 A g^{-1})	93.8% for 10,000 cycles	79
19.	0.5 mM Ni(NO3)2 + 1 mM Co (NO3)2 + 2 mM NH4F + 2.5 mM urea + 30 mL DI water + 90 ◦C for 12 h.	Hydrothermal	2 M KOH	372 (1 A g^{-1})	88.3% after 2000 cycles	80
20.	0.58 g Co(NO3)2 + 0.29 g Ni(NO3)2 + 40 mL DI water + 0.08 g of NH4F + 0.30 g of urea + 120 ◦C for 4 h.	Hydrothermal	2M KOH	2193 (1 A g^{-1})	Good cyclic stability	81
21.	**NiCo2O4@rGO** 60 mL GO + 3 mM Ni(NO3)2 + 6 mM Co(NO3)2 + (60 mM) of urea + 60 mL of DI water + 100 ◦C for 24 h.	Hydrothermal	6M KOH	1315 (10 mA cm^{-2})	55% after 2000 cycles	82
22.	**NiCo2O4@rGO** [20 mL 0.5% GO + 1 mL Ethanol + NF + 120 ◦C for 2 h + 80 ◦C for 12 h on rGO NF] [0.1 M Ni(NO3)2 + 0.2 M Co(NO3)2 + 0.9 m urea + 124.85 ◦C for 1 h on rGO NF]	Hydrothermal	2M KOH	1427 (8 A g^{-1})	83.8 % after 10,000 cycles	83
23.	**rGO wrapped NiCo2O4** 30 mg GO + 40 mL DI water + 0.119 g NiCl2 + 0.273 g CoCl2 + 10 mL Di water + NH4OH (25%) + 180 ◦C for 24 h.	Hydrothermal	2M KOH	1185 (2 A g^{-1})	98% after 10,000 (2 A g^{-1})	84
24.	**NiCo2O4@ rGO** 1 mM Ni(NO3)2 + 2 mM Co(NO3)2 + 8 mL DI water + 20 mL ethanol + 80 mg GO solution + 6 mM urea + 120 ◦C for 6 h.	Hydrothermal	1M KOH	882 (1 A g^{-1})	93.8% after 3000 cycles	85
25.	**NiCo2O4@N-doped graphene** [36.34 mg Ni(NO3)2 + 72.73 mg Co(NO3)2 + 40 mL isopropanol + 8 mL glycerol + 180 ◦C for 6 h. = NiCo2O4] + [30 mg NiCo2O4 + 50 mL Ethanol + 3 mL Ammonia + 8 mL N2H4 + 180 ◦C for 12 h.]	Hydrothermal	-	563 (1 A g-1)	90.5% after 5000 cycles	86

26.	**NiCo2O4-MnO2@GF** [1.5 mM Ni(NO3)2 + 3 mM Co(NO3)2 + 18 mM urea + 30 mL DI water + 110 ◦C for 10 h = NiCo2O4/ GF] [NiCo2O4/GF + 30 mL KMnO4 + 150 ◦C for 5 h.]	Hydrothermal	6M KOH	2577 (1 A g^{-1})	94% over 5000 cycles	87
27.	0.253 g MnSO4 + 0.021 g Co(NO3)2 + 30 mL DDW: ethanol (50:50) + 0.07 g PVP + pH 10 by NH3 + 160 ◦C for 12 h.	Hydrothermal	2M KOH	252 (1 A g^{-1})	-	88
28.	Mn(NO3)2 :Co(NO3)2 (1:2) + T-Spoon of Ethylene glycol + 10 mL DI water required amount of NaOH + 120 ◦C for 36 h.	Hydrothermal	1M KOH	671 (5 mV s^{-1})	92% after 1000 cycles	89
29.	CoCl2:MnCl2) Stoichiometric amount + 0.06 g Urea + 10 mL DI water + 105 ◦C for 6 h.	Hydrothermal	2M KOH	718.75 (0.5 A g^{-1})	Good cyclic stability	90
30.	**MnCo2O4@graphene** 0.01 M Mn(CH3COO)2 + 0.02 M Co(CH3COO)2 + 200 mL DI water :Ethanol (9:1) + 100 mg Ex-GO + 0.05 M Urea + 120 ◦C for 6 h.	Hydrothermal	3M KOH	890	95% over 2000 cycles	91
31.	**MnCo2O4/graphene** GO suspension (2 mg/mL) + 1.2 mM CoCl2 + 0.6 mM MnCl2 + 3.6 mM NaOH + 0.6 mM SDS + 180 ◦C for 10 h.	Hydrothermal	3M KOH	503 (1 A g^{-1})	97.4% retention after 5000 cycles	92
32.	2 mM MgCl2 + 4 mM CoCl2 + 12 mM Urea + 80 mL DI water + 120 ◦C for 6 h on NF	Hydrothermal	2M KOH	1079.6 (1 A g^{-1})	91% after 10,000 cycles	93
33.	4 mM Co(NO3)2 + 2 mM Mg(NO3)2 + 12 mM Urea + 60 mL DI water + 120 ◦C for 6 h.	Hydrothermal	2M KOH	508 (2 A g^{-1})	95.9% after 2000 Cycles	94
34.	2.5 mM Mg(NO3)2 + 5 mM Co(NO3)2 + 24 mM CO(NH2)2 + 80 mL DI water + 120 ◦C for 6 h on NF	Hydrothermal	2M KOH	804 (1 A g^{-1})	87% after 2000 cycles	95
35.	**rGO modified MgCo2O4** 5 mM Mg(CH3COOH) + 10 mM Co(CH3COOH) + 9 mM Urea + 2.5 mM CTAB + 100 mL water + 100 ◦C for 12 h.	Hydrothermal	3M KOH	600 (2 mV s^{-1})	Good cyclic stability	96
36.	2.19 g Co(NO3)2 + 0.97 g FeCl3 + 50 mL DI water + 400 μL + oleic acid + 0.48 g + urea + 6 mL ammonia + 30 mL + DI water + 180 ◦C for 12 h	Hydrothermal	3 M KOH	960 (2 A g^{-1})	94 % after 10,000	97
37.	262 mg Co(NO3)2 + 72.5 mg Fe(NO3)3 + 30 mL DI water + 100 mg NH4F + 162 mg urea + 100 ◦C for 18 h.	Hydrothermal	3M KOH	969 (2 A g^{-1})	Superior cyclic stability	98
38.	**Graphene/FeCo2O4** 0.05 M Fe(NO3)2 + 0.1 M Co(NO3)2 + 0.5 M Urea + 0.2 M NH4F + 40 mL DDW + 4 mg/mL GO + CC + 100 ◦C for 12 h	Hydrothermal	1 M Na2SO4	1710 (3 A g^{-1})	94% after 5000 CV cycles	99

2.6. Vanadium oxide (V_2O_5) Based supercapacitors :-

Among various transition metal oxide materials, vanadium pentoxide (V_2O_5) reveals predominant property. Due to its high theoretical capacitance, multiple oxidation valences (V^{2+}, V^{3+}, V^{4+}, and V^{5+}), low-cost, easy synthesis, layered structure, and low toxicity, it could be a potential candidate for supercapacitor [100]. On this basis, the charge storage mechanism of V_2O_5 can be illuminated by the following equation:

$V_2O_5 + xA^+ + xe^- \leftrightarrow AxV_2O_5$ (A = Li, K, Na, etc.) [101].

V_2O_5 possesses superhigh theoretical capacitance of 2120 F g−1 (under broad potential window of 1 V), which is ascribed to the higher oxidation valence of vanadium to transfer even more electron [102]. To obtain diverse morphology and structure of V_2O_5, many methods have been designed, such as hydrothermal method, electrospinning, sol–gel method [103] and so on. Jeyalakshmi et al. have synthesized β-V_2O_5/Ni (5 wt. %) nanofilms via sol–gel spin coating method and got excellent specific capacitance (417 F g^{-1} at a scan rate of 5 mV s–^{1}) with good cycling capacity (retaining 80% capacitance after 100 cycles), and energy density (231 W h kg^{-1} at a power density of 4.2 k W kg^{-1}) compared with pure V_2O_5 or other doping content composites.[104] A simple chemical bath deposition method was used to synthesize V_2O_5/MWCNTs electrodes which were successfully integrated into a flexible solid-state supercapacitor device. The flexible solid-state device exhibits superior cycling stability of 96% charge retention after 4000 cycles.[105] Balamuralitharan et al. have synthesized V_2O_5 nanotube by hydrothermal way, which reveals a high specific capacitance of 417.3 mF cm^{-2} at a scan rate of 5 mV s^{-1} in 0.5 M Na_2SO_4 and good cycling stability of 80% original capacitance retention over 3000 charge–discharge cycles[106]. A simple hydrothermal method has been reported for the preparation of ternary V_2O_5/CNTs– super activated carbon (SAC) nanosheets by Wang et al. These nanocomposites show a high specific capacitance of 357.5 F g^{-1} at a current density of 10 A g^{-1} and only 0.5% capacitance lost for 1000 charge–discharge cycles [107].Saravanakumar et al. (2014) have exploited V_2O_5/f-MWCNT nanocomposites via simple progresses. This nanocomposite reveals high specific capacitance (up to 410 F g^{-1} at 0.5 A g^{-1}), excellent rate stability (retaining 68.3% as the current density increased from 0.5 to 10 A g^{-1}) and good cycling capacity (retaining 86% after 600 cycles).[108] Yang et al. study self organized method and synthesize V_2O_5–TiO_2 nanotube arrays. The as-obtained composites exhibit capacitance of 220 F g^{-1} and an energy density of 19.56 Wh. kg^{-1} with perfect reversibility and excellent cycling capacity [109]. With the activated carbon as negative electrode material and V_2O_5 nanotubes as positive electrode material, the electrochemical characteristic of asymmetric device is presented and analysed. It shows specific capacitance of 103 F g^{-1} at current density of 1 A g^{-1}, good rate stability of 79.6% capacitance retention (current density increases from 1 to 10 A g^{-1}), excellent cycle capacity even 10,000 charge–discharge cycles, and energy density of 46.35 W h kg^{-1} with power density of 1800 W kg^{-1}.[110]

Conclusion and Prospectives: -

In summary, this overview has looked into the recent advances and challenges in transition metal oxide, transition metal hydroxide and their derivatives for promoting their application in supercapacitors (SCs). The great advantages of the transition metal oxides are in terms of abundant resource and low production cost. Besides, they have a higher specific capacitance as compared to carbon-based materials and conductive polymers.However, it is realized that the major roadblock faced towards the large-scale commercial applications is their relatively low electrical conductivity that restricts the high charge/discharge kinetics of the electrode material. Therefore, many methods have mainly focused on overcoming this problem, including the synthesis of electrode materials with nanostructure and larger active surface area, a composite with an electronically conductive material as well as multiple metals composite with synergistic effect.The synthesis of electrode materials with good electrochemical performance via a green, environmentally friendly, simple and low-cost method is still needed for commercial applications. Now a days carbon-based materials are used as large-scale productive materials for currently practical applications in supercapacitorsdue to their high conductivity, large specific surface area, and high chemical and thermal stability. Active carbon materials as electrode used in commercial supercapacitors can provide a capacitance of 100–500 Fg^{-1} in aqueous and organic electrolytes.The transition metal oxides/hydroxides have been used as one of the most outstanding electrode materials for SCs, due to their intrinsic high electrical conductivity. Up till now these materials are mainly synthesized into various nanostructures. However, their practical capacitance and energy density is still relatively low. Hence, how to control the structure and morphology effectively to improve the electrochemical performance needs a further exploration. For the time being, the preparation process and production cost should also be taken into account.

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