Review Article

Vanessa Quispe-Garrido, Gabriel Antonio Cerron-Calle, Antony Bazan-Aguilar, José G. Ruiz-Montoya, Elvis O. López, Angélica M. Baena-Moncada*

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

https://doi.org/10.1515/chem-2021-0059
received March 22, 2021; accepted May 13, 2021

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 (RuO2, MnO2, V2O5, and Co3O4) 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 (Wh 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].
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...
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, MnO₃, 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].

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

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, 1,300–2,200 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 $P4_{2}m/m$ and $P4\overline{3}$, respectively [41,42]. Besides, commonly a hydrated form of RuO$_2$·xH$_2$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):

\[
\text{RuO}_4(\text{OH})_y + \delta\text{H}^+ + \delta\text{e}^- \leftrightarrow \text{RuO}_x(\text{OH})_y \delta \quad (\delta = 2). \quad (1)
\]

\[
\text{RuO}_2 + \text{H}^+ + \text{e}^- \leftrightarrow \text{RuOOH}. \quad (2)
\]

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$^{3+}$ to Ru$^{4+}$ is observed. In the charge process, in the presence of alkaline electrolytes, RuO$_2$ is oxidized in various forms, from RuO$_2^{2-}$ and RuO$_2$ to RuO$_3$, 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$_3$O$_4$, and V$_2$O$_5$ 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$_2$O$_4$, CoFe$_2$O$_4$, CuCr$_2$O$_4$, and TbMn$_2$O$_5$ [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 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 ($X^+$ = 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]:

\[
\text{MnO}_2 + \text{H}^+ + \text{e}^- \leftrightarrow \text{MnOOH}. \quad (3)
\]

\[
\text{MnO}_2 + \text{X}^+ + \text{e}^- \leftrightarrow \text{MnOOX}. \quad (4)
\]

The second mechanism is based on the adsorption of metallic electrolyte cations on the surface of the MnO$_2$ electrode.

\[
\text{MnO}_2\text{surface} + \text{X}^+ + \text{e}^- \leftrightarrow (\text{MnO}_2\text{X}^+)\text{surface}. \quad (5)
\]

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 Na$_2$SO$_4$ 1.0 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 nm × 0.46 nm and 0.23 nm × 0.23 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
proposed. For example, Qiu et al. [57] electrodeposited different morphologies of MnO₂ 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 Na₂SO₄ 0.5 mol L⁻¹. Xia et al. [58] synthesized nanosheets of δ-MnO₂ 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 δ-MnO₂, and decreasing the resistance of charge transfer. Conversely, the size of the oxides and their composition with

**Figure 4:** Differences in the sizes of interatomic channels of the δ-MnO₂ and α-MnO₂ phases, and possible diffusions of Na⁺ ions in these channels [55].

**Figure 5:** Comparison of the electrochemical behavior between the α-MnO₂ and δ-MnO₂ 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 MnO$_2$@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 KOH 6 mol L$^{-1}$ as an electrolyte.

Furthermore, the addition of other oxides such as Cu$_2$O contributes to the pseudocapacitance of MnO$_2$. For example, Purushothaman et al. [31] electrodeposited consecutively CuMnO$_2$ and Cu$_2$O (Cu$_2$O@CuMnO$_2$@Cu) and obtained a specific capacitance of 257 F g$^{-1}$ at the scan rate of 5 mV s$^{-1}$ in Na$_2$SO$_4$ 0.1 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 MnNiCoO$_2$@MnO$_2$ mesoporous ternary systems supported in carbon cloth (CC) have been reported, with a specific capacitance of 1,931 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 KOH 6 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 PANI/MnO$_2$/carbon nanofibers presented a stability of 91% after 1,000 charge–discharge cycles and a specific capacitance of 289 F g$^{-1}$ [61]. Furthermore, α-MnO$_2$ nanoparticles deposited on platinum electrodes in the form of films have shown specific capacitances of 1,380 F g$^{-1}$, which is higher than the theoretical value (∼1,370 F g$^{-1}$) [23].

2.3 Vanadium oxide

Vanadium oxide has several oxidation states from 0 to +5 to form VO$_2$, V$_2$O$_3$, and V$_2$O$_5$ [62]. Depending on the physical and chemical conditions such as temperature, pressure, and medium (acidic or basic solution), it is possible to reduce V$_2$O$_5$ to VO$_2$ (oxidation state from +5 to +4) [63,64]. V$_2$O$_5$ is the most studied oxide and has been used in electrodes for ion batteries (Li$^+$, Na$^+$, and Mg$^{2+}$) [65,66]. In addition, V$_2$O$_5$ has been proposed in the development of SCs due to its high specific capacitance and low acquisition cost. The orthorhombic phase of V$_2$O$_5$ makes it a promising material for energy storage applications due to its high ion storage capacitance. V$_2$O$_5$ 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$_2$O$_5$ 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]:

$$\text{(V}_2\text{O}_5)_{\text{surface}} + x\text{M}^+ + xe^- \leftrightarrow (\text{M},\text{V}_2\text{O}_5)_{\text{surface}}.$$  (6)

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$_2$O$_5$ 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$_2$O$_5$, 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$_2$O$_5$ 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 m$^2$ 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$_2$O$_5$ was obtained as a consequence of the channel formed by 2D thin sheets of V$_2$O$_5$. This structure improved the diffusion of ions, resulting in a capacitance of 451 F g$^{-1}$ higher than stacked V$_2$O$_5$ (314 F g$^{-1}$) and bulk V$_2$O$_5$ (108 F g$^{-1}$), all of them measured at a current density of 0.5 A g$^{-1}$ in Na$_2$SO$_4$ 1 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$_2$O$_5$ capacitance is dependent on the morphology. Qian et al. [71] reported the synthesis of different morphologies composed by crystalline V$_2$O$_5$, such as nanowire, flower-like flakes, and curly bundled nanowires. 1D V$_2$O$_5$ nanowires showed a high capacitance of 349 F g$^{-1}$ with a surface area of 123 m$^2$ g$^{-1}$; however, this material presented a poor capacitance retention of 27.6%
after 200 charge and discharge cycles. Likewise, in the case of hydrated V2O5 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 V2O5 with capacitances of 556, 641, and 609 F g⁻¹, respectively, at 0.5 A g⁻¹ in LiClO4 1.0 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 V2O5 3D architecture, stacked film, and bulk electrodes [25].

Figure 6: FESEM images of V2O5: (a) commercially available bulk, (b) staked films, and (c) 3D architecture constructed from (b). Electrochemical performance of 3D V2O5, 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 Na2SO4 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 V2O5 3D architecture, stacked film, and bulk electrodes [25].

These results indicate a rapid diffusion of ions and an increase in capacitive values for V2O5 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 V₂O₅-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 V₂O₅, 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 V₂O₅/poly(3,4-ethylenedioxythiophene) with oxygen vacancy gradient (G-V₂O₅/PEDOT). G-V₂O₅/PEDOT presented a capacitance of 614 F g⁻¹ at a current density of 0.5 A g⁻¹ using 1 mol L⁻¹ Na₂SO₄. Moreover, crystallographic results of VOₓ showed an amorphous structure that is attributed to the oxygen vacancies of V₂O₅ and PEDOT. These vacancies generate vanadium oxidation states of V⁴⁺ and V⁵⁺ 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 V₂O₅ 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 V₂O₅@ACF. This composite showed a specific capacitance of 1,098 F g⁻¹ at 5 mV s⁻¹ in K₂SO₄ 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 V₂O₅ 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, V₂O₅ showed a highly crystalline diffraction planes

Figure 7: SEM images of (a) butterfly-like, (b) rhombohedral, and (e) flower-like V₂O₅. Electrochemical performance of butterfly-like, rhombohedral, and flower-like V₂O₅: (d) specific capacitances of V₂O₅ with different morphologies calculated from GCD curves at different current densities and (e) cycling performance of V₂O₅ with different morphologies collected at 100 mV s⁻¹ [72].
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

$\text{Co}_3\text{O}_4$ has a cubic structure formed by two oxidation states of cobalt, and $\text{Co}^{2+}$ and $\text{Co}^{3+}$ present tetrahedral and octahedral coordination with the oxygen atoms, respectively (Figure 9) [79,80]. Likewise, $\text{Co}_3\text{O}_4$ 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 $\text{Co}_3\text{O}_4$ electrodes and alkaline electrolytes such as KOH can be expressed as shown in equations (7) and (8):

\[
\text{Co}_3\text{O}_4 + 6\text{H}_2\text{O} + 3\text{e}^- \leftrightarrow 3\text{CoOOH} + 3\text{H}_3\text{O}^+.
\]

(7)

\[
\text{CoOOH} + 2\text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^-.
\]

(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 $\text{Co}_3\text{O}_4$ 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 $\text{Co}_3\text{O}_4$ 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, $\text{Co}_3\text{O}_4$ 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 $\text{Co}_3\text{O}_4$ 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 $\text{Co}_3\text{O}_4$ 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 $\text{Co}_3\text{O}_4$ nanorods [92]. Liu et al. [91] obtained
core-shell type mesoporous nanospheres of crystalline \( \text{Co}_3\text{O}_4 \) 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, \( \text{Co}_3\text{O}_4@\text{CoS} \) 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 \( \text{Co}_3\text{O}_4 \) 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].
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 Co₃O₄ spinel structure on graphene nanospheres and thereby obtained a specific capacitance of 650 F g⁻¹ at 5 mV s⁻¹ in 1 KOH 1.0 mol L⁻¹ and a capacitance retention of 92% after 1,000 cycles. Development of binary oxide electrodes formed by crystalline NiCo₂O₄ (cubic structure with Fd3m space group) composites on activated carbon also increases notably the capacitance and conductivity due to the redox pairs of Co²⁺/Co³⁺ and Ni³⁺/Ni²⁺. Xu et al. [35] showed that these composites reach specific capacitances of 273.5 F g⁻¹ at 1.0 A g⁻¹ in KOH 6.0 mol L⁻¹ giving a capacitance retention of 96% after 3,000 cycles. The influence of the mesoporous structure of Co₃O₄ in electrochemical performance has also been evaluated. Qiu et al. [57] used a thermal decomposition method, which demonstrated a favorable growth of mesoporous nanocrystalline Co₃O₄ on nanosheets of reduced graphene oxide (NOGR). These materials showed a capacitance of 1,085.6 F g⁻¹ at 2.0 A g⁻¹ in 2 mol L⁻¹ KOH, resulting in a capacitance retention of 82.7% after 10,000 cycles. Sun et al. used biomass-derived activated carbon to obtain carbon–Co₃O₄ 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 Co₃O₄ 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 KOH 6.0 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 Co₃O₄ and MnO₂ (30 nm of crystallite size) supported in graphene oxide (Co₃O₄/MnO₂@GO). The composite had a flake-like structure. The electrodes produced by these composites reached specific capacitance of 1,518 F g⁻¹ at 10 mV s⁻¹ in Na₂SO₄ 1 mol L⁻¹. Besides, Table 1 summarizes the most used TMO for the manufacture of electrodes in supercapacitor systems.

**Figure 9:** Cubic structure of Co₃O₄, showing cobalt ions Co²⁺ and Co³⁺ that shows tetrahedral and octahedral coordinates with oxygen ions, respectively [80].

**Figure 10:** SEM images of Co₃O₄ nanostructures: (a) cotton fibers, preparation of mesoporous carbon microtubes from cotton fibers previously calcined at T = 400°C for (b) 2 h and (c) 3 h; (d) unsupported Co₃O₄ nanostructures. TEM images: (e) in low magnification and (f) in high resolution (HRTEM), showing the composite formed by the Co₃O₄ nanostructures supported in the mesoporous carbon nanotubes previously calcined at T = 400°C for 2 h [99].
Finally, all of these works show excellent capacitive results using nanoparticles composed of unique crystalline phases of Co$_3$O$_4$ with the FCC structure (space group Fd$3$m) [97]. For example, Liu et al. [91] showed that a crystalline structure of Co$_3$O$_4$ in core-shell shape produced a higher specific capacitance than other structures already discussed. Likewise, if these Co$_3$O$_4$ 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, Co$_3$O$_4$ crystalline phase also improved the electrochemical stability after charge–discharge cycles as shown by Zhang et al. [89]. Therefore, the FCC crystalline phase of Co$_3$O$_4$ 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 RuO$_2$, MnO$_2$, V$_2$O$_5$, and Co$_3$O$_4$ 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.

RuO$_2$ 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 dominating 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.

Acknowledgments: The authors wish to thank the Peruvian government agencies CONCYTEC and FONDECYT/World Bank.

Funding information: The Peruvian government agencies CONCYTEC and FONDECYT/World Bank (contract 026-2019 FONDECYT-BM-INC.INV).

Author contributions: Vanessa Quispe-Garrido: writing – original draft; Gabriel Antonio Cerron-Calle: writing – original draft; Antony Bazan-Aguilar: writing – original draft; José G. Ruiz-Montoya: writing – review and editing; Elvis O. López: writing – review and editing; Angélica M. Baena-Moncada: writing – review and editing – project administration-supervision.

Conflict of interest: The authors state no conflict of interest.

Data availability statement: All data generated or analyzed during this study are included in this published article.

Ethical approval: The conducted research is not related to either human or animal use.

References

[1] Nejat P, Jomehzadeh F, Taheri MM, Gohari M, Abd Majid MZ. A global review of energy consumption, CO2 emissions and policy in the residential sector (with an overview of the top ten CO2 emitting countries). Renew Sustain Energy Rev. 2015;43:843–62.
[2] Chang C-P, Zhang LW. Do natural disasters increase financial risks? An empirical analysis. Bul Ekon Monet Dan Perbank. 2020;23:61–86.
[3] Center BP. Annual Energy Outlook 2020. Washington, DC: Energy Inf Adm; 2020.
[4] Viviescas C, Lima L, Diuana FA, Vasquez E, Ludoviique C, Silva GN, et al. Contribution of variable renewable energy to increase energy security in Latin America: complementarity and climate change impacts on wind and solar resources. Renew Sustain Energy Rev. 2019 Oct;113:109232.
[5] Oncel SS. Green energy engineering: opening a green way for the future. J Clean Prod. 2017;142:3095–100.
[6] Gao Z, Zhang Y, Song N, Li X. Biomass-derived renewable carbon materials for electrochemical energy storage. Mater Res Lett. 2017;5(2):69–88.
[7] Meng Q, Cai K, Chen Y, Chen L. Research progress on conducting polymer based supercapacitor electrode materials. Nano Energy. 2017;36(February):268–85.
[8] Holmberg S, Perebivosky A, Kulinsky L, Madou M. 3-D micro and nano technologies for improvements in electrochemical power devices. Micromachines. 2014;5(2):171–203.
[9] Wang J, Zhang X, Li Z, Ma Y, Ma L. Recent progress of biomass-derived carbon materials for supercapacitors. J Power Sources. 2020;451(1January):227794.
[10] Wentker M, Greenwood M, Asaba MC, Leker J. A raw material criticality and environmental impact assessment of state-of-the-art and post-lithium-ion cathode technologies. J Energy Storage. 2019 Dec;26:101022.
[11] Han X, Lu L, Zheng Y, Feng X, Li Z, Li J, et al. A review on the key issues of the lithium ion battery degradation among the whole life cycle. eTransportation. 2019 Aug;1:100005.
[12] Alif A, Rahman SM, Tasfiah Azad A, Zaini J, Islan MA, Azad AK. Advanced materials and technologies for hybrid supercapacitors for energy storage – a review. J Energy Storage. 2019;25(July):100852.
[13] Wang Y, Song Y, Xia Y. Electrochemical capacitors: mechanism, materials, systems, characterization and applications. Chem Soc Rev. 2016;45:5925–50.
[14] Gogotsi Y, Penner RM. Energy storage in nanomaterials – capacitive, pseudocapacitive, or battery-like? ACS Nano. 2018;12(3):2081–3.
[15] Muzaffar A, Ahamed MB, Deshmukh K, Thirumalai J. A review on recent advances in hybrid supercapacitors: design, fabrication and applications. Renew Sustain Energy Rev. 2019;101(October 2018):123–45.

[16] Mohd Abdah MAA, Azman NHN, Kulandaivelu S, Sulaiman Y. Review of the use of transition-metal-oxide and conducting polymer-based fibres for high-performance supercapacitors. Mater Des. 2020;186:108399.

[17] Muralee Gopi CVV, Vinodh R, Sambasivam S, Obaidat IM, Kim HJ. Recent progress of advanced energy storage materials for flexible and wearable supercapacitor: from design and development to applications. J Energy Storage. 2020;27(September 2019):101035.

[18] Saha S, Samanta P, Murmu NC, Kuila T. A review on the heterostructure nanomaterials for supercapacitor application. J Energy Storage. 2018;17:181–202.

[19] Moulson AJ, Herbert JM. Electroceramics: materials, properties, applications. 2nd ed. England: John Wiley & Sons; 2003.

[20] Shi X, Zheng S, Wu ZS, Bao X. Recent advances of graphene-based materials for high-performance and new-concept supercapacitors. J Energy Chem. 2018;27(1):25–42.

[21] Li J, Huang X, Cui L, Chen N, Qu L. Preparation and supercapacitor performance of assembled graphene fiber and foam. Prog Nat Sci Mater Int. 2016;26(3):212–20.

[22] Kate RS, Khalate SA, Deokate RJ. Overview of nanostructured metal oxides and pure nickel oxide (NiO) electrodes for supercapacitors: a review. J Alloy Compd. 2018;734:89–111.

[23] Toupin M, Brousse T, Bélanger D. Charge storage mechanism of MnO2 electrode used in aqueous electrochemical capacitor. Chem Mater. 2004;16(16):3184–90.

[24] Nwankwo MC, Nwanya AC, Agbagwu A, Ekwealor ABC, Ejikeme PM, Bucher R, et al. Electrochemical supercapacitive properties of SILAR-deposited Mn3O4 electrodes. Vacuum. 2018;158(July):206–14.

[25] Zhu J, Cao L, Wu Y, Gong Y, Liu Z, Hoster HE, et al. Building 3D structures of vanadium pentoxide nanosheets and application as electrodes in supercapacitors. Nano Lett. 2013;13(11):5408–13.

[26] Lee KK, Chin WS, Sow CH. Cobalt-based Compounds and composites as electrode materials for high-performance electrochemical capacitors. J Mater Chem A Mater Energy Sustain. 2014;2(16):2017–21.

[27] Liu CF, Liu YC, Yi TY, Hu CC. Carbon materials for high-voltage supercapacitors. Carbon. 2019;145:529–48.

[28] Nabi G, Raza W, Kamran MA, Alharbi T, Rafique M, Tahir MB, et al. Role of cerium-doping in CoFe2O4 electrodes for high performance supercapacitors. J Energy Storage. 2020;29:101652. Available from: https://www.sciencedirect.com/science/article/pii/S2352512X19318547.

[29] Shayan JS, Sadeghnia M, Sialat SOR, Ehsani A, Rezaei M, Omidi M. A novel route for electrosynthesis of CuCr2O4 nanocomposite with p-type conductive polymer as a high performance material for electrochemical supercapacitors. J Colloid Interface Sci. 2017;496:401–6. Available from: https://www.sciencedirect.com/science/article/pii/S0021979717301625.

[30] Saadeghi S, Mohammad Shiri H, Ehsani A, Oftadeh M. Electrosynthesis of high-purity TbMn2O5 nanoparticles and its nanocomposite with conjugated polymer: surface, density of state and electrochemical investigation. Solid State Sci. 2020;105:106227. Available from: https://www.sciencedirect.com/science/article/pii/S1293255820301540.

[31] Purushothaman S, Jeyasubramanian K, Muthuselvi M, Hikku GS. Cu2O nanosheets decorated CuMnO2 nanosphere electrodeposited on Cu foil as high-performance supercapacitor electrode. Mater Sci Semicond Process. 2021;121:105366. Available from: https://www.sciencedirect.com/science/article/pii/S1369800120313020.

[32] Tamaddoni Saray M, Hosseini H. Mesoporous MnNiCoO3@MnO2 core-shell nanowire/nanosheet arrays on flexible carbon cloth for high-performance supercapacitors. Electrochim Acta. 2016;222:505–17. Available from: https://www.sciencedirect.com/science/article/pii/S0013468616323349.

[33] Zhang J, Yuan B, Cui S, Zhang N, Wei J, Wang X, et al. Facile synthesis of 3D porous Co3V2O9 nanoropes and 2D NiCo2V2O8 nanoflakes for high performance supercapacitors and their electrocatalytic oxygen evolution reaction properties. Dalt Trans. 2017;46(10):3295–302.

[34] Hosseini H, Shahrokhsian S. Advanced binder-free electrode based on core–shell nanostructures of mesoporous Co3V2O8-Ni3V2O7 thin layers@porous carbon nanofibers for high-performance and flexible all-solid-state supercapacitors. Chem Eng J (Internet). 2018;341:10–26. Available from: https://www.sciencedirect.com/science/article/pii/S2358594718302158.

[35] Xu J, Liu F, Peng X, Li J, Yang Y, Jin D, et al. Hydrothermal synthesis of NiCo2O4/activated carbon composites for supercapacitor with enhanced cycle performance. ChemistrySelect. 2017;2(18):5189–95.

[36] Al Zoubi W, Kamil MP, Fatimah S, Nashrah N, Ko YG. Recent advances in hybrid organic-inorganic materials with spatial architecture for state-of-the-art applications. Prog Mater Sci. 2020;112:100663. Available from: https://www.sciencedirect.com/science/article/pii/S003810981930272X.

[37] Zhang J, Cui Y, Shan G. Metal oxide nanomaterials for pseudocapacitors. arXiv Prepr arXiv190501766. 2019.

[38] Hu Y, Wu Y, Wang J. High-performance energy storage: manganese-oxide-based electrode materials for energy storage applications: how close are we to the theoretical capacitance? (Adv. Mater. 47/2018). Adv Mater. 2018 Nov;1(30):47;1870364. Available from: https://doi.org/10.1002/adma.201807036.

[39] Maksooud MIAA, Fahim RA, Shalan AE, Abdk Elokodous M, Olojede SO, Osman AI, et al. Advanced materials and technologies for supercapacitors used in energy conversion and storage: a review. Environ Chem Lett. 2021;19:375–439.

[40] Jiang Y, Liu J. Definitions of pseudocapacitive materials: a brief review. Energy Environ Mater. 2019;2:30–7.

[41] Boman C.E. Refinement of the crystal structure of ruthenium dioxide. Acta Chem Scand. 1970;24(1):116–22.

[42] Haines J, Leger JM, Schmidt MW, Petitet JP, Pereira AS, Da Jornada JAH, et al. Structural characterisation of the Pa3-type, high pressure phase of ruthenium dioxide. J Phys Chem Solids. 1998;59(2):239–43.

[43] Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. Energy Environ Sci. 2014;7(5):1597–614.
[44] González A, Gokkolea E, Andoni J, Mysyk R. Review on supercapacitors: Technologies and materials. Renew Sustain Energy Rev. 2016;58:1189–206.

[45] Wang J-G, Kang F, Wei B. Engineering of MnO2-based nanocomposites for high-performance supercapacitors. Prog Mater Sci [Internet]. 2015;74:51–124. Available from: https://www.sciencedirect.com/science/article/pii/0079642515000390.

[46] Ma J, Wei H, Liu Y, Ren X, Li Y, Wang F, et al. Application of Co3O4-based materials in electrocatalytic hydrogen evolution reaction: a review. Int J Hydrog Energy [Internet]. 2020;45(41):21205–20. Available from: https://www.sciencedirect.com/science/article/pii/S0008622319321558.

[47] Iqbal N, Wang X, Ge J, Yu J, Kim H-Y, Al-Deyab SS, et al. Cobalt oxide nanoparticles embedded in flexible carbon nanofibers: attractive material for supercapacitor electrodes and CO2 adsorption. RSC Adv [Internet]. 2016;6(57):52171–9. doi: 10.1039/C6RA06077C.

[48] Xu L, Zhang L, Cheng B, Yu J. Rationally designed hierarchical NiCo2O4–C@Ni(OH)2 core-shell nanofibers for high performance supercapacitors. Carbon N Y. 2019;152:652–60. Available from: https://www.sciencedirect.com/science/article/pii/S0008622319306384.

[49] Panigrahi K, Howli P, Chattopadhyay KK. 3D network of V2O5 nanorods grown on V2O5 nanoribbon as high performance anode electrodes for flexible symmetric supercapacitor. Electrochim Acta. 2020;337:135701.

[50] Harsojo, Dolokaribui M, Prihandoko B, Priyono S, Subhan A, Lestaringinsih T. The effect of reduced graphene oxide on the activated carbon metal oxide supercapacitor. Mater Today Proc. 2019;13:181–6.

[51] Vimuna VM, Athira AR, Dinesh Babu KV, Xavier TS. Simultaneous stirring and microwave assisted synthesis of nanoflakes MnO2/rGO composite electrode material for symmetric supercapacitor with enhanced electrochemical performance. Diam Relat Mater. 2020;110:108129. Available from: https://www.sciencedirect.com/science/article/pii/S0925963520306828.

[52] Zhi M, Xiang C, Li J, Li M, Wu N. Nanostructured carbon–metal oxide composite electrodes for supercapacitors: a review. Nanoscale. 2013;5(1):72–88.

[53] Thackery MM. Manganese oxides for lithium batteries. Prog Solid State Chem. 1997;25(1):1–71. Available from: https://www.sciencedirect.com/science/article/pii/0079678697810035.

[54] Devaraj S, Mundianraiah N. Effect of crystallographic structure of MnO2 on its electrochemical capacitance properties. J Phys Chem C. 2008;112(14):4406–17.

[55] Li Y-Q, Shi X-M, Lang X-Y, Wen Z, Li J-C, Jiang Q. Remarkable improvements in volumetric energy and power of 3D MnO2 microsupercapacitors by tuning crystallographic structures. Adv Funct Mater. 2016 Mar 1;26(11):1830–9. Available from: doi: 10.1002/adfm.201504886.

[56] Wang T, Chen HC, Yu F, Zhao XS, Wang H. Boosting the cycling stability of transition metal compounds-based supercapacitors. Energy Storage Mater. 2019;16:545–73. Available from: https://www.sciencedirect.com/science/article/pii/S2405829718305294.

[57] Qiu D, Ma X, Zhang J, Zhao B, Lin Z. In situ synthesis of mesoporous Co3O4 nanorods anchored on reduced graphene oxide nanosheets as supercapacitor electrodes. Chem Phys Lett. 2018;710:188–92. Available from: https://www.sciencedirect.com/science/article/pii/S0009261418307188.

[58] Xia A, Wu Y, Yi J, Tan G, Ren H, Liu C. Synthesis of porous δ-MnO2 nanosheets and their supercapacitor performance. J Electroanal Chem. 2019;839:25–31. Available from: https://www.sciencedirect.com/science/article/pii/S1572667919305159.

[59] Feng W, Liu G, Wang P, Zhou J, Gu L, Chen L, et al. Template synthesis of a heterostructured MnO2@SnO2 hollow sphere composite for high asymmetric supercapacitor performance. ACS Appl Energy Mater. 2020;3(8):7284–93.

[60] Kong S, Jin B, Quan X, Zhang G, Guo X, Zhu Q, et al. MnO2 nanosheets decorated porous active carbon derived from wheat bran for high-performance asymmetric supercapacitor. J Electroanal Chem. 2019;850:131432.

[61] Dirican M, Yaniılmaz M, Asiri AM, Zhang X. Polyaniline/MnO2/porous carbon nanofiber electrodes for supercapacitors. J Electroanal Chem. 2020;861:113995. Available from: https://www.sciencedirect.com/science/article/pii/S1572667920301788.

[62] Wang T, Chen HC, Yu F, Zhao XS. Boosting the cycling stability of transition metal compounds-based supercapacitors. Energy Storage Mater. 2019;16:545–73.

[63] Ningyi J, Jinhua L, Chenglu L. Valence reduction process from sol–gel V2O5 to VO3 thin films. Appl Surf Sci. 2002;191(1):176–80. Available from: https://www.sciencedirect.com/science/article/pii/S016943320001800.

[64] Beke S. A review of the growth of V2O5 films from 1885 to 2010. Thin Solid Films. 2011;519(6):1761–71. Available from: https://www.sciencedirect.com/science/article/pii/S0040609010015373.

[65] Tanik R, Honma I. Mg secondary batteries using nano-crystalline V2O5. ECS Trans. 2017;75(22):25.

[66] Gao X-T, Zhu X-D, Le S-R, Yan D-J, Qu C-Y, Feng Y-J, et al. Boosting high-rate lithium storage of V2O5 nanowires by self-assembly on N-doped graphene nanosheets. ChemElectroChem. 2016 Nov 1;3(11):1730–6. doi: 10.1002/celc.201600305.

[67] Daubert JS, Lewis NP, Gotsch HN, Mundy JZ, Monroe DN, Dickey EC, et al. Effect of meso- and micro-porosity in carbon electrodes on atomic layer deposition of pseudocapacitive V2O5 for high performance supercapacitors. Chem Mater. 2015;27(19):6524–34.

[68] Qu Q, Zhu Y, Gao X, Wu Y. Core–shell structure of polypyrrole grown on V2O5 nanoribbon as high performance anode material for supercapacitors. Adv Energy Mater. 2012;2(8):950–5.

[69] Majumdar D, Mandal M, Bhattacharya SK. V2O5 and its carbon-based nanocomposites for supercapacitor applications. ChemElectroChem. 2019;6(6):1623–48.

[70] Uchaker E, Zheng YZ, Li S, Candelaria SL, Hu S, Cao GZ. Better than crystalline: amorphous vanadium oxide for sodium-ion batteries. J Mater Chem A. 2016;4(14):18208–14.

[71] Qian A, Zhuo K, Shin MS, Chun WW, Choi BN, Chung C. Surfactant effects on the morphology and pseudocapacitive behavior of V2O5·H2O. ChemSusChem. 2015;8(14):2399–406.

[72] Zheng J, Zhang Y, Hu T, Lv T, Meng C. New strategy for the morphology-controlled synthesis of V2O5 microcrystals with...
enhanced capacitance as battery-type supercapacitor electrodes. Cryst Growth Des. 2018;18(9):5365–76.

[73] Engstrom AM, Doyle FM. Exploring the cycle behavior of electrodoposited vanadium oxide electrochemical capacitor electrodes in various aqueous environments. J Power Sources. 2013;228:120–31.

[74] Bi W, Wu Y, Liu C, Wang J, Du Y, Gao G, et al. Gradient oxygen vacancies in V2O5/PEDOT nanocables for high-performance supercapacitors. ACS Appl Energy Mater. 2018;2(1):668–77.

[75] Lee S-M, Park Y-J, Kim J-H, Lee K. Effects of annealing on electrochemical performance in graphene/V2O5 supercapacitor. Appl Surf Sci. 2020;512:145626.

[76] Zhang Y, Li L, Su H, Huang W, Dong X. Binary metal oxide: advanced energy storage materials in supercapacitors. J Mater Chem A. 2015;3(4):1–53.

[77] González JM, da Silva MI, Toma HE, Angnes L, Martins PR, Araki K. Tridimensional nickel vanadium layered double hydroxides nanosheets grown on carbon cloth for high-performance flexible supercapacitor applications. Nanoscale Adv. 2019;1(6):2400–7.

[78] Tyagi A, Joshi MC, Agarwal K, Balasubramaniam B, Gupta RK. Three-dimensional nickel vanadium layered double hydroxide nanostructures grown on carbon cloth for high-performance flexible supercapacitor applications. J Mater Chem A. 2020;8(21):10534–70.

[79] Ke X, Cao J, Zheng M, Chen Y, Liu J, Ji G. Molten salt synthesis of single-crystal Co3O4 nanorods. Mater Lett. 2007;61(18):3901–3. Available from: https://www.sciencedirect.com/science/article/pii/S0167577X06015424.

[80] Ribeiro RAP, de Lazaro SR, Gracia L, Longo E, Andrés J. Theoretical approach for determining the relation between the morphology and surface magnetism of Co3O4. J Magn Magn Mater. 2018;453:262–7.

[81] Shi Y, Pan X, Li B, Zhao M, Pang H, Co3O4 and its composites for high-performance Li-ion batteries. Chem Eng J. 2018;342:427–46.

[82] Reddy BN, Deshagani S, Deepa M, Ghosal P. Effective pseudocapacitive charge storage/release by hybrids of poly(3,4-ethylenedioxythiophene) with Fe3O4 nanospheres or Co3O4 nanorods. Chem Eng J. 2018;334:1328–40. Available from: https://www.sciencedirect.com/science/article/pii/S1385894717319980.

[83] Obodo RM, Nwanya AC, Ekwealor ABC, Ahmad I, Zhao T, Osuji RU, et.al. Influence of pH and annealing on the optical and electrochemical properties of cobalt (II) oxide (Co3O4) thin films. Surf Interfaces. 2019;16(April):114–9.

[84] Yadav AA, Hunge YM, Mathe VL, Kulkarni SB. Photocatalytic degradation of salicylic acid using BaTiO3 photocatalyst under ultraviolet light illumination. J Mater Sci Mater Electron. 2018;29(17):15069–73.

[85] Yadav AA, Hunge YM, Kulkarni SB. Chemical synthesis of Co3O4 nanowires for symmetric supercapacitor device. J Mater Sci Mater Electron. 2018;29(19):16401–9.

[86] You Y, Zheng M, Ma L, Yuan X, Zhang B, Li Q, et al. Galvanic displacement assembly of ultrathin Co3O4 nanosheet arrays on nickel foam for a high-performance supercapacitor. Nanotechnology. 2017;28(10):105604.

[87] Zhao C, Huang B, Fu W, Chen J, Zhou J, Xie E. Fabrication of porous nanosheet-based Co3O4 hollow nanocubes for electrochemical capacitors with high rate capability. Electrochim Acta [Internet]. 2015;178:555–63. Available from: https://www.sciencedirect.com/science/article/pii/S0013468615303978.

[88] Qing X, Liu S, Huang K, Lv K, Yang Y, Lu Z, et al. Facile synthesis of Co3O4 nanoflowers grown on Ni foam with superior electrochemical performance. Electrochim Acta. 2011;56(14):4985–91. Available from: https://www.sciencedirect.com/science/article/pii/S0013468611005019.

[89] Zhang F, Yuan C, Lu X, Zhang L, Che Q, Zhang X. Facile growth of mesoporous Co3O4 nanowire arrays on Ni foam for high-performance electrochemical capacitors. J Power Sources [Internet]. 2012;203:250–6. Available from: https://www.sciencedirect.com/science/article/pii/S0378775311023755.

[90] Wang Y, Lei Y, Li J, Gu L, Yuan H, Xiao D. Synthesis of 3D-nanotet hollow structured Co3O4 for high capacity supercapacitor. ACS Appl Mater Interfaces. 2014;6(9):6739–47.

[91] Liu Z, Zhou W, Wang S, Du W, Zhang H, Ding C, et al. Facile synthesis of homogeneous core-shell Co3O4 mesoporous nanospheres as high performance electrode materials for supercapacitor. J Alloy Compd. 2019;774:137–44. Available from: https://www.sciencedirect.com/science/article/pii/S0925858818336065.

[92] Venkatachalav V, Alsalwele A, Jayavel R. Shape controlled synthesis of rod-like Co3O4 nanostructures as high-performance electrodes for supercapacitor applications. J Mater Sci Mater Electron. 2018;29(7):6509–67.

[93] Lu Y, Yang W, Li W, Chen M, Shuai I, Qi P, et al. Room-temperature sulfuration for obtaining Co3O4/Co3O4 core-shell nanosheets as supercapacitor electrodes. J Alloy Compd. 2020;818:152877.

[94] Naveen AN, Manimaran P, Selladurai S. Cobalt oxide (Co3O4)/graphene nanosheets (GNS) composite prepared by novel route for supercapacitor application. J Mater Sci Mater Electron. 2015;26(11):8988–9000.

[95] Sun D, He L, Chen R, Liu Y, Lv B, Lin S, et al. Biomorphic composites composed of octahedral Co3O4 nanocrystals and mesoporous carbon microtubes templated from cotton for excellent supercapacitor electrodes. Appl Surf Sci. 2019;465:232–40.

[96] Obodo RM, Onah EO, Nsude HE, Agbogu A, Nwanya AC, Ahmad I, et al. Performance evaluation of graphene oxide based Co3O4/GO, MnO2/GO and Co3O4/MnO2/GO electrodes for supercapacitors. Electroanalysis. 2020;32(12):2786–94.

[97] Picard JP, Baud G, Besse JP, Chevalier R. Croissance cristalline et étude structurale de Co3O4. J Less Common Met. 1980;75(1):99–104.

[98] Periasamy P, Krishnakumar T, Sandhiya M, Sathish M, Chavali M, Siril PF, et.al. Preparation and comparison of hybridized VO2–V2O5 nanocomposites electrochemical supercapacitor performance in KOH and H2SO4 electrolyte. Mater Lett. 2019;236:702–5.

[99] Hosseini H, Shahrokhsian S. Advanced binder-free electrode based on core−shell nanostructures of mesoporous Co3V2O9−Ni3V2O9 thin layers @ porous carbon nano fibers for high-performance and flexible all-solid-state supercapacitors. Chem Eng J. 2018;341(January):10–26.
[100] Tyagi A, Joshi MC, Agarwal K, Balasubramaniam B, Gupta RK. Nanoscale advances three-dimensional nickel vanadium layered double hydroxide nanostructures grown on carbon cloth for high-performance flexible supercapacitor. Nanoscale Adv. 2019;1(May):2400–7.

[101] Chen H, Xue C, Hai Z, Cui D, Liu M, Li Y, et al. Facile synthesis of 3D gem shape Co$_3$O$_4$ with mesoporous structure as electrode for high-performance supercapacitors. J Alloy Compd. 2020;819:152939.

[102] Naveen AN, Selladurai S. Tailoring structural, optical and magnetic properties of spinel type cobalt oxide (Co$_3$O$_4$) by manganese doping. Phys B Condens Matter. 2015;457:251–62. Available from: https://www.sciencedirect.com/science/article/pii/S0921452614008217.