Review Article

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Advances in the design and application of transition metal oxide-based supercapacitors

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Abstract: In the last years, supercapacitors (SCs) have been proposed as a promising alternative to cover the power density deficiency presented in batteries. Electrical double-layer SCs, pseudocapacitors, and hybrid supercapacitors (HSCs) have shown very attractive features such as high-power density, long cycle life, and tunable specific capacitance. The advances of these energy storage devices made by transition metal oxides (TMOs) and their production in pseudocapacitors and HSCs depend on chemical composition, crystalline structure, morphology, theoretical capacitance, and oxidation states. In this way, this critical review considers several metal oxides (RuO_2 , MnO_2 , V_2O_5 , and Co_3O_4) and their different configurations with diverse carbon-based materials. Energy storage mechanisms and fundamental principles to understand the promising effect of metal oxides in SCs devices are thoroughly described. Special attention as regards to the energy storage mechanisms relative to the specific capacitance values is presented in the reviewed articles. This review envisages the TMO as a key component to obtain high specific capacitance SCs.

Keywords: transition metal oxides, specific capacitance, energy storage mechanisms, hybrid supercapacitors

1 Introduction

Global warming and climate change are directly associated with the consumption of fossil fuels due to different anthropogenic activities [1]. Among the consequences of climate change, natural disasters that trigger global financial crises can be highlighted [2]. Nevertheless, as fossil fuels are finite resources, it is necessary to find new, clean, and efficient sources of energy. The annual report of the Energy Information Administration (EIA) shows that the consumption of fossil fuels will decrease slowly until the year 2050 (Figure 1). This report showed an increment of 21% in renewable energy consumption from 2010 to 2020. Based on this result, it is projected that between 2020 and 2050, there will be a 42% increase in renewable energy consumption [3]. However, the extensive use of these clean energy sources (e.g., solar and wind) is limited by the intermittency in the energy density because this value depends on environmental conditions [4]. Hence, various studies have been conducted on the development of sustainable energy conversion and storage systems [5].

The drawback in the intermittent energy provided by renewable energy sources (e.g., solar, wind, hydroelectric, and geothermal) could be solved from the use of modern energy storage technologies. In this sense, supercapacitors (SCs) and batteries are capable of storing electrical energy from a renewable source and distributing it independently of the conventional electrical grid [6]. Thus, several studies and applications emphasize the development of electrochemical energy storage systems, highlighting the scope of lithium-ion batteries (LIBs), double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors, due to their high power (W kg^{-1}) or energy density (W h kg^{-1}) (Figure 2) [7]. Comparing both variables in Ragone diagram, capacitors and ultracapacitors have a high-power density and a low-energy density in contrast to batteries [8]. Therefore, an ideal electrochemical energy storage device must have an extended high electrical charge density for long periods of use [9].

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Figure 1: Electric energy production from various conventional and renewable sources in the United States in 2020, and its estimate for 2050 (adapted from the Annual Energy Outlook 2020) [3].

Figure 2: Ragone diagram for different energy storage devices [8].

Nowadays, there is a big concern in the limitation of extensive use of electrochemical energy storage devices, which is not only associated with performance parameters. For example, LIBs have a high production cost [10], but when exposed to extensive charge and discharge cycles, they have shown the formation of highly volatile compounds, which are prone to ignition of the device, preventing its recycling and generating soil contamination [11]. In this context, electrochemical capacitors based on transition metal oxides (TMO) are effective devices due to their high specific power, electrochemical stability during long charge–discharge cycles, easy scaling, and sustainability [12].

The advantages in performance and application are attributed to the electrode composition in these devices, specifically, to the type of mechanism that governs the

process of electronic transport and storage of electrical charge. In relation to this mechanism, electrochemical capacitors can store the electrical charge through a process of electrical polarization in the electrode–electrolyte interface (the capacitive process of the double electrical layer) or through an electronic transfer process from a reversible redox reaction developed in the same interface (pseudocapacitive process; Figure 3) [13,14]. Based on these mechanisms, three classes of electrochemical capacitors are reported: (1) electric double-layer capacitors (EDLCs), (2) pseudocapacitors (PCs), and (3) hybrid supercapacitors (HSCs), which present both electrical charge storage mechanisms [15].

In contrast, the limitations in energy density (widely reported in the design of SCs) are attributed mainly to resistances in electric and ionic transport. In this sense, EDLCs show limitations in electrical transport associated with poor electrical contact with the current collector, low surface area, high polarization potential, restricted range of capacitive potential, or corrosion lability. Conversely, PCs and HSCs may present restrictions in ionic transport, poor conductivity, mass transfer, electrode stability, low faradaic character, and irreversibility in the charge–discharge processes [14,16,17]. In this sense, different approaches focus on obtaining advanced materials free of the electrical or ionic limitations, previously exposed. The study of these materials emphasizes several physicochemical and electrochemical parameters that reveal the efficiency of these advanced materials in isolated or integrated charge storage devices. Some of these parameters are as follows: high values of specific capacitance, electrochemical stability, compatibility with various more eco-friendly

Figure 3: Classification of supercapacitors according to energy storage mechanisms: electrochemical double layer capacitors, pseudocapacitors, and hybrid capacitors [16].

electrolytes, and so on [18]. In this way, it is important to understand the dielectric properties of ceramic materials due to the strong dependence on the energy gap, the polarizability, and other resonance effects associated with the crystalline lattice of these materials (defects, vacancies, and dopants) [19]. These physical properties have been little studied in this subject of the application.

In relation to electrode composition, studies have been developed with graphene materials [20], carbon fibers from synthetic and/or natural sources [21]. Likewise, the design of electrodes composed of TMOs, such as NiO [22], MnO₂ [23], Mn₃O₄ [24], V₂O₅ [25], Co₃O₄ [26], and others transition bimetallic oxides [27–35] is highlighted in this study. Figure 3 outlines the main classes of SCs and the advanced materials that form the part of their structure [16]. Therefore, this review aims at the most relevant advances in electrodes composed of RuO₂, MnO₂, V₂O₅, and Co₃O₄ supported on carbon-based materials. A relationship is also made between the physicochemical and electrochemical properties such as: crystallography, composition, morphology, topology, and the specific capacitance, the range of working potential and the capacitive retention, respectively. Besides, the development of new microstructures and nanostructures with complex morphologies are highlighted [36].

Regarding to the chemical composition, RuO₂-based electrodes are widely studied due to its theoretical capacitance of 1,300–2,200 F g⁻¹ [37]. MnO₂ and Co₃O₄ have been extensively investigated owing to their remarkable capacitances of 1,370 and 3,560 F g⁻¹ [26,38], respectively.

Likewise, micro- and nano-structured electrodes based on crystalline arrangements of MnO₂, V₂O₅, or Co₃O₄ are highlighted. It is also possible to observe that these structures induce not only the increase of the surface area of the materials but also increase their electroactive area, as well as their specific capacitance [36]. At the same time, it is noteworthy to note that the crystalline order formed by these TMO materials also improves the chemical stability in extensive charge–discharge cycles; hence, it is important to highlight the microstructural characterization of these studied articles.

Finally, the limitations and future perspectives of these materials are compiled and discussed to extend the state of the art and achieve further understanding of the physicochemical and electrochemical processes that govern the performance of SCs based on TMO.

2 TMOs for SCs applications

Several attempts have been made to study the physicochemical and electrochemical properties of TMO applied in the development of high-efficiency SCs. This high efficiency achieved is attributed to the dependence between their capacitive behavior and the versatility in the oxidation state of these metals. Likewise, it is associated with the crystalline phase, particle size, ion exchange capacity, and inherent thermal and chemical stability [13,39,40].

2.1 High-performance ruthenium oxide-based SCs

In particular, ruthenium oxide (RuO_2) is intensively investigated due to its high specific capacitance (theoretical capacitance, $1,300\text{--}2,200\text{ F g}^{-1}$), high ionic conductivity, reversible redox reactions, high thermal stability, and long cyclic life [37]. Charge transfer on RuO_2 surface is caused by reversible storage of protons in interaction with the electrolyte, which is influenced by the type of crystalline phase that the oxide presents. RuO_2 can form two preferential crystalline structures, the tetragonal and cubic systems with space groups of $P4_2/mnm$ and $Pa\bar{3}$, respectively [41,42]. Besides, commonly a hydrated form of $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ is observed. The hydrated form affects the storage of electric charge, facilitating the diffusion of protons (H^+) and electrons (e^-) [43]. The storage of protons, in its hydrated form, can be expressed according to reactions (1) and (2):

The pseudocapacitive behavior of RuO_2 involves different reactions in acidic and basic electrolyte solutions. In the presence of acid electrolytes, a reversible rapid electron transfer and electro-adsorption of protons occur at the surface, and a change in the oxidation state from Ru^{2+} to Ru^{4+} is observed. In the charge process, in the presence of alkaline electrolytes, RuO_2 is oxidized in various forms, from RuO_4^{2-} and RuO_4^- to RuO_4 , and in the discharge process, the oxide is reduced to RuO_2 [44]. This behavior makes RuO_2 a promising material for the development of SCs, but its toxicity, low abundance, and high cost make it necessary to search for alternative materials. Thus, TMOs such as MnO_2 , NiO , Co_3O_4 , and V_2O_5 supported on carbon, activated carbon, and polymers have been investigated since they present some advantages such as greater abundance, lower cost, and lower environmental impact than RuO_2 [16,45–49]. In addition, these oxides are used to increase the capacitance of the carbon electrodes, also increasing the working potential window [50]. Otherwise, new research has shown the use of mixed TMOs such as NiCo_2O_4 , CoFe_2O_4 , CuCr_2O_4 , and TbMn_2O_5 [27–30].

2.2 Manganese oxide

Manganese oxide, MnO_2 (Mn with oxidation state +4), has received great attention due to its high theoretical

specific capacitance (around $1,370\text{ F g}^{-1}$), low cost, abundant availability, and environmentally friendly nature [38,51,52]. In this way, MnO_2 is widely used in energy storage applications such as electrodes for lithium batteries and SCs [45,53]. Charge storage mechanisms in MnO_2 are based on processes of intercalation and deintercalation of protons (H^+) or electrolytic alkaline ions ($\text{X}^+ = \text{Li}^+$, K^+ , and Na^+) adsorbed on the surface of MnO_2 and absorbed in the volume of its crystalline structures. These mechanisms are shown in reactions (3)–(5) [54]:

The second mechanism is based on the adsorption of metallic electrolyte cations on the surface of the MnO_2 electrode.

The pseudocapacitive properties of MnO_2 are influenced by its crystalline structure as MnO_2 has several crystalline phases such as α , β , γ , δ , and λ - MnO_2 , where each crystalline structure has an arrangement of different atoms, leaving interatomic channels where small ions can diffuse (Figure 4) [55]. This diffusion process has an influence on the acceleration and/or deceleration of the intercalation–deintercalation processes of H^+ and alkali ions that are dependent on the atomic channels of MnO_2 and grown crystals topography, which leads to a direct influence on their specific capacitance [55,56].

MnO_2 has a low electrical conductivity around 10^{-6} to 10^{-5} S cm^{-1} and a low structural stability that generates a decrease in electronic transport. Furthermore, a low structural stability has been observed in extensive cycling processes of charge–discharge [38,53]. Depending on the crystalline structure, MnO_2 presents differences in its electrochemical properties, as reported by Li *et al.* [55]. In the case of δ - and α - MnO_2 phases deposited on gold, the current collector showed a specific capacitance of 922 and 617 F cm^{-3} , respectively, at 5 mV s^{-1} in $\text{Na}_2\text{SO}_4\text{ }1.0\text{ mol L}^{-1}$. This difference is due to the crystalline structure, for example: in the case of δ - MnO_2 has an interlayer distance of 0.7 nm, whereas α - MnO_2 presents channels of $0.46\text{ nm} \times 0.46\text{ nm}$ and $0.23\text{ nm} \times 0.23\text{ nm}$ in its structure. By theoretical calculations such as DFT, energy barrier of migration of electrons between δ and α - MnO_2 was calculated and thus obtaining a value of 0.56 and 2.5 eV, respectively. It means that there is greater resistance to ion diffusion in the α - MnO_2 structure compared to the δ - MnO_2 phase (Figure 5).

To optimize the electrochemical properties of MnO_2 , various modifications to its morphology have been

Figure 4: Differences in the sizes of interatomic channels of the $\delta\text{-MnO}_2$ and $\alpha\text{-MnO}_2$ phases, and possible diffusions of Na^+ ions in these channels [55].

proposed. For example, Qiu et al. [57] electrodeposited different morphologies of MnO_2 on paper fiber carbon, such as nanospheres, nanosheets, nanoflowers, and nanorods, showed a specific capacitance of 134, 226.3, 235.6, and 362.5 F g^{-1} , respectively, at 0.5 A g^{-1} in Na_2SO_4 0.5 mol L^{-1} . Xia et al. [58] synthesized nanosheets of $\delta\text{-MnO}_2$ by hydrothermal method and showed a high

specific capacitance of 411 F g^{-1} at 5 mV s^{-1} and 332.7 F g^{-1} at 0.5 A g^{-1} , with a capacitance retention of 93% after 10,000 cycles. This high value was attributed to the porosity of the material, increasing the electroactive sites, creation of short distances for ions diffusion in $\delta\text{-MnO}_2$, and decreasing the resistance of charge transfer. Conversely, the size of the oxides and their composition with

Figure 5: Comparison of the electrochemical behavior between the $\alpha\text{-MnO}_2$ and $\delta\text{-MnO}_2$ phases deposited on a gold current collector: (a) cyclic voltammetry, (b) charge and discharge profiles, (c) volumetric capacitance, and (d) specific capacitance [55].

other transition metals is also discussed. Feng *et al.* [59] synthesized $\text{MnO}_2@\text{SnO}_2$ spheres by the hydrothermal method, in which MnO_2 presented a pseudocapacitive behavior, while the SnO_2 intensified the electrical conductivity. Finally, the authors obtained a high specific capacitance of 541.6 F g^{-1} at a current density of 1 A g^{-1} , with a retention of capacitance of 92% after 1,500 charge and discharge cycles, using $\text{KOH } 6 \text{ mol L}^{-1}$ as an electrolyte.

Furthermore, the addition of other oxides such as Cu_2O contributes to the pseudocapacitance of MnO_2 . For example, Purushothaman *et al.* [31] electrodeposited consecutively CuMnO_2 and Cu_2O ($\text{Cu}_2\text{O}@\text{CuMnO}_2@\text{Cu}$) and obtained a specific capacitance of 257 F g^{-1} at the scan rate of 5 mV s^{-1} in $\text{Na}_2\text{SO}_4 \text{ } 0.1 \text{ mol L}^{-1}$ as an electrolyte. In addition, hybrid systems using MnO_2 nanoparticles grown on highly porous carbonaceous materials (carbon nanotubes, graphene, activated carbon, and carbon fibers) show specific capacitances between 258 and 330 F g^{-1} at a current density of 1.0 A g^{-1} [60]. Likewise, 3D $\text{MnNiCoO}_4@\text{MnO}_2$ mesoporous ternary systems supported in carbon cloth (CC) have been reported, with a specific capacitance of $1,931 \text{ F g}^{-1}$ at a current density of 0.8 A g^{-1} and a retention of capacitance of 91.2% at 6 A g^{-1} after 6,000 charge–discharge cycles in $\text{KOH } 6 \text{ mol L}^{-1}$. This high capacitance is due to the ternary composite in a 3D porous structure that intensifies electroactive area and improves ion transport [32]. Another ternary system composed of $\text{PANI}/\text{MnO}_2/\text{carbon nanofibers}$ presented a stability of 91% after 1,000 charge–discharge cycles and a specific capacitance of 289 F g^{-1} [61]. Furthermore, $\alpha\text{-MnO}_2$ nanoparticles deposited on platinum electrodes in the form of films have shown specific capacitances of $1,380 \text{ F g}^{-1}$, which is higher than the theoretical value ($\sim 1,370 \text{ F g}^{-1}$) [23].

2.3 Vanadium oxide

Vanadium oxide has several oxidation states from 0 to +5 to form VO_2 , V_2O_3 , and V_2O_5 [62]. Depending on the physical and chemical conditions such as temperature, pressure, and medium (acidic or basic solution), it is possible to reduce V_2O_5 to VO_2 (oxidation state from +5 to +4) [63,64]. V_2O_5 is the most studied oxide and has been used in electrodes for ion batteries (Li^+ , Na^+ , and Mg^{2+}) [65,66]. In addition, V_2O_5 has been proposed in the development of SCs due to its high specific capacitance and low acquisition cost. The orthorhombic phase of V_2O_5 makes it a promising material for energy storage applications due to its high ion storage capacitance. V_2O_5 has an

n-type conductivity and is the most stable among all vanadium oxides, reaching a melting point of 685°C [64]. The pseudocapacitive nature of V_2O_5 is due to the processes of intercalation that occurs within its structure, inducing distortions in its morphology and surface chemistry, as shown in the following reaction [67]:

The pseudocapacitive behavior is mainly attributed to its structure in the form of 2D layers and its complex 3D structure where interconnected channels are formed. These channels facilitate a rapid diffusion of electrolytic ions. The pseudocapacitive process in V_2O_5 in aqueous and organic electrolytes is well known due to its structural stability in these media and the use of large windows potential [68]. In theory, a monolayer of V_2O_5 , according to reaction (6), participates in the adsorption process of ions from the electrolytic solution, which leads to a maximum theoretical capacitance of 883.3 F g^{-1} in a working potential range of 1.2 V [69]. Likewise, intercalation processes depend on porosity and oxide morphological structure. Zhu *et al.* [25] compared various structures of V_2O_5 crystalline nanoparticles in the form of bulk, stacked, and 3D (Figure 6a–c) and demonstrated higher electrochemical efficiency for complex 3D structures (Figure 6c). This increase in electrochemical efficiency (specific capacitance, power density, and energy density) is associated with the higher surface area (about $133 \text{ m}^2 \text{ g}^{-1}$) than other structures. Furthermore, according to the diffraction results, a crystalline phase of the bulk structure with planes at (001), (003), (004), (005), (006), and (007) was observed. However, 3D structure only showed planes at (001), (003), and (004) with preferred orientation at (001). As a result, the high surface area for 3D V_2O_5 was obtained as a consequence of the channel formed by 2D thin sheets of V_2O_5 . This structure improved the diffusion of ions, resulting in a capacitance of 451 F g^{-1} higher than stacked V_2O_5 (314 F g^{-1}) and bulk V_2O_5 (108 F g^{-1}), all of them measured at a current density of 0.5 A g^{-1} in $\text{Na}_2\text{SO}_4 \text{ } 1 \text{ mol L}^{-1}$ (Figure 6d–g) [25].

In general, homogeneous amorphous oxides have a lower energy loss than crystalline oxides since they present channels that increase the ionic diffusion [70]. The optimization of V_2O_5 capacitance is dependent on the morphology. Qian *et al.* [71] reported the synthesis of different morphologies composed by crystalline V_2O_5 such as nanowire, flower-like flakes, and curly bundled nanowires. 1D V_2O_5 nanowires showed a high capacitance of 349 F g^{-1} with a surface area of $123 \text{ m}^2 \text{ g}^{-1}$; however, this material presented a poor capacitance retention of 27.6%

Figure 6: FESEM images of V_2O_5 : (a) commercially available bulk, (b) staked films, and (c) 3D architecture constructed from (b). Electrochemical performance of 3D V_2O_5 , staked films, and bulk for supercapacitors: (d) specific capacitances calculated from the cyclic voltammetry curves, (e) galvanostatic charge/discharge at a current density of 0.5 $A g^{-1}$ in the range of -1.0 to $+1.0$ V in Na_2SO_4 1 mol L^{-1} aqueous solution, (f) specific capacitances calculated from galvanostatic charge/discharge with various current densities and (g) power density and energy density of V_2O_5 3D architecture, staked film, and bulk electrodes [25].

after 200 charge and discharge cycles. Likewise, in the case of hydrated V_2O_5 curly bundled nanowires after cycling, there was an increase in 42 to 127 $F g^{-1}$ due to the presence of nanopores in its structure [71]. Furthermore, Zheng et al. [72] reported the synthesis of microstructures in the shape of a butterfly-like, rhombohedral, and a flower-like V_2O_5 with capacitances of 556, 641, and 609 $F g^{-1}$, respectively, at 0.5 $A g^{-1}$ in $LiClO_4$ 1.0 mol L^{-1} (Figure 7a–d). Also, these microstructures were formed by a crystalline phase of V_2O_5 with an orthorhombic structure. Likewise, the high capacitance was mainly

attributed to the V_2O_5 rhombohedral structure, explained by its simple morphology, which induces easy surface polarization at low electrolyte concentrations. Conversely, butterfly-like and flower-like V_2O_5 structures were polarized at higher electrolyte concentrations. In addition, electrochemical impedance spectroscopy showed resistivities of 1.22, 1.17, and 0.76 Ω for butterfly-like, flower-like, and rhombohedral structures, respectively. These results indicate a rapid diffusion of ions and an increase in capacitive values for V_2O_5 of the rhombohedral structure. Also, butterfly-like, flower-like, and

rhombohedral structures showed a capacitive retention of 132.6, 70.4, and 119.8% after 2,000 charge and discharge cycles, respectively (Figure 7e). The increase in the capacitance during the cycling process is attributed to the porosity of the material [72].

Previous reports had shown that some V_2O_5 -based materials present intrinsic limitations such as low conductivity, loss of mass due to the formation of soluble species during extensive charge and discharge processes, affecting its morphology and crystal structure and resulting in serious degradation problems [73]. Several strategies have been studied to improve the electrochemical properties of V_2O_5 , one of these is to modify the structure by generating oxygen vacancies through the chemical reduction caused by the oxidative polymerization of conductive polymers [68], also improving its intrinsic conductivity and pseudocapacitive charge storage kinetics [74]. Bi *et al.* [74] used the vapor phase polymerization method to synthesize V_2O_5 /poly(3,4-ethylenedioxythiophene) with oxygen vacancy gradient (G- V_2O_5 /PEDOT). G- V_2O_5 /PEDOT presented a capacitance of 614 F g^{-1} at a current density of 0.5 A g^{-1} using $1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$. Moreover, crystallographic results of VOx showed an

amorphous structure that is attributed to the oxygen vacancies of V_2O_5 and PEDOT. These vacancies generate vanadium oxidation states of V^{4+} and V^{3+} on the material surface, facilitating charge transfer kinetics with a capacitance retention of 122% after 50,000 cycles. HRTEM microscopy revealed that the core nanoparticles corresponded to a crystalline phase.

Furthermore, the insertion of V_2O_5 nanostructures in carbonaceous matrices (such as nanowires, nanofibers, and nanotubes) generates a synergistic effect between pseudocapacitive properties and the electrochemical double layer [75]. For example, Panigrahi *et al.* [49] developed a composite material from activated carbon fabric (ACF) as a support and obtained a flexible network of V_2O_5 @ACF. This composite showed a specific capacitance of $1,098 \text{ F g}^{-1}$ at 5 mV s^{-1} in K_2SO_4 0.5 mol L^{-1} . This high capacitance is due to the carbonaceous material porous structure, which promotes the dispersion and increment of electroactive sites of V_2O_5 nanoparticles. The diffraction pattern of this flexible 3D carbon network presented a broad peak at 25.75° and small peak at 43.42° , corresponding to a low crystalline order of hexagonal graphite structure. Meanwhile, V_2O_5 showed a highly crystalline diffraction planes

Figure 7: SEM images of (a) butterfly-like, (b) rhombohedral, and (c) flower-like V_2O_5 . Electrochemical performance of butterfly-like, rhombohedral, and flower-like V_2O_5 : (d) specific capacitances of V_2O_5 with different morphologies calculated from GCD curves at different current densities and (e) cycling performance of V_2O_5 with different morphologies collected at 100 mV s^{-1} [72].

at (110), corresponding to an orthorhombic structure. The composite showed a retention capacity of 92% after 10,000 galvanostatic charge–discharge cycles at 15 A g^{−1} [49].

Another important tendency is the design of binary and ternary oxides with improved electrochemical properties, especially oxides with higher conductivity, stability, energy, and power density [76]. The binary and ternary oxides compounds are interesting due to the synergy of metal atoms with different oxidation states, improving the properties such as electronic conductivity, structure stability, ion diffusion rate, electrochemical activity, and high sites active [77]. Zhang et al. [33] synthesized 3D nanoroses of Co₃V₂O₈ and 2D nanoplates of NiCo₂V₂O₈ by the solvothermal method (Figure 8a and b) and obtained surface areas of 112.97 and 131.76 m² g^{−1}, respectively. Co₃V₂O₈ and NiCo₂V₂O₈ oxides showed an orthorhombic phase with a slight distortion in the unit cell of NiCo₂V₂O₈ due to Ni ion insertion within the Co₃V₂O₈. Moreover, when Ni is added an increment of the capacitive current is observed (Figure 8c). The specific capacitances obtained were 371 and 1,098.9 F g^{−1}, respectively, at 1 A g^{−1} in KOH 2.0 mol L^{−1} (Figure 8d). The rate capability shown an increment of the pseudocapacitance due to Ni presence (Figure 8e). Furthermore, both oxides demonstrated good capacitive retention of 89.6 and 68% after 7,000 charge and discharge cycles at 4 A g^{−1} (Figure 8f). This decrease in capacitance retention of ternary oxide during cycling is influenced by the distortion caused by the substitution of Ni ion in the Co₃V₂O₈ structure, which shows greater structural instability.

Other interesting results were obtained by adding carbonaceous materials in hybrid composites of binary or ternary oxides, improving the electrical conductivity and the mechanical properties, as is the case of the thin layers of Co₃V₂O₈/Ni₃V₂O₈ adsorbed on binder-free porous carbon nanofibers. This material presented a synergistic behavior among Co, V, Ni, and porous carbon, which improves the diffusion and migration of ions, and obtained a specific capacitance of 1,731 F g^{−1} at a current density of 1.0 A g^{−1} in 3.0 mol L^{−1} KOH with 88.5% capacitance retention after 3,000 cycles [34]. The use of carbon cloth as support of Ni–V nanosheets also improves the flexibility and mechanical properties, showing a high specific capacitance of 2,790 F g^{−1} at 1.0 A g^{−1} in KOH 2.0 mol L^{−1} [78].

According to the aforementioned studies, a strong relationship has been observed between parameters such as crystallite sizes, morphology of the nanostructures, and their obtained capacitances. These results are mainly due to the direct influence of the capacitance with surface area and electroactive sites at the electrode–electrolyte interface. Apart from that, binary and ternary oxides

showed a synergy for the metals present in the structure, generating several redox centers. The evidence from this study suggests a certain influence of crystallinity on the structure stability during charge and discharge processes. In addition, the substitution of a metal in the structure alters the crystal lattice decreasing the stability after the charge–discharge process.

2.4 Cobalt oxide

Co₃O₄ has a cubic structure formed by two oxidation states of cobalt, and Co²⁺ and Co³⁺ present tetrahedral and octahedral coordination with the oxygen atoms, respectively (Figure 9) [79,80]. Likewise, Co₃O₄ has a large theoretical specific capacitance of about 3,560 F g^{−1} [26]. In addition, cobalt oxide is harmless, is eco-friendly, and has a low acquisition cost [46,72,81]. Reactions produced between Co₃O₄ electrodes and alkaline electrolytes such as KOH can be expressed as shown in equations (7) and (8):

The oxidation mechanism of different cobalt compounds presents intermediate reactions involving cobalt hydroxides, oxyhydroxides, and others. These intermediate reactions are crucial factors to know the electrochemical and thermal stability of Co₃O₄ electrodes [26]. However, the capacitance and the stability while cycling are limited by the structural rigidity and low conductivity of these electrodes [57]. To overcome these limitations, various studies aim the control of Co₃O₄ morphology to increase the surface area. Different morphologies have been studied, such as nanoparticles, nanorods [82,83], nanowires [84], nanowires [85], nanosheets [86], hollow nanosheets [87], and nanoflowers [88]. For example, Co₃O₄ nanowires on nickel foam reach a specific capacitance of 1,160 F g^{−1} at 2.0 A g^{−1} and a retention of 90.6% after 5,000 cycles (performed at 8 A g^{−1}) [89].

Wang et al. synthesized structured nanonetworks of crystalline Co₃O₄ in 3D via heterogeneous precipitation method, which reported a specific capacitance of 820 F g^{−1} at 5 mV s^{−1} using KOH 6 mol L^{−1} showing a capacitance retention of 90.2% after 1,000 of charge and discharge cycles [90]. Liu et al. [91] synthesized Co₃O₄ nanorods in the 1D via hydrothermal method showing a capacitance of 655 F g^{−1} at 0.5 A g^{−1} in KOH 1.0 mol L^{−1}. This increase in capacitance is related to the high crystallinity rod-like structure of Co₃O₄ nanorods [92]. Liu et al. [91] obtained

Figure 8: Scanning electron microscopy (SEM) image of (a) $\text{Co}_3\text{V}_2\text{O}_8$ (CVO) with nanorose structures and (b) $\text{NiCo}_2\text{V}_2\text{O}_8$ (CNVO) with nanoplate structures. Electrochemical performance characterization of porous 3D $\text{Co}_3\text{V}_2\text{O}_8$ nanoroses and 2D $\text{NiCo}_2\text{V}_2\text{O}_8$ nanoplates: (c) CV curves of $\text{Co}_3\text{V}_2\text{O}_8$ nanoroses and $\text{NiCo}_2\text{V}_2\text{O}_8$ nanoplates modified electrode at scan rate of 5 mV s⁻¹. (d) The corresponding galvanostatic charge-discharge curves at a current density of 1 A g^{-1} . (e) Capacitance retention rate as a function of current density. (f) Cycling performance of $\text{Co}_3\text{V}_2\text{O}_8$ and $\text{NiCo}_2\text{V}_2\text{O}_8$ at a constant current density of 4 A g^{-1} for 7,000 cycles [33].

core-shell type mesoporous nanospheres of crystalline Co_3O_4 by the solvothermal method, showing values of 837.7 F g^{-1} at 1.0 A g^{-1} and a good capacitance retention of 87% after 2,000 cycles at 5.0 A g^{-1} . The authors attribute the high capacitance to the type of mesoporous core-shell structure. Similarly, Co_3O_4 @CoS composites with core shell

morphology present a specific capacitance of 1,658 F g^{-1} at 1.0 A g^{-1} and a capacitive retention of 92% after 10,000 cycles. A crystalline cubic phase of Co_3O_4 was observed by X-ray diffraction. The authors did not detect a CoS crystalline phase due to its lower concentration localized on the core shell structure [93].

Figure 9: Cubic structure of Co_3O_4 , showing cobalt ions Co^{2+} and Co^{3+} that shows tetrahedral and octahedral coordinates with oxygen ions, respectively [80].

Besides, many authors report that the insertion of carbonaceous materials such as graphene in composites improves conductivity. Because of that, Naveen et al. [94] synthesized Co_3O_4 spinels structure on graphene nanospheres and thereby obtained a specific capacitance of 650 F g^{-1} at 5 mV s^{-1} in $1 \text{ KOH } 1.0 \text{ mol L}^{-1}$ and a capacitance retention of 92% after 1,000 cycles. Development of binary oxide electrodes formed by crystalline NiCo_2O_4 (cubic structure with $Fd3m$ space group) composites on activated carbon also increases notably the capacitance and conductivity due to the redox pairs of $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{2+}$. Xu et al. [35] showed that these composites reach specific capacitances of 273.5 F g^{-1} at 1.0 A g^{-1} in $\text{KOH } 6.0 \text{ mol L}^{-1}$ giving a capacitance retention of 96%

after 3,000 cycles. The influence of the mesoporous structure of Co_3O_4 in electrochemical performance has also been evaluated. Qiu et al. [57] used a thermal decomposition method, which demonstrated a favorable growth of mesoporous nanocrystalline Co_3O_4 on nanosheets of reduced graphene oxide (NOGR). These materials showed a capacitance of $1,085.6 \text{ F g}^{-1}$ at 2.0 A g^{-1} in $2 \text{ mol L}^{-1} \text{ KOH}$, resulting in a capacitance retention of 82.7% after 10,000 cycles. Sun et al. used biomass-derived activated carbon to obtain carbon- Co_3O_4 composites, and in this study, an increase in capacitance and conductivity of the material was observed. The authors used the hydrothermal synthesis method, followed by a calcination at 400°C where octahedral nanostructures composed by crystalline cubic phase of Co_3O_4 were supported on cotton-derived mesoporous carbon microtubes (Figure 10a–f). These composites showed a capacitance of 284.2 F g^{-1} at 1.0 A g^{-1} in $\text{KOH } 6.0 \text{ mol L}^{-1}$, and a capacitance retention of 91.95% was also observed after 3,000 cycles [95]. Obodo et al. [96] used the hydrothermal method to synthesize crystalline nanoparticles of Co_3O_4 and MnO_2 (30 nm of crystallite size) supported in graphene oxide ($\text{Co}_3\text{O}_4/\text{MnO}_2@\text{GO}$). The composite had a flake-like structure. The electrodes produced by these composites reached specific capacitance of $1,518 \text{ F g}^{-1}$ at 10 mV s^{-1} in $\text{Na}_2\text{SO}_4 \text{ } 1 \text{ mol L}^{-1}$. Besides, Table 1 summarizes the most used TMO for the manufacture of electrodes in supercapacitor systems.

Figure 10: SEM images of Co_3O_4 nanostructures: (a) cotton fibers, preparation of mesoporous carbon microtubes from cotton fibers previously calcined at $T = 400^\circ\text{C}$ for (b) 2 h and (c) 3 h; (d) unsupported Co_3O_4 nanostructures. TEM images: (e) in low magnification and (f) in high resolution (HRTEM), showing the composite formed by the Co_3O_4 nanostructures supported in the mesoporous carbon nanotubes previously calcined at $T = 400^\circ\text{C}$ for 2 h [99].

Table 1: Some transition metal oxides and their electrochemical parameters for application in supercapacitors

Material	C ($F g^{-1}$)	i ($A g^{-1}$)	Electrolyte	Cycles	Capacitance retention (%)	References
MnO ₂ /C	258	1.0	Na ₂ SO ₄ 0.5 mol L ⁻¹	10,000	93	[60]
PANI/MnO ₂ /FC	289	5.0	H ₂ SO ₄ 1.0 mol L ⁻¹	1,000	91	[61]
3D-V ₂ O ₅	1,098	5.0	K ₂ SO ₄ 1.0 mol L ⁻¹	10,000	92	[49]
WO ₃ -V ₂ O ₅	173	1.0	KOH 6.0 mol L ⁻¹	5,000	99	[98]
Nanoplates 2D NiCo ₂ V ₂ O ₈	1,098.9	4.0	KOH 2.0 mol L ⁻¹	7,000	68	[33]
Co ₃ V ₂ O ₈ -Ni ₃ V ₂ O ₈ @NF-C	1,731	1.0	KOH 3.0 mol L ⁻¹	3,000	88.5	[99]
Carbon cloth/nanosheets of Ni-V	2,790	1.0	KOH 2.0 mol L ⁻¹	2,000	75	[100]
Co ₃ O ₄ @CoS	1,658	1.0	KOH 6.0 mol L ⁻¹	10,000	92	[93]
Co ₃ O ₄ /Ni	1,060	1.0	KOH 6.0 mol L ⁻¹	5,000	99	[101]
Hollow nanonetwork 3D Co ₃ O ₄	820	5.0	KOH 6.0 mol L ⁻¹	1,000	90.2	[90]
Co ₃ O ₄ nanorods	655	0.5	KOH 1.0 mol L ⁻¹	1,000	82.7	[92]
Mesoporous Co ₃ O ₄ nanospheres	837.7	1.0	KOH 2.0 mol L ⁻¹	2,000	87	[91]
Co ₃ O ₄ nanoparticles@graphene nanospheres	650	5.0	KOH 1.0 mol L ⁻¹	1,000	92	[102]
Activated carbon/NiCo ₂ O ₄	273	1.0	KOH 6.0 mol L ⁻¹	3,000	96	[35]
Co ₃ O ₄ nanoparticles/NOGR nanosheets	1,085.6	2.0	KOH 2.0 mol L ⁻¹	10,000	82.7	[57]
Carbon microtubes/Octahedral Co ₃ O ₄ nanocrystals	284.2	1.0	KOH 6.0 mol L ⁻¹	3,000	91.95	[95]

C is the specific capacitance ($F g^{-1}$), i is the current density ($A g^{-1}$), and ξ is the efficiency or capacitive retention (%).

Finally, all of these works show excellent capacitive results using nanoparticles composed of unique crystalline phases of Co₃O₄ with the FCC structure (space group *Fd3m*) [97]. For example, Liu et al. [91] showed that a crystalline structure of Co₃O₄ in core-shell shape produced a higher specific capacitance than other structures already discussed. Likewise, if these Co₃O₄ core-shell structures are covered by small amounts of CoS, the specific capacitance obtained is enhanced, as shown by Lu et al. [93]. In addition, Co₃O₄ crystalline phase also improved the electrochemical stability after charge-discharge cycles as shown by Zhang et al. [89]. Therefore, the FCC crystalline phase of Co₃O₄ is a promising material for the development of high-capacitive and low-cost electrodes for energy storage.

3 Conclusions and key insights

Metal oxides with supercapacitive behavior provide a variety of electrode materials that means obtaining high specific capacitance in devices. This study has been focused on the understanding and development of these materials in different configurations. In this context, the mechanisms of energy storage for RuO₂, MnO₂, V₂O₅, and Co₃O₄ were well discussed. Among these mechanisms, this review described reversible redox reactions, the intercalation and deintercalation of electrolyte, and phase changing due to synthesis conditions or different crystalline structures.

RuO₂ presents a mechanism based on the interaction of electrode-electrolyte, which depends on the solution

media to produce reversible redox reactions. Related to manganese oxide, the stored energy depends on intercalation and deintercalation of electrolyte due to different oxide phases. In the case of vanadium oxide, the intercalation and deintercalation of electrolyte is the predominating mechanism due to the complex 3D structure. The mechanism for cobalt oxide is based on reversible redox reactions that involve different intermediate species. The addition of other metallic oxides or metals generate the increase of electroactive sites, multiple valences, porosity, conductivity, and electrochemical stability, which create composites with better electrochemical properties. In this sense, the addition of carbon supports increases the specific capacitance due to the insertion of another capacitive mechanism EDLC, and at the same time, the increase in conductivity and the greater stability in cycling make the contribution of these composites important.

Research efforts on understanding the energy storage mechanism are associated with the domain of key parameters such as crystalline structure, oxidation states, interaction electrode–electrolyte, morphology, and specific surface area, and all of these parameters directly relates to the electronic transport and stability of these materials. The new electrode configuration, which involves carbon materials, is due to its high specific surface area, TMO, conductivity, and dielectric properties, which leads to increase in specific capacitance and EDLC. Hence, the study of energy storage mechanisms on metal oxide is a key factor to improve the supercapacitor electrode and then to increase the efficiency of supercapacitor devices.

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