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Mn$_3$O$_4$ nanoparticles encapsulated in carbon cages as the electrode of dual-mechanism supercapacitors

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**A B S T R A C T**

This article reports the production of Mn$_3$O$_4@$C nanocomposites as electrodes for high-performance supercapacitor applications. A facile and low-cost synthesis method combining DC arc discharge and annealing in air at different temperatures is used. The influence of the oxidation temperatures on product microstructure and electrochemical performance is studied in detail. The Mn$_3$O$_4@$C nanocomposite obtained under 200°C annealing owns the highest specific capacitance of 422 Fg$^{-1}$, with a specific energy density of 36 Whkg$^{-1}$ and excellent stability after 1000 cycles. The enhanced electrochemical response is attributed to a well-defined core-shell structure that has a defect-enriched carbon shell and pseudocapacitive Mn$_3$O$_4$ core. Carbon promotes the ion exchange with electric double-layer capacitance, while Mn$_3$O$_4$ contributes the pseudocapacitance during its faradaic redox reactions.

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1. Introduction

The development of eco-friendly energy storage and conversion technologies is the key to remediate the climate change situation, where supercapacitors might be the most advantageous choice in the near future [1]. Supercapacitors are divided according to their energy storage mechanisms, i.e., by means of an electric double-layer capacitance (non-Faradaic) or by a redox pseudocapacitance (Faradaic) [2]. Carbon materials with large surface areas, a huge number of pores, and intrinsic high conductivity, like activated carbon, carbon nanotubes (CNT), and graphene, are suitable to serve as electric double-layer capacitors (EDLCs) [3]. The fast electrostatic process provides them with a noteworthy reversibility and a long-life cycling stability (>500,000 cycles), where high power densities over 10 kWkg$^{-1}$ can be achieved [4]. On the other hand, pseudocapacitors are distinguished by reversible redox reactions and adsorption of ions from the electrolyte on their surface. They provide far higher capacitance and energy density (around 1–10 Whkg$^{-1}$) than EDLCs but lack long-term stability and power density (>2 kWkg$^{-1}$) [1,2]. The most popular pseudocapacitive material is ruthenium oxide (RuO$_2$) because of its high specific capacitance (>1000 Fg$^{-1}$). However, its main drawback is its high toxicity, which is a determining factor to pursue the study of a suitable replacement [5].

In this regard, polyvalent and environmentally friendly transition metal oxides are now intensively explored, where the versatility of manganese stands out due to a variety of stable oxides and a wide diversity of crystal structures. Hausmannite (Mn$_3$O$_4$) is an important representative of manganese oxides because it has a defect chemistry, morphology, and porosity (from ultramicropores to mesopores) that play a significant role in the electrochemical properties when it is used as electrode materials [6]. In consequence, its potential application for supercapacitors has been demonstrated [7–11]. Unfortunately, two factors such as low conductivity ($10^{-8}$ Scm$^{-1}$) and poor cycling stability restrict the real application of Mn$_3$O$_4$ as the electrode material [7,12,13]. Recently, many researchers focus on finding alternative ways to overcome these deficiencies by producing Mn$_3$O$_4$ nanoparticles decorated on the surface of graphene sheets. Hummers’ method has been applied for the synthesis with many different strategies to attach Mn$_3$O$_4$ nanoparticles on the surface of graphene layers, such as, the modified Hummers’ method with KNO$_3$ [7], hydrothermal reduction of MnOOH [8], chemical decomposition of manganese hexacyanoferrate [9], ultrasonication of MnO$_2$ organosol [14], etc. [10,12,13,15,16]. Furthermore, the activated carbon has also been a suitable conductive component. For instance, some composites...
such as activated carbons-MnO_x-Carbon black [17] and MnO_2-activated carbon [11] were characterized as electrode materials, but their capacitive performance was not completely satisfactory. All the studies mentioned previously obtained the maximum capacitance ranging from 131 to 312 F g\(^{-1}\), which still is not competitive enough. The best design of high-class supercapacitors is to merge the assets of carbonaceous materials and pseudocapacitive materials into one heterogeneous-structure electrode similar to a core-shell formation. This unified structure offers a higher synergistic relationship by reinforcing the electroactivities of each component [5]. Chen et al. [18] demonstrated in their study that the capacitance of MnO_2 nanoparticles dispersed on the outer surface of CNTs (790 F g\(^{-1}\)) was outperformed by that of MnO_2 nanoparticles confined inside CNTs (1250 F g\(^{-1}\)). Such a great difference in capacitance was attributed to the core-shell structure. Moreover, Liu et al. produced onion-like C shells using the arc discharge method. The as-produced carbon layers possessed high flexibility and electrical conductivity, which were used as matrices for Co_3O_4 [22] and Mn_3O_4@C-200 nanoparticles that were synthesized by Mn_3O_4@C-200 oxidation temperature is optimized at 200 °C. The outstanding electrochemical performance and cyclability attained by MnO_2@C-200 F g\(^{-1}\) nanocomposite were endorsed to its ideal configuration (large deal of defects and wrinkles in the graphitic layer, sufficiently open MnO_2 crystal structure) and its synergetic bonding among these electrochemically active materials, ensuring a rapid ion-exchange process within the microstructure. Accordingly, it is reasonable to affirm that this may lead to an alternative method for manufacturing new supercapacitor material.

2. Experimental section

2.1. Fabrication of Mn_xC_y@C nanoparticles

DC arc discharge plasma method has been adopted to fabricate various nanostructures such as metal-based nanoparticles [22], graphene [23], and carbon-coated nanoparticles for energy storage [24–26]. Following the same DC arc discharge methodology described in those previous works, a carbon rod was set as the cathode and Mn bulk (99.99% purity) as the anode on a water-cooled copper stage. Once the vessel compartment was vacuumed to 10\(^{-2}\) Pa, a mixture of methane (0.02 MPa) and argon (0.02 MPa) was introduced. The arc discharge was ignited at a steady current of 90 A with a voltage of about 40 V. The Mn bulk was evaporated for 15 min. The evaporated nanoparticles were deposited on the cooling chamber wall. After being passivated in air for 8 h, the Mn_xC_y@C nanoparticles were finally collected from the chamber wall.

2.2. Synthesis of manganese oxide@C nanocomposites

The following step was the annealing of Mn_xC_y@C nanoparticles that were first deposited in an alumina crucible and then placed in the central zone of the quartz tube to ensure uniformity of heat transfer. The powder was heated at a rate of 3 °C min\(^{-1}\) from room temperature (R.T.) to 200 °C and kept for 2 h at 200 °C still in air to get the sample. The same procedure was implemented at 300 and 400 °C.

2.3. Characterization

The phases of Mn_xC_y@C and MnO_2@C nanopowders were confirmed by X-ray diffraction (XRD, PANalytical Empyrean) using Cu Kα radiation (λ = 1.5416 Å). Raman spectra were recorded by using an inVia spectrometer (Renishaw, England) with an excitation wavelength of 632.8 nm. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in a DSC822/TGA/SDTA851 from 25 °C to 700 °C, with a heating rate of 10 °C min\(^{-1}\) in oxygen. The morphology and structure analyses were performed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using an FEI Tecnai G20 S-type Twin.

2.4. Electrochemical measurements

Nickel foam is chosen as the substrate and a current collector in our work because it serves as excellent conducting backbone, and its porous structure provides excellent mechanical stability and allows easy access of electrolyte ions to electroactive surfaces via short pathways, as many other investigations have demonstrated [7,12,27–32]. Thus, to exclude its pseudocapacitive contribution, the nickel foam was sonicated in a 3 M HCl solution for 20 min. In this way, possible oxides and hydroxides were cleaned off the surface of the electric collector. After that, it was sonicated in deionized water for 10 min to wash off the acid, and then it was dried in the oven for 2 h. The working electrode preparation consisted in mixing the active material, carbon black and poly-(vinyl difluoride) in N-methyl pyrrolidone at a weight ratio of 85:10:5 until it formed a slurry paste. Then it was coated onto the Ni foam, dried in vacuum at 100 °C for 10 h, and finally pressed under a pressure of 10 MPa. The mass loading of the active material was 2 mg cm\(^{-2}\). The electrochemical measurements were performed on the workstation CHI760e. A standard three-electrode cell was set with the active material on the nickel foam as the working electrode, Ag/AgCl as the reference electrode, Pt foil as the counter electrode, and 30% w/w KOH solution as the electrolyte. Cyclic voltammograms (CV) were performed at scan rates of 1, 5, 10, 50, 100, and 500 mVs\(^{-1}\). CV results were calculated using the following equation: \( C_{S} = \frac{\int_{V}^{V_{0}} \frac{dV}{dI}}{2mAV} \), where \( C_{S} \) is the specific capacitance in Fg\(^{-1}\), I is the current in Amp, m is the mass of the entire active material in g, \( \Delta V \) is the potential window in V, and V is the scan rate in Vs\(^{-1}\). Current densities used for galvanostatic charge-discharge were 0.3, 0.5, 0.8, 1, 2, and 3 A g\(^{-1}\), under a potential window of −0.4 to 0.4 V. Charge-discharge results were calculated using the following equation: \( C_{S} = \frac{mA}{mAV} \), where A is the discharge time in s. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 0.01 Hz–100 kHz, with AC amplitude of 5 mV.

3. Results and discussion

To determine the chemical composition and crystallite phases, XRD analysis is performed on the precursor, as displayed in Fig. 1(a). The curve for the nanoparticles owns main characteristic peaks at 2θ = 39.76°, 40.35°, 42.6°, and 44.66°, and they are indexed as the crystal planes of (015), (201), (105), and (115) in the orthorhombic Mn_xC_y [JCPDS 01-089-6159]. This strongly indicates that manganese is an active element to react with carbon. A diffraction peak around 26° is attributed to the characteristic (002) plane of graphitic carbon structure [JCPDS 001–0646]. The carbon sourcing from the graphite anode and methane gas both is plenty in the chemical reaction with Mn where a mixture of C and Mn_xC_y is attained as the final product, as it is illustrated in Mn–C phase.
diagram [33]. According to Scherrer’s equation, \( C_{\text{size}} = \frac{K \lambda}{\beta \cos \theta} \), where \( C_{\text{size}} \) is the apparent crystallite size in Å, \( K \) is shape factor, \( \beta \) is the instrument broadening in radians, \( \theta \) is Bragg angle in radians, and \( \lambda \) is radiation wavelength; the approximate size range of the Mn7C3 grains was calculated to be around 26 nm [34].

Raman spectroscopy of carbons provides not only unique vibrational and crystallographic information but also unique information about physical properties that are pertinent to electrons and phonons. Therefore, to characterize the degree of graphitization, Raman spectroscopy is performed on the as-produced nano-composite. As it can be seen in Fig. 1(b), D, G, and 2D peaks are present in the sample’s spectra around 1343.7, 1574.5, and 2692.9 cm\(^{-1}\). The D peak arises from the disorder associated with structure defects, amorphous carbon, or edges that can break the carbon symmetry, and it can always be found in multilayer or rich-defect graphene sheets. G, a primary in-plane vibrational mode, is strictly related to the presence of six-fold aromatic rings. The other main peak is 2D, which is a second-order overtone of a different in-plane symmetric C-C stretching vibration peak D. D and 2D peak positions are dependent on the laser excitation energy, which means that they have a dispersive nature [35,36].

A Lorentzian function fitting is used to calculate the areas for the ratios \( \text{I}_D/\text{I}_G \). At a fixed \( \lambda \), \( \text{I}_D/\text{I}_G \) is a pointer to confirm the degree of graphitization or defect density in carbon materials, and increased \( \text{I}_D/\text{I}_G \) value represents more disordered structure in graphitic carbon [37]. In our research, 0.02 MPa CH\(_4\) nanocomposite owns a low value of 0.23, which means that it possesses a high degree of graphitized carbon. These findings agree well with TEM and HRTEM images. Using the Tuinstra and Koenig’s formula [38], \( L_a \), the in-plane crystallite size, can be calculated as \( \frac{\lambda^2}{2D} = \frac{A}{\text{I}_D/\text{I}_G} \), where \( A \) is a constant value of 102 nm\(^2\) [39]. It is demonstrated that the electrical conductivity of graphitic carbons is enhanced in direct proportion with the size of the crystalite [23,40]. In our case, the \( L_a \) size was around 21.1 nm which ensures the conductivity of the carbon as an energy storage material.

The TEM morphologies of the Mn7C3@C precursor are shown in Fig. 1(c) and (d). Fig. 1(c) shows a conformation of spherical nanoparticles in well-dispersed distribution without visible agglomeration. The mean size of the particles is about 70 nm. A lot of tiny granules, as they are found within several nanometers, clinched together around the nanoparticles. This is a common morphology of the particles formed in the arc discharge process. The large temperature difference between the wall surface and the arc plasma stimulates spontaneous nucleation of the ionized particles, whereas the particle growth is limited due to the fast cooling condition [41]. High-resolution TEM, shown in Fig. 1(d), is conducted on the single nanoparticle, and its microstructure is clearly confirmed as core-shell configuration. The carbon shell is onion-like graphitic cage consisting 5–7 carbon layers within the thickness of 1.5 nm. A large deal of defect and mismatch of the layers can be observed, which is similar to most carbon-coated nanostructures produced by the arc discharge method [23]. Inside the carbon cage, the solid core displays the crystallized Mn7C3 nanosphere composed of several fine grains, whose boundaries are distinguishable, shown as the meshwork of dash lines in Fig. 1(d). The inset of Fig. 1(d) provides the inverse fast Fourier transform images of the selected rectangular region 'i' in the nanocore. One can measure the (114) planes of Mn7C3 with a spacing distance of 0.235 nm. Hence, the precursor we have obtained is defined accurately as Mn7C3@C nanocapsules. In the succeeding process,
the precursor will be oxidized in controlled temperature and progressive degree, ensuring that the Mn$_7$C$_3$ nanocore is oxidized into manganese oxide without altering the carbon cage.

To select the proper temperature of oxidation, TGA and DTA are conducted from R.T. to 700°C in an oxygen atmosphere, the result of which is illustrated in Fig. 2(a). In the TGA curve, 3 stages can be divided at the temperature range of R.T. — 176°C, 176°C — 262°C, and 262°C — 700°C. The first stage depicts a 1.9% mass loss due to the removal of the physically and chemically bonded water [19,30]. For the second, there is a conspicuous weight increase of 2.2% (262°C), which can be attributed to the Mn$_7$C$_3$ nanoparticles oxidation to Mn$_3$O$_4$, i.e., $3\text{Mn}_7\text{C}_3 + 14\text{O}_2 \rightarrow 7\text{Mn}_3\text{O}_4 + 9\text{C}$. The last phase witnesses a sharp mass loss of 22.6% until 531°C, which can be ascribed as burning of carbon into CO$_2$. The oxidation terminates after 531°C, and the mass of the sample keeps unvaried until 700°C. As for DTA, two main exothermal peaks can be appreciated; the first belongs to the completion of the oxidation process of Mn$_7$C$_3$ to Mn$_3$O$_4$ at 297°C, in good accordance with the weight gain from the TGA curve. There is a 75.63% mass loss corresponding to the carbon content, and 24.37% mass remained corresponding to the Mn$_3$O$_4$. Thus, this represents a mass ratio of Mn$_3$O$_4$ : C = 1:3.1. The second peak belongs to the promoted oxidation of the Mn$_3$O$_4$ phase into Mn$_2$O$_3$ at 370°C, $4\text{Mn}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Mn}_2\text{O}_3$. As it can be confirmed, the oxidation of bulky Mn$_7$C$_3$ can be realized at least over 1300°C [33]. The Mn$_7$C$_3$ core, as it is characterized in the HRTEM, consists of ultrafine nanograins, which store a large excess energy in the grain boundaries or as the form of in-grain defects such as dislocations. These non-equilibrium defects constitute an extra driving force and enable the oxidation to proceed at relatively low temperature. The oxidation of the Mn$_7$C$_3@$C NCs, based on the thermal analysis, is set

Fig. 2. (a) TGA and DTA curves for the Mn$_7$C$_3@$C nanoparticle precursor; (b) XRD patterns of (b1) MOC-200, (b2) MOC-300, and (b3) MOC-400; (c) Raman spectra of MOC-200. XPS spectra of the as-prepared nanoparticles, (d, e, and f) Mn 2p region of MOC-200, MOC-300, and MOC-400; (d’, e’, and f’) Mn 3s region of MOC-200, MOC-300, and MOC-400; (d”, e”, and f”) O 1s region of MOC-200, MOC-300, and MOC-400. TGA, thermogravimetric analysis; DTA, differential thermal analysis; XPS, X-ray photoelectron spectroscopy.
at the temperature of 200, 300, and 400 °C. The corresponding oxidized samples are speculated chemically as manganese oxide in carbon cage, and for the sake of convenience, they are labeled in the abbreviated form of MOC-200, MOC-300, and MOC-400 in the following discussions.

The XRD patterns of the as-annealed samples are depicted in Fig. 2(b), referring to the standard spectra from JCPDS cards. The sample MOC-200 (b1) owns main characteristic peaks at 2θ = 28.9°, 31.1°, 32.53°, and 36.19° corresponding to the (112), (200), (103), and (211) planes of tetragonal Mn3O4 hausmannite, respectively. The remains of the Mn7C3 peaks at 2θ = 40.3°, 42.6°, and 44.6° reveal an incomplete oxidation process of the core at 200 °C. MOC-300 (b2) shows the primality of the Mn1O4 phase. The peaks of the Mn7C3 fall to an inappreciable extent, indicating the Mn7C3 nanocores have been approaching the full-oxidated state. In the curve of MOC-400 (b3), the peaks of Mn2O3 phase are found coexisting with those of Mn3O4. This identifies the possibility of the upgraded oxidation from Mn3O4 to Mn2O3, which arrives at good agreement with the TGA-DTA results, where an exothermal peak around 370 °C is displayed for such oxidation process. The Raman spectra of MOC-200 in Fig. 2(c) indicates that the carbon structure after the oxidation process has the changes in the structure related to disorder and induced defects in the graphitic layers. This is demonstrated with an increase of ID/IG from 0.23 to 0.38 and the reduction of the size of Lq crystallite from 21.1 to 16.4 nm.

X-ray photoelectron spectroscopy was performed to verify the electronic states of Mn in the as-prepared MOC-200, MOC-300, and MOC-400 nanocomposites. The high resolution spectra of Mn 2p is shown in Fig. 2(d)-(f). Two characteristic peaks for Mn species arose at 641.9 and 653.63 eV for MOC-200, 641.89 and 653.63 eV for MOC-300, and 641.75 and 653.45 eV for MOC-400 attributed to Mn 2p1/2 and 2p3/2, respectively. The energy separation of all the samples was 11.7 eV, which is in accordance with previous studies [42]. The peaks for binding energy level of Mn 3s are located at 83.77 and 89.27 eV for MOC-200, 83.77 and 89.27 eV for MOC-300, and 83.56 and 89 eV for MOC-400. The energy separation of this spin orbit splitting is really important to determine the possible valence of Mn [43]. According to some references [44,45], the theoretical values for the energy separation of Mn1O4 and Mn2O3 are 5.5 and 5.4 eV, respectively. Fig. 2(d’)-(f’) show that there is a difference in energy separation between MOC-200 and MOC-300 ($\Delta E = 5.5$) with the one of MOC-400 ($\Delta E = 5.44$), which represents the change in the chemical state of the nanocomposite once the temperature reaches 400 °C and matches what was seen in XRD measurements (Fig. 2(b)). In agreement with theoretical values of Mn 2p and 3s spectra, the energy separation of MOC-200 and MOC-300 corresponds to Mn1O4. In contrast, MOC-400 owns an energy separation of 5.44 eV in Mn 3s spectra and additionally has two satellite peaks in Mn 2p spectra at 641.6 and 642.3 eV, which are related to Mn12 and Mn13, respectively [46,47]. These two factors are evidence of the coexistence of Mn3O4 and Mn2O3 species in MOC-400. Finally, O 1s spectra shows (Fig. 2(d’)-(f’)) one main peak at 529.9, 529.9, and 530.1 eV for MOC-200, MOC-300, and MOC-400, respectively, which are consistent with the binding energy values for Mn–O bond found in other studies [43,48]. Two satellite peaks can be found in all the samples, which belong to C–O and C=C–O bonds [48].

Fig. 3(a) and (a’) show the TEM and HRTEM morphologies of MOC-200, where the core-shell configuration is still maintained in the less-sintered nanoparticles. One can easily see that the carbon cage, after oxidation, is thickened to near 6 nm and preserves the large extent of the defect-rich multilayered structure. The exceeding increment of the graphitic layers is driven by the fast growth of carbon, the main product when oxygen reacts with Mn7C3. With the constraint of the existing carbon cage, the expelled growth of carbon, the main product when oxygen reacts with Mn7C3, the expelled growth of carbon, the main product when oxygen reacts with Mn7C3, the expelled growth of carbon, the main product when oxygen reacts with Mn7C3, the expelled growth of carbon, the main product when oxygen reacts with Mn7C3, the expelled growth of carbon, the main product when oxygen reacts with Mn7C3, the expelled growth of carbon, the main product when oxygen reacts with Mn7C3.

![Fig. 3](image-url) Structural evolution of Mn3O4@C composite nanomaterials. TEM images of (a) MOC-200, (b) MOC-300, and (c) MOC-400. HRTEM images of (a’) MOC-200, (b’) MOC-300, and (c’) MOC-400. TEM, transmission electron microscopy; HRTEM, high-resolution transmission electron microscopy.
Mn$_3$O$_4$ core, in the direction of the arrows shown in Fig. 3(b), leaving the core half exposed. Apparently, unlike the MWCNTs, which consist of parallel unidirectional carbon layers, the carbon wires are made up of piles of tiny and curved graphene segments, just as they were found previously in the carbon cages. With the help of the thermal convex during the annealing of the Mn$_7$C$_3$@C NCs, the graphene segments in the carbon cages are driven to flow in one direction, which are linked to each other by the van der Waals’ force. In Fig. 3(c) and (c'), MOC-400 sample displays two disengaged set of structures, broken graphitic layers and Mn$_3$O$_4$ nanoparticles agglomerate. Thus, when the protection of carbon cages is lost, the Mn$_3$O$_4$ nanoparticles are apt to agglomerate due to the spontaneous tendency of decreasing their surface energy. The carbon, at the same time, is continuously burnt into CO$_2$, leading to heavy destroyed structures in pieces of fragments (Fig. 3(c')).

Scanning electron microscopy images of all the as-prepared nanoparticles are shown in Fig. 4. As it can be seen in Fig. 4(a) and (b), Mn@C precursor and MOC-200 nanoparticles preserve an isolated spherical morphology. Accordingly, the core-shell structure is intact after the oxidation at 200 °C. Furthermore, MOC-300 and MOC-400 images clearly illustrate the process of carbon disengagement from the core Mn$_3$O$_4$ after the annealing in air at 300 and 400 °C, respectively. One can easily see carbon wires on the side of the agglomerated Mn$_3$O$_4$ nanoparticles (Fig. 4(c) and (d)). These results are consistent with what was observed in the TEM images shown in Fig. 3.

The mechanism of Mn$_7$C$_3$@C nanocomposite production and its subsequent oxidation process to synthesize Mn$_3$O$_4$@C are shown in Fig. 5(a). When the electric discharge produces the flame between the carbon rod and manganese block, Mn atoms along with carbon, hydrogen, and argon atoms are evaporated into a plasma state. Constant collisions transport the atoms away from the hot zone of the arc. The cooling process happens in the large temperature gradient away from the plasma to the chamber room where all atoms are prompted to come closer to each other for the vapor-liquid-solid growth to begin [22]. This is a critical stage of the formation mechanism because unlike traditional physical deposition using the arc discharge technique [23,25], a reaction between carbon and manganese is produced right after the condensation. After the temperature reaches 1300 °C approximately, Mn$_7$C$_3$ is crystalized, and the excess carbon is precipitated. As demonstrated before, these crystals are in spherical shape, which is a sign of high surface tension of the liquid or semiliquid Mn carbide. The excessive C atoms deposit on the carbide surface to form a continuous carbon layer surrounding the spherical carbide-manganese particles. Therefore, the initial layer of carbon creates a preferential growth for the rest of the carbon layers [49]. However, this step happens so fast (due to the high-temperature gradient on the wall of the chamber) that there is no time for the upcoming layer to match perfectly with the subjacent one. On the other hand, the spherical shape of the nanoparticles induces serious bending, which breaks the continuity of the graphitic layer. In consequence, a large density of defects is formed. The as-prepared Mn$_7$C$_3$@C is annealed in air at different temperatures afterward. The core-shell structure is conserved only after the 200°C oxidation, which owns a thicker graphitic carbon layer. This is due to a reaction of Mn carbide with oxygen, i.e., $3\text{Mn}_7\text{C}_3 + 14\text{O}_2 \xrightarrow{200^\circ\text{C}} 7\text{Mn}_3\text{O}_4 + 9\text{C}$, which produces carbon and Mn$_3$O$_4$. The nanocore undergoes a shrinkage after the reaction while the graphitic cage grew at the expense of this reaction.

The main features of the core-shell architecture that are essential to achieving a dual-mechanism are represented in Fig. 5(b). First, the electric double-layer capacitance achieved by the graphitic carbon satisfies all the requirements, such as high conductivity, high area, electrochemical stability, and open porosity [1,4], for the delivery of double-layer capacitance proposed by the Stern model [50]. Furthermore, its electronic conductivity provides fast charge transfer from/to the current collector (nickel foam) by
reducing the contact resistance. Another advantage is that it constrains the volume expansion of the core during cycling and protects it from dissolution in the electrolyte as well. Second, the faradaic redox pseudocapacitance involves the surface adsorption or intercalation of electrolyte cations (C\(^+\) = H\(^+\), Li\(^+\), Na\(^+\), and K\(^+\)) on the surface and in the bulk of electrode. In both charge-storage routes, redox reactions between the II, III, and IV oxidation states of Mn ions occur [6,51]. The synthesized Mn\(_3\)O\(_4\) spinel structure is formed by interconnected tunnels and high volume of pores enabling the intercalation of protons and ions necessary for fast redox reactions, ensuring high pseudocapacitance and energy density [51]. Such a smart approach tailors the virtues of dual mechanisms, which will ensure high performance of the electrochemical supercapacitor.

With the purpose of comparing the capacitive properties of the as-synthesized Mn\(_3\)O\(_4\)@C nanocomposites, CV and galvanostatic charge-discharge tests are performed in KOH 30% w/w as the electrolyte, under a potential window of 0.8 V (−0.4 - 0.4 V), as illustrated in Fig. 6(a) and (b). According to the area of the loops in Fig. 6(a), the largest capacitance belongs to the MOC-200 sample, followed by MOC-300 and MOC-400 samples. Their shapes differ from the ideal rectangular shape of double-layer capacitors [16,52]; instead, two sharp anodic peaks with their corresponding cathodic pair are easily distinguished, which comes from the process of...
intercalation/deintercalation of cations (K\(^+\)) and/or protons (H\(^+\)) from the electrolyte [53–55], due to the spinel 3D-interconnected tunnels arrangement of the pseudocapacitive material. Such an opened structure improves cation diffusion through the Mn\(_3\)O\(_4\) microstructure [51,56]. The redox peaks reflect the redox transitions of Mn between different valence states (Mn\(^{2+}/\)Mn\(^{3+}\), Mn\(^{3+}/\)Mn\(^{4+}\)) in an alkaline medium, including the following equations:

\[
2(\text{Mn}_3\text{O}_4\cdot 2\text{H}_2\text{O}) + 5\text{OH}^- \rightarrow 6\text{MnO}_2\cdot 5\text{H}_2\text{O} + 3\text{H}^+ + 8\text{e}^- \quad (1)
\]

\[
\text{MnO}_2\cdot 5\text{H}_2\text{O} + \text{H}^+ + \text{e}^- \rightarrow \text{MnOOH} + 5\text{H}_2\text{O} \quad (2)
\]

where MnOOH indicates the interfacial manganese oxyhydroxide species under a higher oxidation state [27,57]. This behavior resembles the one from porous Mn\(_3\)O\(_4\) nanocrystal–graphene electrodes [15], with the only difference that peaks are sharper in our work, which makes it reasonable that the type of carbon by our method plays a major role in the redox reactions. In other words, these cations and protons can be energetically attracted and wrapped within the defects and interlayer misalignments, boosting the pseudocapacitance feature reflected in the redox peaks pair around −0.25 V [23,24]. Efficient crystallization of the Mn\(_3\)O\(_4\) core produced during annealing under air ambient is also a key factor for the peak enhancement during the ion exchange process [58]. As for the MOC-400 sample, an evident shift during cathodic and anodic processes could be originated from greatly reduced electric and ionic conductivity across the whole electrode interface due to the breakage of the carbon shell and the voids between the metal and carbon structures after oxidation, as shown above in Fig. 3(c) and (d) as well as in Fig. 4(d) and (d′). The maximum values of capacitance attained at 1 mVs\(^{-1}\) for MOC-200, MOC-300, and MOC-400 were 422, 213, and 136 Fg\(^{-1}\) (based on the total mass of carbon and Mn oxides), respectively. The CV results are confirmed by the galvanostatic curves shown in Fig. 6(a). The pseudocapacitive response is also recorded in all the discharge curves through two potentials plateaus at −0.05 and −0.25 V. High electrochemical performance for MOC-200 nanocomposite can be ascribed to the enhanced interaction of well-defined core-shell structure, where open-layered and defect-enriched carbonaceous shells can deliver sufficient ions to the Mn\(_3\)O\(_4\) core. Furthermore, the remaining manganese carbide helps decrease the contact resistance between Mn\(_3\)O\(_4\) and the outer graphitic layer [27].

Charge-discharge results for MOC-200 are shown in detail in Fig. 6(c). The maximum value calculated from the curves is 401 Fg\(^{-1}\) (based on the total mass of carbon and Mn\(_3\)O\(_4\)), which corresponds to the current density of 0.3 Ag\(^{-1}\). It is noticeable the decreasing tendency of capacitance when the scan rate or current density increases. The reason for this decrease is the electrolyte penetration in pores and defects of the carbon shell, thus the amount of ions is less available near the surface of the electrode. Moreover, the number of defects formed in the carbon shell during the oxidation process may have caused the mismatch among the layers. Once this misalliance is produced, the electronic and ionic conductivity will be attenuated, thus having great influence on the rate capability. Conversely, at low charge rates, electrolyte ions have time to diffuse into the depth of the pores, and the additional surface area is reached, which could be close to the full use of the electrode material, which can be confirmed in Fig. 6(d) and (e) [4,59]. These encouraging results are superior to previously reported capacitances: δ-MnO\(_2\) nanofibers (380 Fg\(^{-1}\) at 5 mVs\(^{-1}\)) [47], doped Mn\(_3\)O\(_4\) nanocrystals (272 Fg\(^{-1}\) at 0.5 Ag\(^{-1}\)) [60], Mn\(_3\)O\(_4\)-graphene oxide (276.5 Fg\(^{-1}\) at 0.4 Ag\(^{-1}\)) [48], Mn\((\text{MnO})_{\text{Mn}_3\text{O}_4}\)CNT (378.9 Fg\(^{-1}\) at 2 mVs\(^{-1}\)) [27], Mn\(_3\)O\(_4\)-graphene nanosheets (271.5 Fg\(^{-1}\) at 0.1 Ag\(^{-1}\)) [13], porous Mn\(_3\)O\(_4\) nanocrystal-graphene (213.3 Fg\(^{-1}\) at 1 Ag\(^{-1}\)) [15], and multilevel porous graphite foam-Mn\(_3\)O\(_4\) composite (260 Fg\(^{-1}\) at 1 mVs\(^{-1}\)) [61]. Furthermore, the stability of the MOC-200 composite is evaluated after 1000 cycles at 100 mVs\(^{-1}\) (Fig. 6(f)), demonstrating acceptable capacitance retention of 81%, which is ascribed to its exceptional structure arrangement. Here, we show the cyclability only until 1000 cycles due to the sudden drop in capacitance after 1200 cycles to 100 Fg\(^{-1}\). The rapid descent in capacitance was caused by severe damage in the structure of the carbon shell. We presume that the volume change of the core was large enough to destroy the nanocomposite’s cage. After the annealing process, the carbonaceous material underwent high tensile stress during the growing step as the core was oxidized, producing the increase of defects, which in consequence weakened the graphitic structure, affecting also its electronic conductivity. This will be confirmed in the next section.

The HRTEM technique is used to study the microstructure change that occurs during the electrochemical process (Fig. 7) to clarify the reasons for the capacitance fading during cycling. Three distinctive images are found as the main representatives of the microstructure modifications. Fig. 7(a) shows those encapsulated nanoparticles, of which neither their core-shell structure nor their carbon layer has been altered. After the oxidation process of the precursor, the core of the nanoparticles decreased and the outer shell increased, as shown in Fig. 3(a′). Thus, the confinement effect by the enlarged shell alleviates the volume expansion during the continuous cycling, for these nanoparticles with the thickest carbonaceous shell for these nanoparticles. Fig. 7(b) represents the partially encapsulated nanoparticles. The failure is produced due to the
insufficient protection of the less prominent carbon layers in comparison with the previous ones. Therefore, an obvious distortion of the shell is produced along with an increase in size and morphological change from spherical to rectangular. As for the bare nanoparticles (Fig. 7(c)), the size expansion and structural change of the in-core particle are much larger than the tolerance of the carbon shell. The average size of the nanoparticles before and after cycling was measured to be 30 nm and 41 nm, respectively. This represents a notable volume expansion and morphology modification whose deleterious effect was reflected on the cyclability of the electrode material. The lattice fringes on the particle are measured to be 0.52 nm, corresponding to (010) planes of MnOOH. It confirms that the degeneration of the electrochemical performance is aroused by the microstructure transformation from Mn$_3$O$_4$ to MnOOH. Furthermore, the produced MnOOH is not considered as an electroactive material for supercapacitors [62]. In other words, this material does not possess any pseudocapacitive behavior, which explains the decrease of capacitance throughout the stability test.

Further studies are being carried out to find a stable Mn$_3$O$_4$ crystal structure so that the formation of MnOOH is avoided. Lower oxidation temperature and longer annealing time are being tested to maintain the integrity of the graphitic layers. One of the most effective methods to achieve this is by doping the Mn$_3$O$_4$ nanoparticles with ions, i.e., Na$^+$ which has been done before by Li et al. [63] with V$_2$O$_5$. With the same concept, Liu et al. [64] synthetized an NCN$_2$-doped MnO electrode material for Li-ion batteries and supercapacitors. In these two examples, the doped ion not only stabilized the structure but also improved the rate capability by promoting the mobility of ions from the electrolyte.

EIS measurements for MOC-200, MOC-300, and MOC-400 electrodes are performed to provide further evidence of the interfacial phenomena in Fig. 8(a). With this in mind, EIS was also tested for MOC-200 electrode before cycling and at the 1000$^{th}$ cycle (Fig. 8(b)) to deepen what is discussed in the electrochemical performance and TEM sections. The electrical equivalent circuit and the fitting the parameters for all the impedance spectra are shown in Fig. 8(c) and (d), where R1 and R2 correspond to the electrolyte resistance and charge transfer resistance or pseudocapacitive resistance. CPE1 and CPE2 are the constant phase elements for modeling the double-layer capacitance and pseudocapacitance, respectively. For a simplified circuit representation, a clear semicircle appears at high frequencies, and during low frequencies, a line with 45-degree angle; however, in our case, the semicircle is depressed and the line appears between 90$^\circ$ and 45$^\circ$. This can be associated with a non-uniform contact of the active material and the current collector across the electrode surface, which supports the usage of CPE1 and CPE2 [65]. $W_1$ accounts for the Warburg impedance during the dynamics of a diffusion-controlled process. It is embodied by a diagonal line with a slope of 45$^\circ$. Diffusion can create an impedance known as the Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies, the Warburg impedance is small because diffusing reactants do not have to move very far. At low frequencies, the reactants have to diffuse farther, thereby increasing the Warburg impedance.

When the impedance curve of MOC-200 composite is compared with that of its counterparts MOC-300 and MOC-400 (Fig. 8(a)), they corroborate the enhanced ion diffusion of the carbon constraint Mn$_3$O$_4$ nanoparticles. The charge transfer resistance values were calculated to be 2.9 and 3.2 $\Omega$ for MOC-300 and MOC-400, respectively, which are much higher than the one of MOC-200 (0.1 $\Omega$). Once more, this is endorsed to the core-shell arrangement and the benefit of owning a carbon shell with superior conductivity,

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Fig. 8. (a) Nyquist plots for MOC-200, MOC-300, and MOC-400 electrodes, (b) Nyquist plots for MOC-200 prior cycling and at the 1000$^{th}$ cycle, (c) the EIS electrical equivalent circuit, (d) fitting data for each impedance element of MOC-200 electrode prior cycling and at the 1000$^{th}$ cycle. The inset of (a) and (b) shows the magnified region of the Nyquist plot. EIS, electrochemical impedance spectroscopy.
matching the findings of electrochemical results. EIS results after
cycling showed in the inset of Fig. 8(b) depict an enlargement of the
compressed semicircle at high frequencies, which is consistent with
the increment of the charge transfer limitation at electrode-electrolyte
interface, and its diameter is equivalent to the Faradaic charge
transfer resistance $R_2$ [8,65]. After adequately fitting the data, the
approximate values for $R_2$ before cycling and at the 1000th cycle are
found to be 0.1 and 0.2 $\Omega$, respectively. Small values of charge
transfer resistance demonstrate the effectiveness of ion exchange.
The capacitive decay is directly affected by the increased resistance,
that is, reduction of ion exchange within the electrode-electrolyte
interface as displayed by the EIS results.

The applicability of the electrochemical supercapacitor depends
on the relationship between two crucial factors: energy density and
power density. The goal is to fulfill the requirements of high-energy
storage matching with high power of delivery over a range of cur-
rent densities. Thus, the performance of the samples is calculated at
a current density of 0.3 $\text{A g}^{-1}$, shown in Fig. 9.

Fig. 9 shows the electrode performance using the values of the
capacitances from the charge-discharge tests, and this is why the
power and energy density were not represented in a standard
Ragone plot for full cell configurations such as asymmetric super-
capacitors. MOC-200 owns the highest energy density of 36 $\text{Wh kg}^{-1}$
and power density of 120 $\text{W kg}^{-1}$. These values are su-
perior in comparison with the EDLC-type supercapacitors [66,67]
and even outperform MnO$_2$ supercapacitors [68], graphene-MnO$_2$,
and graphene-Mn$_3$O$_4$ electrodes [7,69]. The perfor-
mance ratifies the importance of the dual mechanism of the core-
shell nanostructure, that is, pseudocapacitive Mn$_3$O$_4$ core encap-
sulated in a highly conductive graphitic shell.

Based on the results obtained previously, high electrochemical
performance of the Mn$_3$O$_4$@C nanostructure can be ascribed to the
carbon shell whose graphitization level plays an essential role in
the intercalation-deintercalation of cations and protons from the
electrolyte, the manganese carbide that enhances the overall con-
ductivity, and the Mn$_3$O$_4$ core possessing high-energy storage of
inherent pseudocapacitance.

4. Conclusions

In summary, Mn$_3$O$_4$@C nanocomposites have been synthesized
using a facile, environmentally friendly, low-cost, and industry-
oriented technique that combines the arc discharge method with a
direct oxidation process. Microstructure analysis revealed that the
sample retained a distinct core-shell structure after the annealing
at 200 °C. The electrochemical results show high performance
including excellent specific capacitance and remarkable capaci-
tance retention. Dual-mechanism capacitance, i.e., the electric
double-layer capacitance of the carbon shell and the pseudocapa-
tance from the Mn$_3$O$_4$ core, has been achieved simultaneously in
the core-shell nanostructure, which can be a promising alternative
for future high-performance supercapacitors.

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