### Nanostructured MnO<sub>2</sub> films for 3D micro-supercapacitors: from new insights of the growth mechanism to the fine tuning of areal capacitance values

Botayna Bounor<sup>1,2,3,4</sup>, Bouchra Asbani<sup>1,3</sup>, Camille Douard<sup>2,3</sup>, Dominique Deresmes<sup>1</sup>, Didier Stiévenard<sup>1</sup>, Pascal Roussel<sup>4</sup>, Frederic Favier<sup>3,5\*</sup>, Christophe Lethien<sup>1,2,6\*</sup> and Thierry Brousse<sup>2,3\*</sup>

<sup>1</sup> Institut d'Electronique, de Microélectronique et de Nanotechnologies, Université de Lille, CNRS, Université Polytechnique Hauts-de-France, UMR 8520 - IEMN, F-59000 Lille, France

<sup>2</sup> Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, 33 rue Saint Leu, 80039 Amiens Cedex, France

<sup>3</sup> Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, 2 rue de la Houssinière BP32229, 44322 Nantes cedex 3, France

<sup>4</sup> Unité de Catalyse et de Chimie du Solide (UCCS), Université de Lille, CNRS, Centrale Lille, Université d'Artois, UMR 8181 – UCCS, F-59000 Lille, France

<sup>5</sup> ICGM, Univ. Montpellier, CNRS, ENSCM, 34293 Montpellier, France

<sup>6</sup> Institut Universitaire de France (IUF), Paris - France

\*Correspondence to: <u>frederic.favier@umontpellier.fr</u> & <u>christophe.lethien@univ-lille.fr</u> & <u>thierry.brousse@univ-nantes.fr</u> **Keywords:** MnO<sub>2</sub>, thin films, electrodeposition, Atomic Force Microscopy, microsupercapacitor

### Abstract

Maximizing the electrochemical performance of 3D micro-supercapacitors based on pseudocapacitive films is crucial for powering the next generation of miniaturized IoT devices. The films have to be nanostructured, must conform the 3D template, and have uniform deposition. To study the growth mechanism of nanostructured  $MnO_2$  films obtained by a pulsed electrodeposition method, *in situ* Atomic Force Microscopy methods operating in liquid mode, Scanning Electron Microscopy, and electrochemical characterization techniques were used. The impact of ON and OFF times during the pulsed electrodeposition process was investigated. The deposition mechanism in Volmer Weber Island growth mode provided some guidelines to tune the deposit morphology to enhance the electrochemical performance of the 3D electrode based on nanostructured  $MnO_2$  films.

### Introduction

The development of autonomous miniaturized electronic systems is a major technological challenge in today's world<sup>1,2</sup>. To meet this challenge, various electrochemical energy storage devices are intensively explored to power the next generation of miniaturized Internet of Things (IoT) devices. To power small, connected sensors operating in a wireless network, proposed solutions include Lithium ion micro-batteries<sup>3–7</sup>, Zn-ion micro-supercapacitors<sup>8</sup>, carbon-based or pseudocapacitive micro-supercapacitors<sup>9–15</sup>, and micro-capacitors<sup>16–18</sup>. Among these options, micro-supercapacitors (MSCs) are a new type of electrochemical capacitors with limited surface footprint that can deliver energy at a low time constant ( $\tau \sim$ second), thus providing fast rate capability. However, such MSCs face the same challenges as regular larger electrochemical capacitors in terms of increasing energy density (here the energy per footprint area for MSC) while maintaining high power density<sup>1,2,19</sup>. Additionally, there is a challenge for MSCs in designing efficient microscale devices with restricted footprint (~ mm<sup>2</sup>). Two different approaches are being pursued to overcome these challenges. The first approach focuses on maximizing the electrode thickness moving from thin to thick films by using deposition sputtering<sup>20-24</sup>, magnetron techniques such as Atomic Layer Deposition<sup>25</sup>, electrophoretic deposition<sup>26</sup>, or electrochemical deposition<sup>27–29</sup>. The second approach involves designing 3D electrodes in which the electrochemical performance of the electroactive material is improved by the large volume to surface ratio of the 3D template or scaffold<sup>11,14,30–32</sup>. In this case, a conformal deposit of the active materials (thin films) should be produced by reliable and scalable deposition methods as demonstrated by V. De Andrade et al <sup>33</sup> in 2021 when a comparison was made between magnetron sputtering deposition and Atomic Layer Deposition of

Nb<sub>2</sub>O<sub>5</sub> films on 3D scaffold. Pulsed deposition techniques such as Atomic Layer Deposition<sup>34,35</sup> (a gas phase process) and pulsed electrodeposition<sup>36,37</sup> (a solution processing route) are well-suited for depositing conformal films on complex 3D scaffolds to produce micro-supercapacitor electrodes and devices with attractive electrochemical performance. The electrodeposition process of pseudocapacitive oxides<sup>11,14,32,38,39</sup> such as MnO<sub>2</sub> or RuO<sub>2</sub> is known to produce nanostructured materials in hydrous forms that could be used as efficient electrodes in MSCs. However, the electrochemical properties of 3D electrodes made by pulsed electrodeposition technique depend greatly on various deposition parameters such as: the deposition period (ON time), the rest period at open circuit (OFF time), cumulative deposition time, pH of the plating solution....

We hence conducted an investigation into the influence of deposition parameters on the morphology of MnO<sub>2</sub> nanostructured films and their corresponding electrochemical properties. In situ atomic force microscopy in liquid mode was used to study the growth mechanisms of MnO<sub>2</sub> films on planar substrates. Then 3D Silicon / platinum micro-tubes scaffold were used as substrates for conformal growth of MnO<sub>2</sub> films to enhance the performance of fabricated electrode. The deposits were investigated using Scanning Electron Microscopy and electrochemical characterization techniques. The thickness of the nanostructured film, opening of MnO<sub>2</sub> nanosheets, and thickness of the nanowalls were found to be modifiable by manipulating the deposition parameters. The impact of ON and OFF times during the pulsed electrodeposition of MnO<sub>2</sub> films was emphasized. By using the Volmer Weber Island growth mode, guidelines were established to tune the morphology of MnO<sub>2</sub> films for maximizing their electrochemical performance as efficient pseudocapacitive electrodes for 3D MSC.

### Methods

### Preparation of electrodes - fabrication of the 3D scaffold

3D electrodes with a surface area of 16 mm<sup>2</sup> were fabricated by micromachining a 3" silicon wafer ((100) oriented). A top down process was carried out to fabricate the 3D silicon scaffold by following two main steps: photolithography combined with deep reactive ion etching (DRIE) technique. The Bosch process (PlasmaPro Estrelas100 equipment) is an etching method consisting in alternating cycles of passivation and etching steps to produce high aspect ratio microstructures. In the present study, 3D electrodes based on vertically aligned silicon micro-tubes were fabricated. After removing the photoresist by  $O_2$  plasma in a PVA TEPLA equipment, a thin film of platinum (50 nm-thick) was deposited on the 3D silicon micro-tubes scaffold by atomic layer deposition (ALD) using a Beneq TFS 200 reactor and was further used as metal electrode for MnO<sub>2</sub> plating. For comparison purpose, planar silicon substrates were also coated by ALD with a 50 nm-thick Al<sub>2</sub>O<sub>3</sub> insulating layer and a platinum film (50 nm-thick).

## Preparation of electrodes - deposition of nanostructured MnO<sub>2</sub> films on planar substrate and 3D scaffold

The anodic deposition of  $MnO_2$  films resulted from the electrolysis of an aqueous plating solution obtained by dissolving 0.1 M  $MnSO_4$  in 0.1 M  $H_2SO_4$ . To identify the suitable potential for  $MnO_2$  anodic electrodeposition process, a linear sweep voltammetry was first carried out from open circuit potential (OCP) to 1.5 V *vs.* Ag/AgCl, using a platinum wire as counter electrode. From this experiment, it was determined that the highest oxidative potential while avoiding oxygen evolution reaction was close to 1.15 V *vs.* Ag/AgCl. To deposit conformal  $MnO_2$  films on planar

substrates as well as on 3D scaffolds, a potential-controlled pulsed deposition technique was selected as its efficiency has already been demonstrated<sup>36,37,39</sup>. The set-up for the pulsed potential deposition profile consisted in alternating a first step at 1.15 V *vs.* Ag/AgCl during a certain time,  $t_{ON}$ , with a second step at OCP during  $t_{OFF}$  (rest period).  $t_{ON}$  and  $t_{OFF}$  were optimized within the framework of the present study. The temperature of the electrolytic solution was kept constant at room temperature. The electrodeposition process was performed without any binder nor conductive additives. After the deposition, the electrode was rinsed with deionized water and dried under flowing N<sub>2</sub>.

The effect of pulse current parameters on the morphological and electrochemical properties of the MnO<sub>2</sub> thin films deposited on 3D Si-Pt microtubes was investigated by varying on-time (t<sub>ON</sub>, duration for the potential to be applied) and off-time (t<sub>OFF</sub>, rest time at OCP) to determine the optimal electrodeposition conditions. To achieve this goal, three series of experiments were carried out on 3D electrodes with the same footprint surface in a 50 mL plating solution of 0.1 M MnSO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> while stirring with a PTFE coated magnetic stirrer at 130 rpm. Platinum grid counter electrode, Ag/AgCl reference electrode and the silicon-based working electrode were vertically arranged keeping 1 cm spacing in between them. In the first series, ton was varied from 100 to 400 ms while  $t_{OFF}$  was kept constant at  $t_{OFF}$  = 500 ms. The OCP step for  $t_{OFF}$  was also set at 100 and 400 ms for samples in the second series while  $t_{ON}$  was kept at 500 ms. The last set of experiments was carried out at t<sub>ON</sub> = t<sub>OFF</sub>. In other words, pulse duty cycle ( $\theta$ ) was fixed in the last series at 50 %, where  $\theta$ =t<sub>ON</sub> / (t<sub>ON</sub>+t<sub>OFF</sub>). **Table 1** summarizes the parameters selected during experiments. All the experiments were set up for a total charge of 3000 mC cm<sup>-2</sup>. Samples were then rinsed with deionized water and dried under  $N_2$  at ambient temperature.

#### Morphological and electrochemical analyses

The growth mode of nanostructured MnO<sub>2</sub> films by pulsed electrodeposition technique was studied by scanning probe microscopy on planar surface. A Bioscope Atomic Force Microscope (AFM) from Bruker was used in contact mode to follow the growth process of manganese dioxide films on planar silicon substrate coated with a 50 nm-thick platinum film deposited by Atomic Layer Deposition. A nanostructured MnO<sub>2</sub> film was electrodeposited on top of the Pt film following the same deposition process as for the deposition on 3D Si-Pt microtubes scaffold.

These *in situ* AFM measurements were performed in a homemade electrochemical cell (**Figure 1a-b**), where a platinum wire was used as counter electrode, Ag/AgCl as reference electrode and the Pt on Si substrate as working electrode. In  $H_2SO_4$  / MnSO<sub>4</sub> (0.1 M / 0.1 M) plating solution, silicon nitride cantilevers with a constant stiffness of k ~ 0.58 N/m were used. Pulsed electrodeposition was achieved at various t<sub>ON</sub> and t<sub>OFF</sub> to investigate the evolution of the growth mechanism vs deposition parameters.

A Zeiss Supra scanning electron microscope (SEM) was used to characterize the morphologies of prepared  $MnO_2$  films. SEM observations were operated at 2 keV for all samples to measure the geometrical dimensions of Si microtubes and  $MnO_2$  film thickness.

To identify the crystalline structure of the as-deposited  $MnO_2$  thin film on Si /  $Al_2O_3$  / Pt planar substrate, X-ray diffraction (XRD) analysis were carried out by using Rigaku

Smartlab equipment with CuK $\alpha$  radiation source and Raman analyses by using Labram HORIBA instrument under UV light source ( $\lambda$  = 471 nm).

The electrochemical behavior of electrodeposited MnO<sub>2</sub> films was investigated by cyclic voltammetry (CV) using a Potentiotat / Galvanostat (VMP2) instrument from Biologic. A platinum wire with a diameter of 0.5 mm was used as counter electrode and Ag/AgCl served as reference electrode in a 5 M LiNO<sub>3</sub> aqueous electrolyte. The potential window was set between 0 V and 1 V vs Ag/AgCl.

### **Results and discussion**

# Investigation of the growth mechanism of electrodeposited nanostructured MnO2 films by *In situ* AFM analysis on planar substrate.

Electrochemical deposition is a powerful method to grow thin/thick films from an electrolytic plating solution directly onto planar or complex conductive substrates. The chemical and physical properties of electrodeposited materials such as morphology, electrical conductivity, porosity, adhesion... could be modified by adjusting deposition parameters. To take benefit from the surface developed by the 3D scaffold, the step-conformal deposition of nanostructured MnO<sub>2</sub> films on the 3D template is critical for maximizing the areal capacitance values. Continuous chronoamperometry or cyclic voltammetry technique performed from Mn<sup>2+</sup> solution such as proposed by S. W. Donne *et al* <sup>29</sup> or D.G. Nocera et al <sup>40</sup> were widely studied for the deposition of nanostructured MnO<sub>2</sub> thin films on flat conductive substrates. However, such continuous deposition methods are not well-suited techniques for depositing conformal MnO<sub>2</sub> films on complex conductive 3D scaffolds. To achieve this goal,

pulsed anodic electroplating from Mn<sup>2+</sup> solution was investigated as a method for depositing homogeneous, porous nanostructured MnO<sub>2</sub> films on 3D templates<sup>39</sup>. The areal capacitance of resulting 3D pseudocapacitive MnO<sub>2</sub> electrodes can be maximized if the deposited MnO<sub>2</sub> layer conforms to the shape of the 3D scaffold<sup>12,14,39</sup>. The growth mechanism<sup>36</sup> of the pulsed electrodeposited MnO<sub>2</sub> film is influenced by various deposition parameters, which can be adjusted to control the film morphology and thus its related electrochemical properties.

The design of the fabricated 3D scaffolds presents a challenge in the electrodeposition process due to the thickness of the deposited films, and thus the size of grain grown, that can be achieved between two micro-tubes. To overcome this limit, it is critical to control the growth of MnO<sub>2</sub> film to ensure a conformal deposit with homogeneous composition and thickness. Improper control may result in overgrowth of MnO<sub>2</sub> films at the top of the 3D structures, leaving the bottom of the micro-tubes uncovered. Hence, it is important to control the nucleation of MnO<sub>2</sub> crystallites as well as the grain growth at the scaffold surface, and to observe the grain coalescence mechanism of nanostructured manganese dioxide films as a function of the deposition time, *i.e.* the film thickness. The present study begins by electrodepositing nanostructured MnO<sub>2</sub> films on a planar silicon substrate coated with a 50 nm-thick platinum layer serving as a current collector. Once optimized the growth of nanostructured MnO<sub>2</sub> films on planar substrate, the pulsed electrodeposition of MnO<sub>2</sub> layers on 3D scaffold was processed to check the conformality of the resulting nanostructured MnO<sub>2</sub> films. Based on the test setup described in **figure 1a-b**, linear sweep voltammetry (LSV) at 1 mV.s<sup>-1</sup> scan rate was performed in MnSO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> solution (0.1 M / 0.1 M) to determine the appropriate potential for oxidizing Mn<sup>2+</sup> cations to form a MnO<sub>2</sub> deposit. Based on the LSV shown

in figure 1c, the deposition potential was set to 1.15 V vs Ag/AgCl. Atomic Force Microscopy (AFM) is a widely used nanoimaging technique that has also been applied to the study of materials for electrochemical energy storage applications<sup>41,42</sup>. In the present study, the electrochemical growth mechanism of MnO<sub>2</sub> film was investigated in situ using AFM on planar a Si/Pt substrate operated in aqueous solution. The evolution of the nanostructured MnO<sub>2</sub> morphology was probed at the nanoscale versus the duration of electrodeposition pulse (ton parameter) from a MnSO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> plating solution. The potential of the WE was set at 1.15 V vs Ag/AgCl during t<sub>ON</sub>, and relaxed to open circuit potential (OCP) during t<sub>OFF</sub> which was set at 2000 ms. The t<sub>OFF</sub> was set sufficiently long to allow the re-homogenization of the plating solution at the electrode/solution interface before the next oxidation pulse, preventing depletion of Mn<sup>2+</sup> ions close to the metallic surface and avoiding a diffusion-controlled deposition reaction. Two ton values (500 ms and 1000 ms, figure 1d-e) were tested and the results are reported in figure 2. For each t<sub>ON</sub> duration, a movie showing the formation of manganese dioxide films under AFM imaging is available in supplementary information section. The AFM top surface images showed that MnO<sub>2</sub> film was electrodeposited through a Volmer-Weber island growth process<sup>29</sup>. Dynamic AFM nanoimaging revealed new insights into the mechanism of nucleation of manganese dioxide on a platinum-coated silicon substrate. The roughness analysis of the MnO<sub>2</sub> films deposited with two different t<sub>ON</sub> is depicted in figure 2a, with two different regimes corresponding to two different growth mechanisms being evidenced. The competition between these two growth mechanisms influences the grain size of the deposited particles and therefore, MnO<sub>2</sub> film morphology. The ton parameter was found to be crucial for controlling the kinetics of the growth mechanism, particularly if deposition on a 3D complex scaffold is desired, as it has a significant influence on current distribution and grain size.

The slope change of the curves determines the threshold time that separates the nucleation / grain growth phase from the coalescence stage. This threshold time ( $\tau_{th}$ ) is dependent on the  $t_{ON}$  parameter with  $\tau_{th} \sim 375$  s for  $t_{ON} = 1000$  ms and  $\sim 1500$  s for  $t_{ON} = 500$  ms. Regardless of the length of  $t_{ON}$ , both nucleation and grain growth mechanisms in the Volmer-Weber mode are observed prior to  $\tau_{th}$ . Once deposition time reaches  $\tau_{th}$ , the slope of the plot changes, indicating a significant increase in roughness value due to grain coalescence during the electrodeposition process. Indeed, that the Volmer Weber Island growth mode is an "ideal" model to explain the growth of electrodeposited film based on simple redox reactions, but the electrodeposition of manganese dioxide is a more complex reaction involving a large number of chemical and electrochemical steps<sup>29</sup>.

The grain coalescence regime results in the formation of a continuous  $MnO_2$  film. For a  $t_{ON} = 1000 \text{ ms} (\tau_{th} \sim 375 \text{ s})$ , the roughness of the  $MnO_2$  film is about 23 nm after 500 s deposition time. For a shorter  $t_{ON}$  (500 ms), the threshold is shifted approximately to 1500 s, with a corresponding roughness of about 3 nm after ~ 1800 s. These observations suggest that to achieve a smooth  $MnO_2$  film with low roughness, it is important to maintain a short  $t_{ON}$  to promote the nucleation / grain growth regime rather than rapid coalescence of  $MnO_2$  particles. The  $t_{ON}$  parameter can be adjusted to modify the threshold time  $\tau_{th}$  and limit the roughness of the film by shifting the coalescence phase. Once the Pt surface is covered by enough  $MnO_2$ crystallites, no additional nucleation is observed, and the existing crystallites continue to grow and merge progressively, forming a smoother surface. Long  $t_{ON}$  values result in the rapid formation of large MnO<sub>2</sub> particles. **Figure 2b** depicts the MnO<sub>2</sub> granular deposit after three electrodeposition durations (5, 200 and 500 s, respectively) and demonstrates the growth and coalescence of three MnO<sub>2</sub> grains to form a large MnO<sub>2</sub> cluster as the electrodeposition progresses. The  $t_{ON}$  and  $t_{OFF}$  times were set to 1000 ms and 2000 ms, respectively. At this  $t_{ON}$  time parameter, the height of the grain in the direction normal to the substrate (h) as well as the Full-Width at Half-Maximum of the grains / cluster (FWHM, diameter of the grain at half maximum) increased rapidly (**figure 2c**). After 500 s of electrochemical deposition, h and FWHM reached 60 nm and 250 nm, respectively. The spacing between two micro-tubes is approximately 1000 nm and the formation of large clusters can quickly clog the void, resulting in heterogeneous and non-conformal deposits that can significantly decrease the areal capacitance values of the corresponding 3D electrodes. Thus, to ensure the conformal deposition of MnO<sub>2</sub> films on 3D scaffolds, the formation of such large clusters should be avoided.

This study aimed to investigate the growth mechanism of electrodeposited  $MnO_2$  film by *in situ* AFM. Our results indicate that longer  $t_{ON}$  times promote the formation of larger  $MnO_2$  particles. This finding led us to define the limits for investigating the effects of the pulse parameters ( $t_{ON}$  and  $t_{OFF}$ , both within the range of 100 – 500 ms) on the electrodeposition process to optimize the areal capacitance values of 3D micro-supercapacitors based on nanostructured  $MnO_2$  films deposited on Si-Pt micro-tubes scaffold. Thus, the  $t_{ON}$  parameter should not exceed 500 ms to achieve a conformal  $MnO_2$  film deposition on 3D silicon micro-tubes scaffolds.

Influence of the pulse parameters ( $t_{ON}$  and  $t_{OFF}$ ) on the electrodeposition process of 3D MnO<sub>2</sub> electrodes The 3D Si / Pt scaffold fabricated in this study is presented in figure 3. Scanning Electron Microscope images and top view analyses

(**figure 3a-b**) were used to measure the geometric dimensions of the scaffold (outer diameter = 3  $\mu$ m, inner diameter = 1  $\mu$ m, spacing = 1  $\mu$ m, outer depth = 27  $\mu$ m), yielding an estimated Area Enhancement Factor (AEF) of 25. This results in a developed surface of about 100 mm<sup>2</sup> (= 25 x 4 mm<sup>2</sup>), taking into account the 2 mm x 2 mm footprint area of the electrode. Conformal MnO<sub>2</sub> thin films were deposited onto 3D conductive scaffolds using a pulsed current electrodeposition technique from MnSO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> solution at a potential of 1.15 V vs Ag/AgCI (~ 150 nm thickness for a total charge of 3000 mC cm<sup>-2</sup>).The film thickness (discussed later and presented in **figure 6a**) was kept constant from top to bottom (**figure 3d**), resulting in a homogenous MnO<sub>2</sub> film with a sand-rose morphology (Figure 3c), as seen in the top view of the film deposited with t<sub>ON</sub> = 500 ms and t<sub>OFF</sub> = 100 ms. This demonstrates the efficiency of the pulsed electrodeposition process in depositing conformal MnO2 films onto the Si/Pt micro-tubes.

The structural analyses were carried out using grazing incidence X-Ray Diffraction combined with Raman spectroscopy at room temperature. Figure 4a displays the diffractogram with the diffraction peaks (201), (111), (211) and (221) at 37.01°, 39.79°, 42.12° and 56.09°, respectively, which are associated to Ramsdellite MnO<sub>2</sub> polymorph<sup>43</sup>. The results were further confirmed by Raman spectroscopy. figure 4b shows the Raman spectrum (RS) of the sample, which demonstrates that all noticeable peaks belong to MnO<sub>2</sub> and correspond to the intrinsic vibration modes of MnO<sub>2</sub> within the range of 200-700 cm<sup>-1</sup>. Four major peaks were identified as v<sub>1</sub> to v<sub>4</sub>. The peak at 580 cm<sup>-1</sup> is assigned to the Mn-O vibration along the chains of MnO<sub>2</sub> framework and has been assigned to Ramsdellite by C. Julien *et al*<sup>44</sup> <sup>44</sup>.Table 1 summarizes the deposition conditions for the various samples prepared during this study using pulsed electrodeposition of MnO<sub>2</sub>. The total charge was kept constant at

3000 mC cm<sup>-2</sup> across the series. SEM analyses (top view images) in figure 5 and figure S1 demonstrate how the morphology of MnO<sub>2</sub> films can be modified by the deposition parameters. Obvious discrepancies between the samples emphasize the impact of the ON and OFF time parameters, with differences observed in the length of the MnO<sub>2</sub> nanosheets leading to nanostructured films with either open or dense morphology. Sample E3, for example, shows quite long nanosheets arranged perpendicular to the top surface of the Si / Pt microtube thus showing rather large cavities between them, unlike sample E4 which exhibits guite short MnO<sub>2</sub> nanosheets organized in a very dense network. For the first batch, increasing ton while keeping toFF constant at 500 ms results in wider open morphologies generated by MnO2 nanosheets. A too short toon, below 250 ms, leads to limited capacitance values as shown by the related cyclic voltammograms, when t<sub>OFF</sub> is kept at 500 ms (figure 5b). The best areal capacitance value (240 mF cm<sup>-2</sup> at 2 mV s<sup>-1</sup>) can be tentatively assigned to the well-organized open morphology for sample E3. In the second batch, there is also an optimum for t<sub>OFF</sub> when t<sub>ON</sub> is kept constant at 500 ms. The highest capacitance (227 mF cm<sup>-2</sup> at 2 mV s<sup>-1</sup>) is obtained for a sample (E5) with a dense morphology, unlike the sample with the highest capacitance in the first batch (E3) with an open morphology (figure 5b). The MnO<sub>2</sub> deposits in the second batch appear smoother in SEM top view images (figure 5a) than those in the first batch. For the third batch, the E8 sample with a  $t_{ON} = t_{OFF} = 300$  ms, exhibits a larger open morphology. While the nanostructured shapes of E7 and E9 samples are similar to those from the second batch (similar capacitance values, figure 5c-d), sample E8 (similar open structure as sample E3) also shows an improved areal capacitance value (240 mF cm<sup>-2</sup> at 2 mV s<sup>-1</sup>) as compared to samples with similar nanostructured shapes (E4, E5, E6, E7 and E9). These capacitance values are in good agreement with those previously reported by our team<sup>12,14,39</sup>.

These results are summarized in **figure 6**. As the total charge is integrated over the  $t_{ON}$  and  $t_{OFF}$  periods, all the samples are assumed to contain the same amount of  $MnO_2$ , disregarding any potential side reactions, such as oxygen evolution reaction, that may have occurred during anodic deposition. It is hypothesized that thicker  $MnO_2$  deposits correspond to the films with more open morphologies and a greater volume of void. Thicknesses measured from SEM images for the three batches of samples are plotted in **figure 6a**, but it is challenging to observe a clear trend. However, the two samples with a thickness of 425 nm exhibit the highest capacitance (240 mF cm<sup>-2</sup> at 2 mV s<sup>-1</sup>). Deposits that are either thicker or thinner lead to lower capacitance values, suggesting that there is an optimal morphology of the  $MnO_2$  films.

The capacitance decay with increasing scan rate is presented in **Figure 6b**. It can be pointed out that the samples with the highest capacitances (E3, E5, and E8) retained a greater portion of their capacitance at 100 mV s<sup>-1</sup>, i.e. 70% of the capacitance measured at 2 mV.s<sup>-1</sup>. Samples with average capacitance values (~ 150-188 mF cm<sup>-2</sup> at 2 mV.s<sup>-1</sup>) retained about 65% of their capacitance at 100 mV.s<sup>-1</sup>, while samples (E1, E2) with the lowest capacitance only retained 50% of it at 100 mV.s<sup>-1</sup>.

The fundamental electrokinetic mechanisms controlling an electrodeposition process are nucleation and growth of crystal grains. The SEM analysis and electrochemical characterizations of nanostructured  $MnO_2$  films, suggest that in the 1<sup>st</sup> batch, the shape of  $MnO_2$  film is primarily controlled by the growth process, leading to larger nanosheets as compared to the 2<sup>nd</sup> batch. Electrochemically, the long t<sub>OFF</sub> period

provides sufficient time for the  $Mn^{2+}$  cations to diffuse near the surface, allowing for the regeneration of the diffusion layer and preferential incorporation of  $Mn^{2+}$  cations into existing crystallites during the oxidation process to  $Mn^{4+}$ ).

This results in a dense structure with slower renewal of  $Mn^{2+}$  species near the surface and preferential creation of new crystallites due to the high  $t_{ON}$  and low  $t_{OFF}$  period.

In the samples of the 2<sup>nd</sup> batch, small grains are observed suggesting that nucleation is favored over growth. This results in a dense structure with slower renewal of  $Mn^{2+}$  species near the surface and preferential creation of new crystallites due to the long  $t_{ON}$  and low  $t_{OFF}$  periods.

### Conclusions

The growth of nanostructured  $MnO_2$  film as efficient pseudocapacitive electrodes for 3D micro-supercapacitors was studied using a combination of *in situ* Atomic Force Microscopy, Scanning Electron Microscopy and electrochemical analyses.

The AFM top surface images showed that the  $MnO_2$  film was electrodeposited (pulsed electrodeposition process) through a Volmer-Weber island growth process. The *in situ* AFM analysis revealed that a lower ON time of less than 500 ms promotes the nucleation and grain growth processes rather than grain coalescence, leading to smooth films on planar Si / Pt substrates. As such, no large grain would be promoted when depositing  $MnO_2$  film on 3D Si / Pt scaffold with ON time lower than 500 ms.

The second part of this study examined the impact of ON and OFF times on the  $MnO_2$  film properties. With  $t_{ON} < 500$  ms, all the tested conditions (9 samples) produced conformally deposited  $MnO_2$  films on 3D Si / Pt micro-tubes scaffolds. Nevertheless, it was important to dismiss the role of the ON and the OFF times on the  $MnO_2$  properties. The electrodeposition process is controlled by the nucleation and growth of crystal grains with large tOFF promoting the growth of large nanosheets rather than germination of small cristals. In contrast, high  $t_{ON}$  and low  $t_{OFF}$ , are promoting small grains from germination preferentially to growth. The resulting dense structure limits the thickness of the  $MnO_2$  films and thus the pseudocapacitance value. This study defined trends that could be followed to optimize the electrodeposition process of  $MnO_2$  films on 3D scaffolds for high performance micro-supercapacitors.

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### **Competing interests**

Authors declare no competing interests.

### Materials & Correspondence

Correspondence to Christophe Lethien, Frédéric Favier & Thierry Brousse.

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### List of the figure captions



**Fig. 1** | Test setup used to monitor the growth of electrodeposited  $MnO_2$  films by Atomic Force Microscopy in aqueous solution. **a.** AFM microscope positioned in the homemade test cell. The working electrode (WE) consists in a 50 nm-thick platinum film deposited on a planar silicon wafer. An Ag/AgCl and a platinum wire are used as the reference and the counter electrodes respectively. **b.** The WE is sandwiched between two half cells (stainless steel bottom cell and Teflon-like top cell). The tank is filled with a small quantity of MnSO<sub>4</sub> (0.1 M) / H<sub>2</sub>SO<sub>4</sub> (0.1 M) electrolyte. **c.** Linear Sweep Voltammetry performed in MnSO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> electrolyte at 1 mV s<sup>-1</sup>. **d.** Pulsed electroplating technique is applied on the WE to deposit nanostructured porous MnO<sub>2</sub> films. Evolution of the potential (vs Ag/Ag/Cl) and the current vs the deposition time taking t<sub>ON</sub> = 1000 ms. **e.** Evolution of the current at two different t<sub>ON</sub>.



**Fig. 2 | a.** Increase of the roughness (2  $\mu$ m x 2  $\mu$ m scanning area) as a function of the deposition time for two different t<sub>ON</sub> (t<sub>ON</sub> = 1000 ms & t<sub>ON</sub> = 500 ms) while keeping t<sub>OFF</sub> at 2000 ms. **b.** AFM top surface images illustrating the formation of MnO<sub>2</sub> clusters occurring during the electrodeposition process at t<sub>ON</sub> = 1000 ms. **c.** Increase of the height (h) and full-width at half maximum (FWHM) vs the deposition time (t<sub>ON</sub> = 1000 ms).



Fig. 3 / SEM top view (a) and cross sectional (b) images of Si / Pt 3D scaffold <u>before</u> the electrochemical deposition of porous  $MnO_2$  films. SEM top view (c) and cross

sectional (d) images of Si / Pt /  $MnO_2$  3D electrodes <u>after</u> the electrochemical deposition of nanostructured  $MnO_2$  films.

Experiment	On-time (ms)	Off-time (ms)	Pulse duty cycle (%)	$t_{on}/t_{off}$	Pulse periode (ms)	Specific capacitance (mF cm <sup>-2</sup> )
Series 1						
E1	100	500	16,66	0,2	600	75
E2	250	500	33,33	0,5	750	85
E3	400	500	44,44	0,8	900	240
Series 2						
E4	500	100	83,33	5	600	150
E5	500	250	66,66	2	750	227
E6	500	400	55,55	1,25	900	186
Series 3						
E7	100	100	50	1	200	180
E8	300	300	50	1	600	240
E9	500	500	50	1	1000	188

**Table 1**: Pulse electrodeposition parameters of the samples.



**Fig. 4** / Structural analyses of planar nanostructured MnO<sub>2</sub> films obtained by pulsed electrodeposition method. **a.** X-ray diffraction pattern obtained by grazing incidence technique. **b.** Raman scattering spectrum of the as-prepared MnO<sub>2</sub> thin film measured on a planar Si / Pt substrate.



**Fig. 5** / **a.** SEM top view images of  $MnO_2$  thin films electrodeposited on 3D Si / Pt scaffold for series 1 (fixed  $t_{OFF}$ ), series 2 (fixed  $t_{ON}$ ) and series 3 ( $t_{ON} = t_{OFF}$ ). **b-d.** CV plots illustrating the electrochemical performance of  $MnO_2$  depending on  $t_{ON}$  and  $t_{OFF}$  parameters (**a.** series 1, **b.** series 2 and **c.** series 3).



**Fig. 6** | Illustration of the ON and OFF times effects on the films morphology and surface capacitance values. **a.** Evolution of the film thickness. **b.** Analysis of the surface capacitance vs the sweep rate for the 3D MnO<sub>2</sub> electrodes optimized vs the electrodeposition parameters.

### **Supplementary Informations**

**Figure S1** - SEM top view images of  $MnO_2$  thin films electrodeposited on 3D Si / Pt scaffold for series 1 (fixed  $t_{OFF}$ ), series 2 (fixed  $t_{ON}$ ) and series 3 ( $t_{ON} = t_{OFF}$ ).

**Movie S1** – *In situ* AFM nanoimaging Movie illustrating the nucleation / grain growth and coalescence phases occurring during the electrodeposition process used for  $MnO_2$  films deposited at  $t_{ON} = 500$  ms

**Movie S2** – *In situ* AFM nanoimaging Movie illustrating the nucleation / grain growth and coalescence phases occurring during the electrodeposition process used for  $MnO_2$  films deposited at  $t_{ON} = 1000$  ms