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**Electrodeposited manganese oxide supercapacitor microelectrodes with enhanced performance in neutral aqueous electrolyte**

C.C.H. Tran\*, J. Santos-Peña\*, C. Damas

Laboratoire de Physico-Chimie des Matériaux et des Electrolytes pour l'Energie, PCM2E (EA 6299), Université François Rabelais, F-37200 Tours, France

\*Corresponding authors: [camhoangtc@yahoo.com](mailto:camhoangtc@yahoo.com), [jesus.santos-pena@univ-tours.fr](mailto:jesus.santos-pena@univ-tours.fr)

## ABSTRACT

1.6-4  $\mu\text{m}$  thick microelectrodes of manganese oxide  $\text{MnO}_2$  were produced by electrolytic deposition on nickel nanowires  $\text{Ni}_{\text{nw}}$  previously electrodeposited on Anodized Aluminium Oxide (AAO).  $\text{MnO}_2/\text{Ni}_{\text{nw}}$  electrodes prepared under optimized pressure, obtained by application of a torque of 0.2-1.5  $\text{N}\cdot\text{m}$  between the electrolytic cell blocks, show significant electrochemical capacities without addition of conductive additive or binder and can compete with current microsupercapacitor electrodes. Thus,  $\text{MnO}_2/\text{Ni}_{\text{nw}}$  microelectrodes provide a large and reproducible capacitance of  $51.8 \text{ mF}\cdot\text{cm}^{-2}$  (per  $\text{MnO}_2$  electrode surface) at a scan rate of  $200 \text{ mV}\cdot\text{s}^{-1}$  in a three-electrode configuration in neutral aqueous  $0.5 \text{ M Na}_2\text{SO}_4$ . Time constant for the electrochemical process are in the 1.4-2.0 s range, which compares quite well with other microelectrodes. After 3400 cycles, two-electrode devices containing activated carbon negative electrode provide a capacity of  $12.76 \text{ mF}\cdot\text{cm}^{-2}$  and an energy density of  $4.17 \mu\text{Wh}\cdot\text{cm}^{-2}$  per total surface area of both electrodes at a cycling rate of  $0.05 \text{ A}\cdot\text{g}^{-1}$  per  $\text{MnO}_2$  electrode mass which turns into a power density of  $3.75 \mu\text{W}\cdot\text{cm}^{-2}$  per total surface of an electrode. Ragone plot shows a high energy density of  $5.4 \text{ Wh}\cdot\text{kg}^{-1}$  ( $2.14 \mu\text{Wh}\cdot\text{cm}^{-2}$ ) for a power exceeding  $0.7 \text{ kWh}\cdot\text{kg}^{-1}$  ( $0.31 \text{ mW}\cdot\text{cm}^{-2}$ ). These results are, overall, significantly higher than those found in the literature for symmetrical or asymmetric devices based on manganese oxide (with or without carbonaceous materials), and even comparable with some 3D microdevices.

*Keywords:* microsupercapacitors, microelectrodes, manganese oxide, nickel nanowires, electrodeposition.

## 1. Introduction

The miniaturization of energy storage devices is essential to meet the growing demand for autonomous electronic systems and wireless technology [1] in many areas of applications, ranging from home automation and industrial tracking to healthcare and environmental monitoring [2]. The term "micro-supercapacitor" refers to a miniaturized supercapacitor that can be used as autonomous or complementary power source for microbatteries with application on self-powered wireless sensors, Radio Frequency Identification (RFID) tags and MicroElectroMechanical System (MEMS). In general, a supercapacitor is an electrochemical capacitor that can store a larger amount of electrical charge compared with an electrolytic capacitor [3] and can deliver 1-2 orders of magnitude higher power density than rechargeable batteries [4]. A supercapacitor stores electrical energy via an adsorption–desorption of ions (electrochemical double layer supercapacitors-EDLCs) or a pseudo-capacitive Faradaic reaction (pseudo-supercapacitors) between an electrode and an electrolyte [5, 6]. Both EDLCs [7-9] and pseudo-supercapacitors [2, 10] have been studied for microelectrode preparation of microsupercapacitor. The charge storage mechanism of EDLCs capacitors is fast but offers relatively low capacitance. At the opposite, pseudo-supercapacitors provide high capacitance but often deliver low power or suffer from poor cycle stability, due to true faradaic processes taking place on the electrode outer surface layers. Transition metal oxides (such as  $\text{RuO}_2$ ,  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$  [11-15]) and electrically conducting polymers (polyaniline, polypyrrole, polythiophene [16-18]) are examples of pseudo-capacitive electrode materials. Manganese oxides appear to be an alternative to ruthenium oxide due to their relatively low cost, low toxicity and theoretical high capacitances ( $1100\text{-}1300 \text{ F}\cdot\text{g}^{-1}$ ) [19].

Here we report the preparation of microelectrodes ( $\leq 4 \mu\text{m}$  thick) based on manganese oxide (without addition of conductive additive or binder) for applications in 2D planar microsupercapacitors. This 2D planar microsupercapacitors configuration is similar to that of macroscopic supercapacitors, but the different layers (corresponding to electrode and electrolyte reservoir, respectively) are deposited alternatively by micro-manufacturing techniques to form the stack [20]. This configuration remains simple to elaborate. However, the microelectrodes are limited in energy density because they can store only a small amount of active material on the basis of their thin character. This limitation cannot be overcome by the development of thickness electrodes because charge transport is hindered, which reduces the power density. In this context, binder-free porous conductive films are promising as greater energy and power density electrodes [21].

Thin films materials are fabricated by a variety of methods such as sputtering (which leads to a reduction in internal porosity, and thus, a decrease in ion transport), CVD, chemical vapor deposition (which limits the load of active material per unit area or volume) and other complex and expensive techniques [21]. We propose here a simple and clean method of preparation, electrodeposition [22], used by the industry for a long time. On the other hand, synthesis of supercapacitor materials via the use of hard template is actually widely described. This approach includes the use of polycarbonate membranes [23], poly (methyl methacrylate) [24], anodic aluminum oxide AAO [25] or mesoporous silica [26].

In this work, AAO approach was initially proposed for the preparation of manganese oxide nanowires [27]. However, and although easy to obtain, the nanowires prepared by our means were easily disconnected from the stainless steel collector. In order to save this drawback, manganese oxide as a spongy film was electrodeposited onto the nickel nanowires ( $\text{Ni}_{\text{nw}}$ ),

previously electrodeposited on the collector. We studied the influence of the pressure maintained on the electrodeposition cell in order to obtain a nickel nanowires layer homogeneous in thickness and with good contact with the substrate.

Thus, the  $\text{MnO}_2/\text{Ni}_{\text{nw}}$  microelectrodes tested in a 3-electrodes configuration in neutral 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte, were able to provide a reproducible specific capacitance of  $51.8 \text{ mF}\cdot\text{cm}^{-2}$  and  $68.8 \text{ mF}\cdot\text{cm}^{-2}$  (per  $\text{MnO}_2$ -based electrode surface) at a scan rate of  $200 \text{ mV}\cdot\text{s}^{-1}$  and  $10 \text{ mV}\cdot\text{s}^{-1}$ , respectively. Time constant were in the 1.4-2.0 s range and suitable for micro-supercapacitor purposes. After 3400 cycles, AC/ $\text{MnO}_2$  asymmetric devices furnished a specific capacitance of  $12.76 \text{ mF}\cdot\text{cm}^{-2}$  and an energy density of  $4.17 \text{ }\mu\text{Wh}\cdot\text{cm}^{-2}$  (corresponding to  $3.75 \text{ }\mu\text{W}\cdot\text{cm}^{-2}$  in power density). These values are higher than those of several micro-supercapacitors reported in the literature. Thus, our results indicate that our  $\text{MnO}_2/\text{Ni}_{\text{nw}}$  based microelectrodes could strongly compete to other microelectrodes found in the literature for symmetrical or asymmetric devices and based on manganese oxide (with or without carbonaceous materials). Improvement of the performance referred to electrodeposited manganese oxide directly on the collector was due to the presence of nickel nanowires. They guaranteed an intimate (modified stainless steel collector)-electroactive material connection which leads to a high capacitance retention in cyclic voltammetry or galvanostatic cycling.

## **2. Experimental**

### *2.1. Electrodeposition of manganese oxide and nickel nanowires.*

Manganese oxide thin layer and nickel nanowires deposits were prepared by anodic electrodeposition <sup>[28]</sup>. The electrolytic cell, shown in Scheme 1, is an adaptation of a membranes wettability test cell. It consisted of two polyethylene blocks containing a depressed part for

installing the system to investigate (membrane or electrode). Electrolyte was injected through two channels connecting the depression until a total filling volume of 5 mL. Distance between plates and thus, the pressure that the testing system experiences, was fixed with four screws. The pressure was measured with dynamometric wrenches (*Manutan*) and the corresponding torque values ranged between 0.0 and 1.5 N·m.

A treatment of the steel surface collector with 20% v/v HNO<sub>3</sub> for 90 s increased the surface roughness and enhanced the deposits (manganese oxide or nickel) adhesion. Then, the substrate was cut as a disk ( $\phi=10$  mm), bonded to a steel current collector rod and finally coated with an insulating resin to control the effective deposition surface. The counter and pseudo-reference electrodes were stainless steel grid (*Goodfellow*, 0.025 mm thick) and Ag wire, respectively. A glass fiber membrane (*Whatman GF/D*, 0.67 mm thick, porosity 2.7  $\mu\text{m}$ ) with diameter of 14 mm and saturated with electrolyte separated the electrodes. All the electrochemical preparations and tests were performed on a Biologic multipotentiostat (models MPG-2 and VMP-3). Prior to cells assembly and test, electrolyte was degassed with argon for 10 minutes.

In a first approach, we tempted the nanostructuration of manganese oxide through the use of AAO template (Whatman, 60  $\mu\text{m}$  thick, 200 nm pore size). For this purpose, an AAO disk ( $\phi=10$  mm) was soaked in an electrolyte based consisting of 0.5 M aqueous solution of Mn(CH<sub>3</sub>COO)<sub>2</sub> (*Sigma-Aldrich*, 98%) for 2 hours and installed on the surface of the steel substrate. The electrodeposition of manganese oxide on the stainless steel was conducted at 20°C, by setting a potential of 0.8 V vs a pseudo-reference Ag wire for 5 minutes [29].

The deposition of Ni<sub>nw</sub> onto stainless steel required the use of AAO template. The electrolyte adapted to the preparation of nickel nanowires consisted of a solution of 526 g·L<sup>-1</sup> NiSO<sub>4</sub>·6H<sub>2</sub>O

(Sigma-Aldrich, 98%), 35 g·L<sup>-1</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich, 99%), 35 g·L<sup>-1</sup> H<sub>3</sub>BO<sub>3</sub> (Sigma-Aldrich, 98%), and 0.6 g·L<sup>-1</sup> sodium dodecyl sulfate SDS (Sigma-Aldrich, 99%) at pH = 2. Electrodeposition took place at 35°C by imposing a constant current density of 40 mA·cm<sup>-2</sup> to the electrode for 2.6 minutes [30] to the electrode. Details on this step will be developed in section 3.2. Same approach was conducted for obtaining a smooth nickel thick film without involvement of AAO. After treatment with a 7M aqueous solution of NaOH (Sigma-Aldrich, 97%), a Ni<sub>nw</sub>/ss composite consisting of a thick (1.6-5 μm) film of nanowires with diameter close to 300 nm, was recovered. The electrodeposition of manganese oxide is then carried out under the conditions earlier defined. The whole process is schematized in Scheme 2.

## 2.2. Materials characterization

The microstructures of the materials were examined by scanning electron microscopy (SEM) with a Zeiss® ULTRA Plus field effect microscope working at 5 kV.

## 2.3. Electrochemical capacitor tests

Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) were performed with *swagelock* type three-electrode cell containing the electrode MnO<sub>2</sub>/Ni<sub>nw</sub>/ss as working electrode, excess AC (NORIT™ with specific gravimetric capacitance, C= 90 F·g<sup>-1</sup>) as counter electrode and Ag/AgCl<sub>(sat)</sub> as reference electrode (E°=0.208 V vs SHE at 20°C). Electrolyte consisted of degassed 0.5M aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich, 99%). CVs were carried out in the 0V-1V window with different scan rates between 1 and 200 mV·s<sup>-1</sup>. Surface capacitance values of the electrode were obtained by employing the formula:

$$C = \frac{\int i dt}{\Delta U} \quad (1)$$



where  $i$  is the intensity developed in the cell,  $\Delta U$ , the potential explored, and  $s$ , the manganese oxide electrode surface.

Galvanostatic cycling was performed in the 0-1 V voltage range for 5000 cycles. The positive ( $\text{MnO}_2$ -based) and negative (AC-based) electrodes of the capacitor device were mass balanced in order to operate in a potential range between 0 V and 1.7 V. Mass of deposited  $\text{MnO}_2$  material,  $m_{\text{MnO}_2}$ , was estimated as  $Q \times MW_{\text{MnO}_2} / 2F$  [31], where  $F$  is Faraday constant.  $Q$ , the total charge crossing the cell during the electrodeposition time, was calculated by integrating the measured current and assuming that no parasitic reaction takes place at 0.8 V vs Ag.

Cell capacitance,  $C_{\text{cell}}$ , values were obtained by employing the formula [32]:

$$C_{\text{cell}} = I \Delta t / S \Delta V \quad (2)$$

where  $S$  the total geometrical surface of the electrodes,  $I$  is the constant current applied,  $\Delta t$  the time of charge crossing and  $\Delta V$ , the voltage window of cycling after correcting the  $iR$  drop.

The energy  $E$  and the power  $P$  delivered during a discharge between the initial potential  $U_0$  (after eliminating the ohmic drop) and the final potential  $U_f$  are equal to:

$$E = \frac{1}{2} C (U_0 - U_f)^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

where  $\Delta t$  is the discharge time.

Electrochemical impedance spectra were obtained by imposing an AC  $\pm 10$  mV signal around the Open Cell Voltage in the frequency range of 200 kHz and 2 mHz. Electrical Series Resistance (ESR) was evaluated from the Nyquist plots by measuring the real impedance axis at a frequency of 1 kHz.

### 3. Results and discussion.

#### 3.1. *MnO<sub>2</sub> deposition templated by AAO*

AAO template was used for preparing MnO<sub>2</sub> nanotubes by electrodeposition for 2 h. Nanotubes length and diameter ranged between 15-20 μm and 250-330 nm, respectively. Please note that the latter values are higher than the pore size of the AAO template, so the tubes underwent condensation during the electrodeposition. Unfortunately, such MnO<sub>2</sub> nanotubes were easily detached from the stainless steel substrate, even with the prior acid treatment of the substrate conducted to enhance deposit adhesion. This lack of connectivity was responsible of poor electrochemical properties of the MnO<sub>2</sub> nanotubes. The only electrochemical test performed with this electrode, a CV in a three electrodes configuration, confirmed a low capacitance of 15.6 F.cm<sup>-2</sup> under voltage steps of 10 mV·s<sup>-1</sup>.

#### 3.2. *Nickel nanowires (Ni<sub>nw</sub>) thin film electrodeposition*

The use of commercial AAO led to some practical difficulties in nanowires Ni electrodeposition. Thus, the contact between such template and the stainless steel substrate had to be guaranteed in order to ensure the nickel filling through the AAO pores. A homogeneous pressure was applied and maintained during electrodeposition. The corresponding torque ranged from 0.0 to 1.5 N·m. As a high pressure could cause a lack of active material from the electrolyte, 1.5 N·m was the maximum pressure level where the supply of active ingredient was guaranteed during the electrodeposition.

Figure S1 shows the chronopotentiograms recorded during electrodeposition of different Ni<sub>nw</sub> materials obtained under the different pressures (0.0-1.5 N·m). For any pressure, it was observed that the cathodic potential (initially of 0.25 V vs. Ag) fell to a value close to -1.45 V vs. Ag after

10 seconds. During the transition time, the amount of substance flown to the electrode was insufficient to consume all the imposed current for its electrolysis. As a result, cell polarized until a potential value allowing the main electrochemical reaction to take place and consume the charge [33]. The curve showed then a voltage plateau around -1.00 V vs. Ag, which corresponded to the reduction potential of Ni(II) to Ni(0). Figure S1 reflects a slight influence of the pressure applied on the cell during the electrolysis on the shape of the chronopotentiogram obtained. Nevertheless, we detected a strong impact on the nickel coating (completion, morphology, thickness and diameter) as discussed next.

At null pressure in the electrolytic cell, the nickel deposition was not homogeneous. According to Figure 1a, one could distinguish nickel-free zones (encircled in yellow), thin and compact Ni<sub>nw</sub> areas (encircled in blue) and finally, thick (>2.5 μm) (Figure 1a.2) and 300 nm-diametered (Figure 1a.3) Ni<sub>nw</sub> deposition zones (encircled in red). The average diameter is close to 300 nm, which is, as for manganese oxide nanotubes, larger than the diameter of the AAO membrane pores. This agrees with condensation of the wires during the electrodeposition.

An improvement in the deposition, providing a thorough coating of the stainless steel surface was obtained when the torque reached 0.1 N·m (Figure 1b.1). Although some thicker deposit areas (encircled in red) were also observed, the surface was mainly recovered of a 2-2.5 μm (Figure 1b.2) thick film of Ni<sub>nw</sub> with average diameter of 300 nm (Figure 1b.3).

Applying a torque of 0.2 N·m, the steel surface was thoroughly and uniformly covered by Ni<sub>nw</sub> (Figure 1c.1). Although the nanowires average diameter remain similar, their lengths shrunk compared to those obtained under a torque of 0.1 N·m, from 2-2.5 to 1.6 μm (Figure 1c.2).

When the pressure on the electrolytic cell rises to a torque equivalent to 1.5 N·m, a 4 μm thick coating (Figure 1d.3) was fairly homogeneous although some craters (yellow circles in Figure

1d.1) were identified. A closer examination of the 300 nm-diametered  $\text{Ni}_{\text{nw}}$  allow to detect a less compact structure than in the earlier presented  $\text{Ni}_{\text{nw}}/\text{ss}$  composites (Figure 1d.2). Both, the depressed zones and the empty space, seemed to be produced during disassembly of the electrolytic cell. In the next section, it will be proved that the space created between the nanowires can accommodate manganese oxide.

In conclusion, a torque equal or superior to 0.1 N·m, made possible to maintain a consequent contact between the membrane of AAO and the stainless steel substrate, leading, after electroplating, to a complete coating of homogeneous in diameter (300 nm) and in length (a few micrometers) nickel nanowires. The four set of electrodes were handled and showed robustness against peeling off, which are consistent with the intimate contact between the stainless steel substrate and the nanowires films observed in the cross-section images.

### *3.3. $\text{MnO}_2$ electrodeposited on Ni nanowires*

The material electrodes based on  $\text{MnO}_2$  were obtained by conducting its electrodeposition at 20°C on the  $\text{Ni}_{\text{nw}}$  electrodes previously deposited at torques equivalent to 0.2 N·m and 1.5 N·m. Manganese(II) ions present in the electrolyte were oxidized at a potential of 0.8V vs Ag for 5 min.

To illustrate this section, we chosen to show the results obtained for  $\text{MnO}_2$  thin film electrodeposition on the  $\text{Ni}_{\text{nw}}$  deposited at a torque of 1.5 N·m. The corresponding images composite is shown in Figure 2. The  $\text{MnO}_2/\text{Ni}_{\text{nw}}$  thin film contained cracks as a result of the pristine  $\text{Ni}_{\text{nw}}/\text{ss}$  composite incompactness (see section 3.2), which is enhanced by some stress induced during the manganese oxide electrodeposition (Figures 2 a-c). These cracks opened the  $\text{Ni}_{\text{nw}}$  structure and provided additional positions to  $\text{MnO}_2$  to deposit, according to Figure 2d, a backscattered electron replicate of Figure 2b. Indeed, two well-differentiated zones are noticed

in the image: nickel nanowires in light gray and manganese oxide film in darker gray. The latter was homogeneously deposited on the top of the nanowires and randomly deposited on their edges. From here, the samples were named MO/Ni<sub>nw</sub>\_0.2N·m/ss and MO/Ni<sub>nw</sub>\_1.5N·m/ss according to the different pressure applied during the nickel nanowires electrodeposition.

### *3.4. Capacitive behavior of MnO<sub>2</sub> thin films deposited on Ni<sub>nw</sub> in three-electrode cells*

#### *3.4.1. Cyclic voltammetry*

For determining the role of substrate where manganese oxide is electrodeposited, the following electrodes were cycled in 0.5M Na<sub>2</sub>SO<sub>4</sub>: MO/Ni<sub>nw</sub>\_0.2N·m/ss, MO/Ni<sub>nw</sub>\_1.5N·m/ss and two additional electrodes containing stainless steel as surface deposition (electrode hereafter called MO/ss and evoked in section 3.1) or a compact Ni film deposited on stainless steel. The latter is produced in a similar way as our MO/Ni<sub>nw</sub>/ss electrodes but without assistance of AAO structuring agent and will be hereafter called MO/Ni/ss electrode. Please note that the latter system is similar to one earlier proposed by Simon et al. [31]

Figure 3 shows the CV corresponding to the four electrodes investigated in a three-electrode cell. For the MO/ss electrode, a large polarization is observed which could denote the lack of suitable connection between the manganese oxide electrodeposited and the stainless steel substrate, as discussed in next sections. Broad and weak bands located at 0.76V and 0.35V, at the anodic and the cathodic waves respectively, were noticed. The maximal capacitance provided by the MO/ss electrode was limited to 21 mF·cm<sup>-2</sup>.

The inclusion of a compact nickel film between the substrate and the MnO<sub>2</sub> film in the MO/Ni/ss electrode, although decreased the system resistance, was not efficient enough to recover the typical box shape of the CV. Thus, large peaks appeared during charge (0.63V and 0.7V) and discharge (0.5 V). Due to the presence of such peaks, the capacitance of this system greatly increased to 53.2 mF·cm<sup>-2</sup>. Simon et al. [31] prepared a conformal 200 nm-thick layer of manganese oxide electrodeposited onto Ni<sub>nw</sub> themselves previously deposited on a nickel substrate. The film of Ni<sub>nw</sub> was 5 nm thick and the wires were 200 nm diameter. Capacitances as high as 100 F·g<sup>-1</sup>·cm<sup>-2</sup> were provided by such MnO<sub>2</sub>/Ni<sub>nw</sub>/Ni electrodes at 100 mV·s<sup>-1</sup>. It should be taken into account that nickel is more costful than stainless steel.

An improved contact between MnO<sub>2</sub> film and collector was obtained by depositing the oxide onto Ni<sub>nw</sub>/stainless steel collector. In Figure 3, we notice a close-to-ideal rectangular CV reflecting a quasi-perfect pseudocapacitive behavior of the MO/Ni<sub>nw\_1.5N·m/ss</sub> electrode. Unlike, CVs of the MO/Ni<sub>nw\_0.2N·m/ss</sub> electrode were not box shaped. Regarding this different behavior, one should notice that the Ni<sub>nw</sub> formed under a torque of 0.2 N·m were very compact (Figure 1c.2). Unlike, the Ni<sub>nw</sub> obtained at 1.5 N·m were a more opened structure with intimate connection with the collector (Figures 2b and 2c). This particular organization offers additional places for the manganese oxide deposition others than the nanowires top surface. As a consequence, the amount of oxide per cm<sup>2</sup> was larger than for a torque of 0.2 N·m (0.18 mg·cm<sup>-2</sup> versus 0.17 mg·cm<sup>-2</sup>). Thus, more active material was exposed to the electrolyte charge storage. Both factors (connectivity and active material amount) contribute to the enhanced capacitance shown by MO/Ni<sub>nw\_1.5 N·m/ss</sub> (68.8 ± 2.8 mF·cm<sup>-2</sup>) versus MO/Ni<sub>nw\_0.2 N·m/ss</sub> (45.9 ± 2.6 mF·cm<sup>-2</sup>). It also should be noted that the capacitance of the MO/Ni<sub>nw\_1.5 N·m/ss</sub> electrode at 100 mV·s<sup>-1</sup>, 276 F·g<sup>-1</sup>·cm<sup>-2</sup> was substantially larger (more than twice) than that found for

MO/Ni<sub>nw</sub>/Ni electrodes developed by Simon et al. [31] and even for a MnO<sub>2</sub>/Ni<sub>nw</sub>/Ti electrode reported by Xu et al. [34] with nickel nanowires array prepared by a modified magnetic-field-driven selective-deposition growth process and a large amount of manganese oxide deposited.

The positive effect of the Ni<sub>nw</sub> collector presence on the electrode capacitance was even more pronounced when scan rates are faster than 10 mV·s<sup>-1</sup>. Figure 4 shows the evolution of the MnO<sub>2</sub> electrodes capacities depending on the scan rate. It was noteworthy that at the slowest regime, the specific capacitance of the MO/Ni/ss electrode was the biggest one on this set of electrodes. This agrees with a larger electrodeposition of manganese oxide in this system (0.25 mg·cm<sup>2</sup>) due to the larger porosity accessible to the electrolyte ions in order to charge storage [31,34]. Nevertheless, pronounced loss of capacitance was observed for all the electrodes when the scan rate increased from 1 to 10 mV·s<sup>-1</sup>. This drop was 13.5% for MO/Ni<sub>nw</sub>\_1.5 N·m/ss, 25.3% for MO/Ni<sub>nw</sub>\_0.2 N·m/ss, 38.5% for MO/Ni/ss and finally 43.9% for MO/ss. Beyond 50 mV·s<sup>-1</sup>, the capacitance of MO/Ni/ss was lower than that of MO/Ni<sub>nw</sub>\_0.2N·m/ss. Best behavior shown by MO/Ni<sub>nw</sub>\_1.5 N·m/ss and MO/Ni<sub>nw</sub>\_0.2 N·m/ss MO/Ni<sub>nw</sub> electrodes highlights the good connection between the MnO<sub>2</sub> film and the nickel nanowires. At fast regimes, only a few nanometers of the outer surface of the material are involved in the electrochemical reaction and the connection between the deposited materials plays a key role on the capacitance retention.

### 3.4.2. Electrochemical impedance spectroscopy

EIS has been applied at OCV on different asymmetric devices based on our microelectrodes and AC. Figure 5a contains the corresponding Nyquist plots. The values of ESR issued from the Nyquist plots are 4.3 Ω, 12.2 Ω, 12.5 Ω and 500 Ω for MO/Ni<sub>nw</sub>\_1.5N·m/ss, MO/Ni<sub>nw</sub>\_0.2N·m/ss, MO/Ni/ss and MO/ss electrodes, respectively. The three first values are

below those obtained for symmetrical  $\text{MnO}_2||\text{GQD}$  (graphene quantum dots) devices using ionic liquids as electrolytes [35] or microelectrodes tested in gel electrolytes [36] and are far below those obtained for bigger size electrodes [37]. The lowest values of ESR for  $\text{MO}/\text{Ni}_{\text{nw}}_{1.5\text{N}\cdot\text{m}/\text{ss}}$  and  $\text{MO}/\text{Ni}_{\text{nw}}_{0.2\text{N}\cdot\text{m}/\text{ss}}$  electrodes, testified for an excellent connectivity between the manganese oxide/nickel nanowires system and the stainless steel collector.

Figure 5b shows the evolution of the imaginary part of the capacitance as a function of the frequency. The curves were characterized by a maximum occurring at the frequency corresponding to the time constant of the electrode, i.e. the time necessary for half discharging the cell. Time constants were 1.4, 2.0, 70 and 150 s for  $\text{MO}/\text{Ni}_{\text{nw}}_{1.5\text{N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}_{\text{nw}}_{0.2\text{N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}/\text{ss}$  and  $\text{MO}/\text{ss}$  electrodes, respectively, demonstrating the accessibility of the electrolyte ions in the pores of the two first electrodes. It is also noteworthy that the two first values were well below those typical of macrodevices (beyond 10s) [38] and are similar to that of systems containing thick carbon electrodes [39] but are three or four times higher than those reported for microelectrodes containing  $\text{MnO}_2/\text{carbone}$  composites [40] and  $\text{MnO}_2/\text{graphene}/\text{Ni}$  [41]. Nevertheless, such microelectrodes are more difficult to elaborate than ours.

Finally, Figure 5b also indicates that bigger capacitances at the lowest frequencies were provided by the  $\text{MO}/\text{Ni}/\text{ss}$  and  $\text{MO}/\text{ss}$  electrodes. This is not contradictory with the above mentioned features. At lowest frequencies, the electrolyte ions trended to accommodate in a maximum of porosity. Both electrodes contained respectively more manganese oxide ( $0.25 \text{ mg}\cdot\text{cm}^{-2}$  and  $0.19 \text{ mg}\cdot\text{cm}^{-2}$ ) than  $\text{MO}/\text{Ni}_{\text{nw}}_{1.5\text{N}\cdot\text{m}/\text{ss}}$  and  $\text{MO}/\text{Ni}_{\text{nw}}_{0.2\text{N}\cdot\text{m}/\text{ss}}$  and thus, a larger accessible porosity for charge storage. In the case of  $\text{MO}/\text{Ni}/\text{ss}$  electrode, this feature compensated the poor



active material/collector connectivity response at the slowest regimes (for instance, CV at 1  $\text{mV}\cdot\text{s}^{-1}$  as in Figure 4).

### 3.4.3. Galvanostatic cycling

The stability during cycling of different devices in the 0-1V range was studied by galvanostatic tests at a regime of  $3.8\ \mu\text{A}\cdot\text{cm}^{-2}$  (corresponding to  $0.05\ \text{A}\cdot\text{g}^{-1}$  of  $\text{MnO}_2$ ) over 3400 cycles. Similar amounts of  $\text{MnO}_2$  are deposited for all the devices. Figures 6a and 6b present, respectively, the evolution of nickel-containing devices capacitance and their coulombic efficiencies as a function of the cycle number.

MO/Ni<sub>nw</sub>\_1.5N·m/ss-based device provided a stable capacitance close to  $13\ \text{mF}\cdot\text{cm}^{-2}$  after 3400 cycles, which represents a retention of 99.4% compared to the first cycle. For the device based on MO/Ni<sub>nw</sub>\_0.2N·m/ss, an increase in specific capacitance was observed during the first 700 cycles. However, this property leveled off to  $11\ \text{mF}\cdot\text{cm}^{-2}$ , a value slightly lower than that shown by the MO/Ni<sub>nw</sub>\_1.5N·m/ss-based one. After 3400 and 4300 cycles, the capacitance provided by the device containing MO/Ni<sub>nw</sub>\_0.2N·m/ss were  $10.9$  and  $10.35\ \text{mF}\cdot\text{cm}^{-2}$ , respectively, representing low retentions (77.9% and 73.5%, respectively). The MO/Ni/ss device showed a high capacitance (around  $15\ \text{mF}\cdot\text{cm}^{-2}$ ) at the beginning of cycling, which dropped to  $10\ \text{mF}\cdot\text{cm}^{-2}$  after 1000 cycles. After 3400 and 5000 cycles, the capacitance retentions were only 66.1% and 63.8%, respectively.

The high capacities reported here for the MO/Ni<sub>nw</sub>\_1.5N·m/ss-based devices are comparable to those found in the literature for other devices such as  $\text{MnO}_2$ /onion-like carbon (symmetric) prepared by printing technology and containing a solid electrolyte (PVA/ $\text{H}_3\text{PO}_4$ :polyvinyl alcohol/phosphoric acid) ( $7.04\ \text{mF}\cdot\text{cm}^{-2}$  at  $20\ \mu\text{A}\cdot\text{cm}^{-2}$  between 0 V and 0.8 V [42]) and

MnO<sub>2</sub>||GQD (graphene quantum dots) (2.98 mF·cm<sup>-2</sup> at 30 μA·cm<sup>-2</sup> between 0 V and 1 V) prepared by electrodeposition [35].

In order to determine if the ohmic drop was responsible for the devices capacitance loss, we studied the galvanostatic first cycle and a test corresponding to 3400<sup>th</sup> cycle (Figure 7). In general, the curves showed a triangular and symmetrical shape revealing a typical capacitive behavior [43] with a high coulombic efficiency (95%-99%). In the first cycle, these devices presented low and stable upon cycling ohmic drop. Thus, the capacitance loss should be better associated to manganese dissolution (as Mn<sup>2+</sup>) upon negative polarization enhanced by the expected changes of the medium pH. Accessorily, we observe a higher ohmic drop for devices based on MO/Ni/ss, compared to that based on MO/Ni<sub>nw</sub>/ss, highlighting the important role of nickel nanowires/substrate connection in composites. It is also noteworthy that in the MO/Ni/ss electrode last test, one could detect small pseudoplateaux in the 0.5-0.6 V region, revealing the apparition of faradaic process others than those stated for pure pseudocapacitor manganese oxide electrode.

#### *3.4.4. Energy and power density of devices*

A Ragone plot (Figure 8) was built in order to compare our micro-devices performance with those of different micro-supercapacitors reported in the literature. The Ragone data correspond to different test regimes involving different intensities. In general, we found a remarkable energy density for the devices based on MO/Ni<sub>nw</sub>, reaching 4.17 μWh·cm<sup>-2</sup> at a power density of 3.75 μW·cm<sup>-2</sup>. This power is greater than that of several last-generation 1V-0.9V micro-supercapacitors working in aqueous Na<sub>2</sub>SO<sub>4</sub> solutions as for instance, asymmetric MnO<sub>2</sub>||GQDs

[35] and symmetric RGMA (RGO/MnO<sub>2</sub>/Ag) GQDs [44]. Our devices power was also higher than those of devices dealing with gel electrolytes such as symmetric MnO<sub>x</sub>/Au in PVA/H<sub>2</sub>SO<sub>4</sub> gel [45] and symmetric LSG/SWCNTs in PVA/H<sub>3</sub>PO<sub>4</sub> gel [46]. However, the power of our devices was lower than that of symmetrical micro-supercapacitor with interdigital 3D electrodes manufactured by Eustache et al. [47] and tested in aqueous electrolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub>, at 0.8 V). These particular devices contain a 350 nm-thick MnO<sub>2</sub> electrodeposited on an interdigitated Si/Al<sub>2</sub>O<sub>3</sub>/Pt electrode and provided energy and power densities close to 10 μWh·cm<sup>-2</sup> and 20 mW·cm<sup>-2</sup>, respectively [47]. One should take into account that elaboration of interdigital 3D electrodes is an expensive and time-consuming process, involving the use of silicon microstructures, alumina and platinum materials as well as more sophisticated techniques than electrodeposition as photolithography and atomic layer deposition technology and deep reactive ion etching.

MO/Ni<sub>nw</sub>\_1.5N·m/ss-based devices may compete with the symmetrical MnO<sub>2</sub>/(SiO<sub>2</sub>/Si)-Pt system reported by Tian et al. [36] and involving the preparation of negative photoresistor SU-8 micro-pillars on a SiO<sub>2</sub>/Si substrate, Ti and Pt double coating and finally, manganese dioxide electrodeposition. A KOH/PVA gel electrolyte is used for the construction of a 1.7 μm-thick all-solid device delivering an energy density of 4 μWh·cm<sup>-2</sup> at 930 μW·cm<sup>-2</sup>.

The power of our devices also remained lower than that of micro-supercapacitors employing ionic liquid as electrolyte, as for instance those based on asymmetrical MnO<sub>2</sub>||GQDs [35] and MnO<sub>2</sub>/Si symmetrical [48] or G/CNTCs symmetrical [49]. This was expected as ionic liquids show larger electrochemical window than water and their based devices can provide higher voltages and, therefore, higher energies and powers.

Our devices have been prepared by a combination of hard templating and electrodeposition technique which remains a simple, inexpensive, reliable and efficient method. This combination provided neutral aqueous electrolyte devices with comparable or even higher energy density than some micro-supercapacitors with 3D architecture elaborated through complex techniques such as CVD (chemical vapor deposition) [48, 49], electron beam evaporation [45] and laser-scribing technology [46]. This performance was certainly related to the low thickness of the manganese oxide electroactive material and its excellent connection with the electronic collector through the nickel nanowires.

Despite the excellent surface energy density, it was difficult to discuss on the devices volume energy density because the assembly of the complete device is still not optimized. Volume quantities are better adapted to evaluate micro-supercapacitor properties. Thus, volumetric capacitances, energies and powers allow comparison of different electrode materials, independently of thicknesses. For this purpose, the thickness of each layer (substrate, current collector, electrolyte, electrode materials) should be controlled and optimized. For instance, in our case, activated carbon-based negative electrode thickness could be limited in order to decrease the total micro-device size. This optimization is beyond the goal of this work. However, our microelectrodes remarkable energetic parameters allow believing that they can be of interest for microsupercapacitor purposes. Further studies must be carried out in order to confirm this hypothesis.

#### **4. Conclusions**

A series of capacitor microelectrodes based on manganese oxide (without addition of conductive additive or binder) were prepared. The oxide was deposited on nickel nanowires  $\text{Ni}_{\text{nw}}$  which have

been previously deposited on a sheet of stainless steel using the AAO template. It is noted that the quality of the nickel nanowires layer was closely related to the pressure conditions exerted on the electrolytic cell during electrodeposition. Thus, the pressure exerted by a torque of 1.5 N·m ensured the formation of a 4 μm thick film of 300 nm-diametered nickel nanowires. The capacitance values of the nanostructured MO/Ni<sub>nw</sub>\_1.5N·m/ss composites when tested in aqueous neutral Na<sub>2</sub>SO<sub>4</sub> electrolyte were high and reproducible: 68.8 mF·cm<sup>-2</sup> at 10 mV·s<sup>-1</sup> and 51.8 mF·cm<sup>-2</sup> at 200 mV·s<sup>-1</sup>. The latter value was 1.9 times, 2.6 times and 9.6 times respectively greater than those of the microelectrodes based on MO/Ni<sub>nw</sub>\_0.2N·m/ss, MO/Ni/ss and MO/ss (27.5 mF·cm<sup>-2</sup>, 19.9 mF·cm<sup>-2</sup> and 5.4 mF·cm<sup>-2</sup>, respectively) tested under the same conditions.

Asymmetric devices built with the manganese oxide/nickel nanowires/stainless steel composites as positive electrode and AC as negative electrode were tested in the same electrolyte in the 0-1V voltage range. Galvanostatic cycling was conducted at a rate of 0.05 A·g<sup>-1</sup> (per MnO<sub>2</sub> electrode weight) or 3.8 μA·cm<sup>-2</sup> (per unit area of electrodes) on all MnO<sub>2</sub>-based devices. The capacitance was 12.76 mF·cm<sup>-2</sup> for the device using MO/Ni<sub>nw</sub>\_1.5N·m/ss at the 3400<sup>th</sup> cycle, values 1.26 and 2.1 times higher than that of the devices based on MO/Ni/ss and MO/ss, respectively, in the 3400<sup>th</sup> cycle. Finally, the time constant for the charge storage process was very fast for the Ni<sub>nw</sub> containing composites, in the 1.4-2.0 s range. Such parameter indicates that devices containing these microelectrodes could operate at high powers. Indeed, Ragone plot (energy density vs. power density) clearly highlighted the particular advantages of the MO/Ni<sub>nw</sub>\_1.5N·m/ss || AC device, with the lowest time constant.

The energy density of 4.17 μWh·cm<sup>-2</sup> (at 3.75 μW·cm<sup>-2</sup>) was higher than that of several micro-capacitors reported in the literature. These values are even more revealing considering that most of the performant systems employ organic, ionic liquid-based electrolytes or more complex

composites. For this reason, the advantageous properties of the manganese oxide/nickel nanowires/stainless steel composite microelectrodes prepared in this work could be of interest for developing microsupercapacitors.

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## Supporting Information

**Figure S1.** Chronovoltammogram corresponding to the electrodeposition of different Ni nanowires at  $40 \text{ mA}\cdot\text{cm}^{-2}$  for 2.6 minutes.

## Legend of Schemes and Figures

**Scheme 1.** Electrolytic cell assembly showing electrodes and separators disposition.

**Scheme 2.** Step-by-step  $\text{MnO}_2/\text{Ni}_{\text{nw}}/\text{ss}$  microelectrode preparation.

**Figure 1.** SEM images of the  $\text{Ni}_{\text{nw}}$  /stainless steel composites prepared at torques of (a) 0 N·m, (b) 0.1 N·m, (c) 0.2 N·m and (d) 1.5 N·m. 1: wide top view, 2: close top view, 3: cross-section view.

**Figure 2.** SEM images of  $\text{MnO}_2/\text{Ni}_{\text{nw}}$  where nickel nanowires were produced at a torque of 1.5 N·m: (a) and (b) top view of different areas; (c) close top view of (a); (d) backscattered electron image of (c).

**Figure 3.** CVs curves of  $\text{MO}/\text{Ni}_{\text{nw}}_{1.5\text{N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}_{\text{nw}}_{0.2\text{N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}/\text{ss}$  and  $\text{MO}/\text{ss}$  electrodes in 0.5M  $\text{Na}_2\text{SO}_4$  recorded between 0 and 1V vs Ag/AgCl at  $10\text{ mV}\cdot\text{s}^{-1}$ .

**Figure 4.** Evolution of the capacitance developed in 0.5M  $\text{Na}_2\text{SO}_4$  by  $\text{MO}/\text{Ni}_{\text{nw}}_{1.5\text{ N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}_{\text{nw}}_{0.2\text{ N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}/\text{ss}$  and  $\text{MO}/\text{ss}$  electrodes as a function of the scan rate (1-200  $\text{mV}\cdot\text{s}^{-1}$ ).

**Figure 5.** (a) Nyquist plots and (b) imaginary part of the capacitance,  $C''$  of devices with  $\text{MO}/\text{Ni}_{\text{nw}}_{1.5\text{N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}_{\text{nw}}_{0.2\text{N}\cdot\text{m}/\text{ss}}$ ,  $\text{MO}/\text{Ni}/\text{ss}$  and  $\text{MO}/\text{ss}$  electrodes as a function of the frequency measured around OCV. Electrolyte = 0.5M  $\text{Na}_2\text{SO}_4$ .

**Figure 6.** Testing of microelectrode-based devices prepared in this work: (a) long-term cycling stability, (b) coulombic efficiency. Cycling conditions:  $j= 3.8\ \mu\text{A}\cdot\text{cm}^{-2}$ , voltage range: 0-1V, electrolyte: aqueous 0.5 M  $\text{Na}_2\text{SO}_4$ .

**Figure 7.** Charge/discharge cycle of microelectrode-based devices prepared in this work: (a): first cycle, (b) last cycle. Cycling conditions:  $j= 3.8\ \mu\text{A}\cdot\text{cm}^{-2}$ , voltage range: 0-1V, electrolyte: aqueous 0.5 M  $\text{Na}_2\text{SO}_4$ .

**Figure 8.** Ragone plot showing the performances of various micro-supercapacitors. Abbreviations: LSG: laser scribed graphene; SWCNTs: single-walled carbon nanotubes; RGO: reduced graphene oxide; CNTCs: Carbon Nanotube Carpet; GQD: graphene quantum dots; RGMA: RGO/ $\text{MnO}_2$ /Ag; ILs: ionic liquid electrolytes; (sym): symmetric device.

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