

Cite this: *RSC Adv.*, 2017, 7, 32038

Received 20th April 2017

Accepted 15th June 2017

DOI: 10.1039/c7ra04481j

rsc.li/rsc-advances

Electrodeposition: a versatile, efficient, binder-free and room temperature one-step process to produce MnO₂ electrochemical capacitor electrodes†

R. Della Noce,^{id}*^a S. Eugénio,^a T. M. Silva,^{ab} M. J. Carmezim^{ac} and M. F. Montemor^a

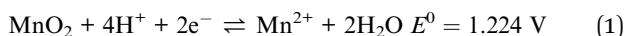
The use of room temperature cathodic electrodeposition to produce MnO₂ electrochemical capacitor electrodes is demonstrated. By employing a permanganate-based bath, birnessite-type MnO₂ electrodes are directly obtained with no further heat treatment. Moreover, a crystalline/amorphous structural transition is observed as the applied current density is increased up to 50 mA cm⁻².

1. Introduction

Manganese oxides are multifunctional materials that display a myriad of applications in advanced catalysis,¹ Li-ion rechargeable batteries,^{2,3} microbial fuel cells,^{4,5} and electrochemical capacitors.^{6,7} They have been produced by a variety of chemical and physical methods such as hydrothermal synthesis,⁸ sol-gel process,⁹ physical vapor deposition (PVD),¹⁰ chemical vapor deposition (CVD),¹¹ and electrodeposition.¹² Among these techniques, electrodeposition has stood out mainly owing to its cost-effectiveness, relatively low temperature operating conditions, lower energy and space requirement, and easily maintained equipment. In fact, Dini showed that PVD processes may be as much as ten times more costly than electrodeposition.¹³ Electrodeposition also allows the deposition of the active material directly on the current collector, eliminating the need for binders and extra-process steps. Furthermore, thickness, and structural and morphological properties of the deposits can be tailored by relatively simple parameters such as potential, current density, bath concentration, pH, and temperature.

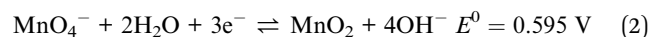
The fabrication of electrodeposited manganese oxides, in particular MnO₂, has been demonstrated by two main routes:^{6,14}

(1) Anodic deposition: by employing sulfate-, nitrate or acetate-based baths according to the following reaction:

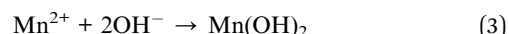


where Mn(II) ions are oxidized to Mn(IV) species leading to the formation of the manganese dioxide. Note that the reaction is

written in the reverse way since the standard reduction potential is shown.¹⁵ (2) Cathodic electrodeposition: one-step deposition from permanganate (MnO₄⁻) bath:



where Mn(VII) ions are directly reduced to Mn(IV) species. Besides these two purely electrochemical approaches, another commonly employed in literature involves a cathodic deposition step plus a chemical one. By applying potential or current from nitrate- or acetate-based bath manganese hydroxide is initially formed as follows:



After subsequent heat treatment, which in general is done at about 300 °C,¹⁶ to dehydrate the manganese hydroxide, MnO₂ is finally obtained.

In this work, the use of room temperature cathodic electrodeposition to produce MnO₂ electrochemical capacitor (EC) electrodes is reported. By employing permanganate (MnO₄⁻)-based bath, birnessite-type MnO₂ electrodes are directly obtained with no further heat treatment. Although, some papers have described the production of MnO₂ EC electrodes by this method,^{12,14,17} as far as we know, the influence of the applied current density on the structure and capacitive performance of MnO₂ electrodes has not yet been described. Here, it is demonstrated by means of X-ray diffractometry (XRD) that a crystalline/amorphous structural transition is observed as the applied current density is increased up to 50 mA cm⁻².

2. Experimental

2.1. MnO₂ electrodeposition

MnO₂ was galvanostatically electrodeposited onto stainless steel (AISI 304, Goodfellow) from a bath composed of 0.01 M KMnO₄ and 0.1 M Na₂SO₄. The bath pH was set to 7 by adding

^aCentro de Química Estrutural-CQE, Department of Chemical Engineering, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal. E-mail: rodrigo.noce@tecnico.ulisboa.pt

^bDepartment of Mechanical Engineering, GI-MOSM, Instituto Superior de Engenharia de Lisboa, 1950-062 Lisboa, Portugal

^cESTSetúbal, Instituto Politécnico de Setúbal, 1959-007 Setúbal, Portugal

† Electronic supplementary information (ESI) available: SEM images and XRD. See DOI: 10.1039/c7ra04481j



dilute NaOH. Analytical grade chemicals were used to prepare all solutions. The MnO_2 deposits were obtained by using a Gamry Interface 5000E potentiostat/galvanostat at room temperature. A three-electrode conventional cell was used for all electrochemical experiments. The applied current density (i_c) was varied from 0.5 up to 50 mA cm^{-2} maintaining the same charge density (2 C cm^{-2}). The mass of MnO_2 deposits was directly measured using an electronic microbalance (Sartorius, model MC 5 $d = 0.01/0.1 \text{ mg}$). The mass loading of the active material was obtained in all cases by subtracting the substrate mass from the total weight. In general, the mass loading of the deposits ranged from 0.3 to 1.45 mg .

2.2. Morphological and structural characterization

The morphology of the deposits was characterized by scanning electron microscopy (SEM) using a JEOL model JSM-7001F field emission gun SEM equipped with energy dispersive X-ray spectroscopy (EDX). The X-ray diffractometry (XRD) measurements were performed using Cu K α radiation (1.5418 \AA) in a Bruker AXS D8 Advance instrument at $0.002^\circ \text{ s}^{-1}$ scan rate, a slow scan rate to avoid peak widening. Raman spectra were acquired (Horiba LabRAM HR800 Evolution) using the radiation source with a solid-state laser operating at 532 nm with an output power of 20 mW. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. The spectra were collected between 200 and 800 cm^{-1} with the sample exposed to the air under ambient conditions and obtained with an acquisition time of 30 s and 15 accumulations. A spectrograph with a 600 lines per mm grating was used. A 50 times objective lens focused the laser beam on the sample surface.

2.3. Electrochemical characterization

The electrochemical performance of MnO_2/SS electrodes was assessed by cyclic voltammetry (CV) and chronopotentiometry (charge–discharge curves). A platinum plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All the experiments were performed in freshly prepared 1 M Na_2SO_4 electrolyte at room temperature. Charge–discharge curves were conducted in a potential range from -0.1 to 0.9 V applying a specific current of 1 A g^{-1} . Furthermore, a long-term cycling test constituted of 5000 cycles at 5 A g^{-1} was carried out to verify the MnO_2/SS electrode ($i_c = 50 \text{ mA cm}^{-2}$) stability. No conditioning was performed prior to the long-term cycling test.

3. Results and discussion

Fig. 1 displays the potential vs. time ($E \times t$) profiles for the galvanostatic electrodeposition of MnO_2 onto SS by applying different current densities in the range 0.5 to 50 mA cm^{-2} . The potential increases with i_c , reaching a maximum of about 5 V at $i_c = 50 \text{ mA cm}^{-2}$. When $i_c = 0.5 \text{ mA cm}^{-2}$, no MnO_2 deposition takes place and then, it can be inferred that MnO_2 is only formed for higher i_c values.

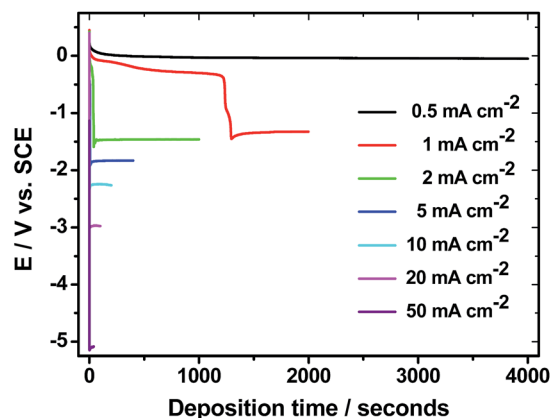


Fig. 1 $E-t$ profiles for the electrodeposition of MnO_2 onto SS by applying different applied current densities. Total charge density: 2 C cm^{-2} .

By using Faraday's law of electrolysis, it is possible to estimate the global current efficiency of the MnO_2 electrodeposition process as follows:¹⁸

$$m = QM/(Fz) \quad (4)$$

where m is the expected mass of MnO_2 deposit, Q (Coulombs) is the total quantity of electric charge for the MnO_2 electrochemical deposition, F is the Faraday constant which is equal to 96485 C mol^{-1} , M (g mol^{-1}) is the molecular weight of MnO_2 and z is the number of electrons transferred from Mn^{2+} to Mn^{4+} . As the mass of the deposits is known, the current efficiency of the MnO_2 electrochemical process can be calculated as summarized in Table 1.

As expected, increasing i_c leads to a decrease of the current efficiency due to the increase of hydrogen evolution reaction. The deposit obtained at 1 mA cm^{-2} shows a current efficiency close to 100%. In fact, in industrial electroplating processes, a high current efficiency is always desirable in order to minimize the electricity consumption. Considering the MnO_2 density as 5.03 g cm^{-3} , the deposits thickness can be also obtained (Table 1). For the same reason, *i.e.* hydrogen evolution reaction, the deposits thickness decreases as i_c increases, ranging from *ca.* $1.2 \text{ }\mu\text{m}$ to 250 nm . Nevertheless, for these

Table 1 Current efficiency (CE) and thickness of MnO_2 deposits obtained by modulating the applied current density in the range 1–50 mA cm^{-2} . The thickness of the MnO_2 deposits was estimated by taking into account the MnO_2 density (5.03 g cm^{-3}) and also by SEM images of the cross-section of the MnO_2 deposits. Total charge density: 2 C cm^{-2}

$i/\text{mA cm}^{-2}$	Deposited mass/mg	CE/%	Thickness/ μm	Thickness (SEM)/ μm
1	1.45	96.6	1.15	—
2	1.05	69.9	0.83	6.4
5	0.80	53.3	0.64	3.9
10	0.65	43.3	0.52	2.3
20	0.50	33.3	0.40	2.0
50	0.30	20.0	0.25	0.9



thicknesses calculations is assumed that the formed films are not porous which is not verified when SEM images (Fig. 2 and 3) are analyzed. For this reason, cross-section SEM images of the MnO_2/SS electrodes have been performed to obtain more realistic values of the deposits thickness, which are also displayed in Table 1. In this case, the values of thickness range from approximately 6.4 to 0.9 μm for the deposits obtained at $i_c = 2$ and 50 mA cm^{-2} , respectively. These values are different from those previously obtained from MnO_2 density consideration and can be explained based on the porosity of the deposits. The same trend, *i.e.* the deposits thickness decreases as i_c increases, is observed in the case of the thicknesses estimation by cross-section SEM images of the MnO_2/SS electrodes. If thicker films are desirable, porous substrates can be employed. Indeed, Su and Zhitomirsky¹⁹ have recently demonstrated that MnO_2 electrodes with mass loading of 13 mg cm^{-2} can be successfully electrodeposited by utilizing a porous Ni plaque as substrate. Most of works related to MnO_2 and other ECs electrodes has been devoted to obtain high mass loadings (on the order of 10 mg cm^{-2})²⁰ materials required for commercial applications, nevertheless, thin films EC electrodes technology has successfully emerged in last decades. In this sense, electrodeposited thin films electrodes have been utilized in semiconductor devices, integrated circuit fabrication, and multilayer ceramic substrates. In these cases, it is difficult to obtain large specific capacitance (SC) values (*e.g.* > 0.1 mF cm^{-2}) with electrostatic capacitor technology but quite easy with using EC technology. Voltage in such circuits is relatively low in which an aqueous electrolyte device as a single cell, especially if of the asymmetric

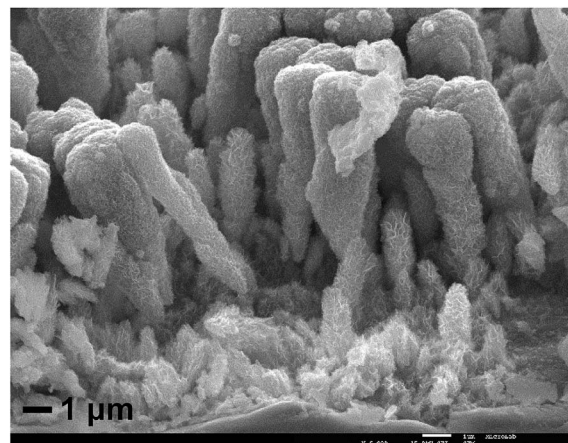


Fig. 3 Cross-section SEM image of MnO_2/SS electrode obtained at 2 mA cm^{-2} .

design, will have sufficient operating voltage. In addition, the most popular process nowadays used to make EC electrodes (both in laboratory and in industry) is slurry coating, which is limited in its minimum thickness to the size of particles in the slurry, typically 1 to 5 micrometers. By employing electrodeposition, much thinner electrodes, even approaching few nanometers thickness, can be obtained. Therefore, electrodeposition can be considered as an efficient and versatile technique to produce either thin or thick MnO_2 EC electrodes by simply modulating the applied current density. In order to analyze the morphology of MnO_2/SS electrodes, scanning microscopy electron (SEM) has been employed. Fig. 2 depicts the top-view SEM images of MnO_2 electrodeposits obtained at various i_c . Microspheres are noticed along the whole deposit which are indeed composed of nanoflakes, as shown in Fig. 1S,† under high magnification. In fact, MnO_2 nanoflakes electrodes have been obtained by anodic electrodeposition as recently reported by Mai *et al.*²¹ Moreover, it is clear that a grain refinement occurs as i_c increases leading to the formation of reduced grains at higher i_c values (see Fig. 2S in ESI†).

As mentioned above, cross-section SEM images have been acquired in order to estimate the deposits thickness. Fig. 3 illustrates the cross-section SEM image of MnO_2/SS electrode obtained at 2 mA cm^{-2} . The average thickness in this case is about 6.4 μm . The average thickness values for the deposits obtained in the range 2–50 mA cm^{-2} are listed in Table 1.

XRD and Raman Spectroscopy have been utilized to determine the structure of the MnO_2/SS electrodes. Fig. 4a shows the XRD patterns of MnO_2/SS electrodes obtained for i_c values in the range 1–50 mA cm^{-2} . The samples obtained at $i_c < 20 \text{ mA cm}^{-2}$ exhibit two main peaks at 12.4° and 24.8°, and one broad peak at 36.9° which correspond to (001), (002) and (020) planes of the $\delta\text{-MnO}_2$ (JCPDS no. 18-0802) confirming the Na-birnessite structure formation.^{12,22} It is important to highlight that the Na-birnessite structure, obtained in this work, is only stabilized by the presence of Na^+ cations which is present in the electrochemical bath. If no Na_2SO_4 is initially present, amorphous electrodeposits are achieved as illustrated in Fig. 3S,† for

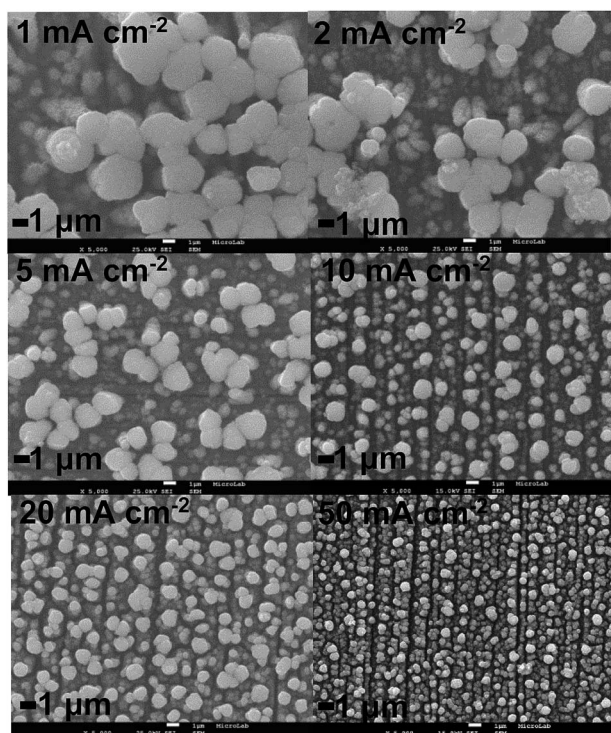


Fig. 2 Top-view SEM images of MnO_2/SS electrodes obtained at various i_c .



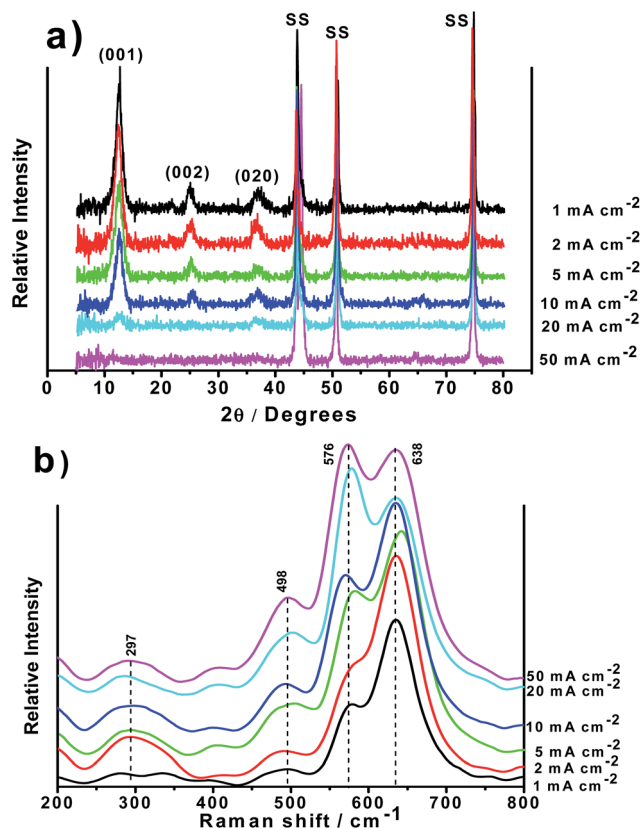


Fig. 4 XRD patterns (a) and Raman spectra (b) of birnessite-type MnO_2/SS electrodes obtained at various i_c .

a sample prepared under the same conditions except the Na_2SO_4 addition to the bath. This observation is in full agreement with the work reported by Tanimoto *et al.*¹² that obtained K-birnessite MnO_2 electrodes from a MnO_4^- -based bath containing K^+ ions. In addition, the XRD patterns show an amorphous (absence of long range order) state for the samples obtained at $i_c = 20$ and 50 mA cm^{-2} . This is attributed to the effect of grain refinement (decreased particle size) as i_c increases, as confirmed by SEM analysis (Fig. 2), which leads to diffraction peak broadening that, ultimately, are not detectable anymore by XRD. The crystalline or amorphous nature of the electrodeposited materials might influence the capacitive performance of the electrodes as will be described below. With regard to the Raman spectra, depicted in Fig. 4b, four major vibrational features corresponding to MnO_2 are observed at 297, 498, 576 and 638 cm^{-1} . The band at 576 cm^{-1} is related to the Mn–O stretching vibration in the basal plane of $[\text{MnO}_6]$ sheets while the band located at 638 cm^{-1} is attributed to the symmetric Mn–O stretching vibration of MnO_6 groups.²³ The bands at 297 and 498 cm^{-1} are of weak intensity as previously reported by Julien *et al.*,²³ and may not be visible depending on the preparation method.

The capacitive performance of the prepared MnO_2/SS electrodes has been analyzed by cyclic voltammetry and chronopotentiometry (charge–discharge curves) in $1 \text{ M Na}_2\text{SO}_4$ solution. Fig. 5a exhibits the cyclic voltammograms (CVs) of the different MnO_2/SS electrodes in $1 \text{ M Na}_2\text{SO}_4$. All CVs show a near-rectangular shape typical of MnO_2 materials with

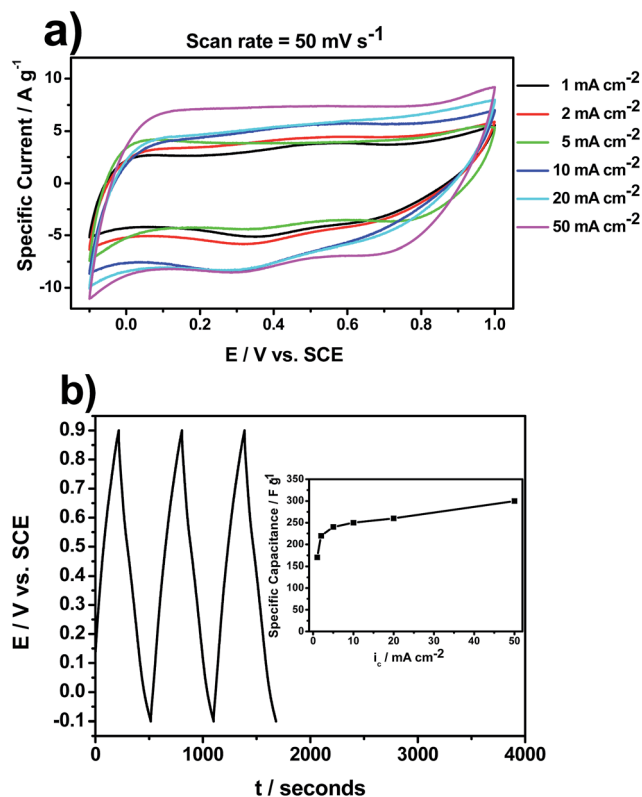


Fig. 5 CVs of MnO_2/SS electrodes obtained at various i_c (a). Typical charge–discharge curve for MnO_2/SS electrode obtained at $i_c = 50 \text{ mA cm}^{-2}$ (b). Inset shows the variation of specific capacitance as function of i_c for all studied MnO_2/SS electrodes. Electrolyte: $1 \text{ M Na}_2\text{SO}_4$.

a working potential window of 1.1 V . In addition, it is noticed that the specific current increases as i_c also increases. This is an indication of higher electrochemical activity which in turn leads to higher materials specific capacitance (inset of Fig. 5b). Knowing the potential limits from CVs, charge–discharge curves have been performed. A characteristic charge–discharge curve of MnO_2/SS electrode obtained at $i_c = 50 \text{ mA cm}^{-2}$ is illustrated in Fig. 5b. All curves, regardless i_c , present the same behavior, a near-triangular curve, with an operating working potential of 1 V , which is representative of pseudocapacitive materials such as MnO_2 and RuO_2 .²⁴ The materials SC calculated from charge–discharge curves, shown in the inset of Fig. 4b, exhibits values from 170 up to 300 F g^{-1} depending on i_c . These SC values are comparable to those found in literature for similar synthetic conditions.^{14,25} For instance, Jacob and Zhitomirsky showed that electrodeposited MnO_2 films, prepared by cathodic reduction of KMnO_4 solutions, with thickness ranging from 0.1 to $2 \mu\text{m}$, display SC values up to 279 F g^{-1} .¹⁴ In other work, the same group studied the effect of heat treatment on the MnO_2/SS electrodes obtained by cathodic electrodeposition at 2 mA cm^{-2} . The highest SC of $\sim 353 \text{ F g}^{-1}$ was obtained for the $45 \mu\text{g cm}^{-2}$ film at a scan rate of 2 mV s^{-1} . The capacitance decreased with increasing scan rate and film thickness. Heat treatment at 200°C resulted in the reduced porosity and enhanced crystallinity of the films. Compared to the as-prepared films, the films heat treated at 200°C exhibited



lower SC at scan rates below 10 mV s^{-1} and higher SC at scan rates above 10 mV s^{-1} .²⁵

It is evident that the deposits thickness plays an important role on SC since MnO_2 displays in general poor electrical conductivity,⁶ hence, a decrease in film thickness leads to an increase in SC. As a matter of fact, it has been demonstrated that MnO_2 thin films can display high gravimetric capacitances, *e.g.* in some cases higher than 2000 F g^{-1} , which strongly depends on the preparation method.²⁶ The SC value in MnO_2 films has been depicted to decrease with increasing film thickness, mostly owing to a combination of reduced electrolyte access and increased distance from the current collector, which lead to increased electrical resistance.²⁷ Additionally, the grain refinement and more amorphous structure that occurs in the electrodeposited films with increasing i_c also contributes to the higher SC values achieved. It has been reported that the NiO SC from bulk contribution may be at least three times larger in

amorphous than in crystalline films for the same surface area.²⁸ Therefore, in the case of MnO_2 -based materials, besides thickness (mass loading), is also important to tailor the crystallinity to exploit their full potential in order to increase SC.

Besides SC, which plays a pivotal role to increase EC's energy density, two other important parameters to evaluate ECs performance are the rate capability and cyclability. Fig. 6a displays the rate capability for all prepared MnO_2/SS electrodes performed from 1 to 10 A g^{-1} . In all cases, there is a considerable decrease in SC as the current density increases which seems to be more pronounced in the samples prepared at low values of i_c . For example, in the case of the sample prepared at 50 mA cm^{-2} , about 60% of its SC is retained while for $i_c = 1 \text{ mA cm}^{-2}$ the SC retention is only 45%.

As mentioned above, this is due to the MnO_2 poor electrical conductivity that directly affects the electrodes SC. If one desires to circumvent this MnO_2 drawback, in order to obtain high

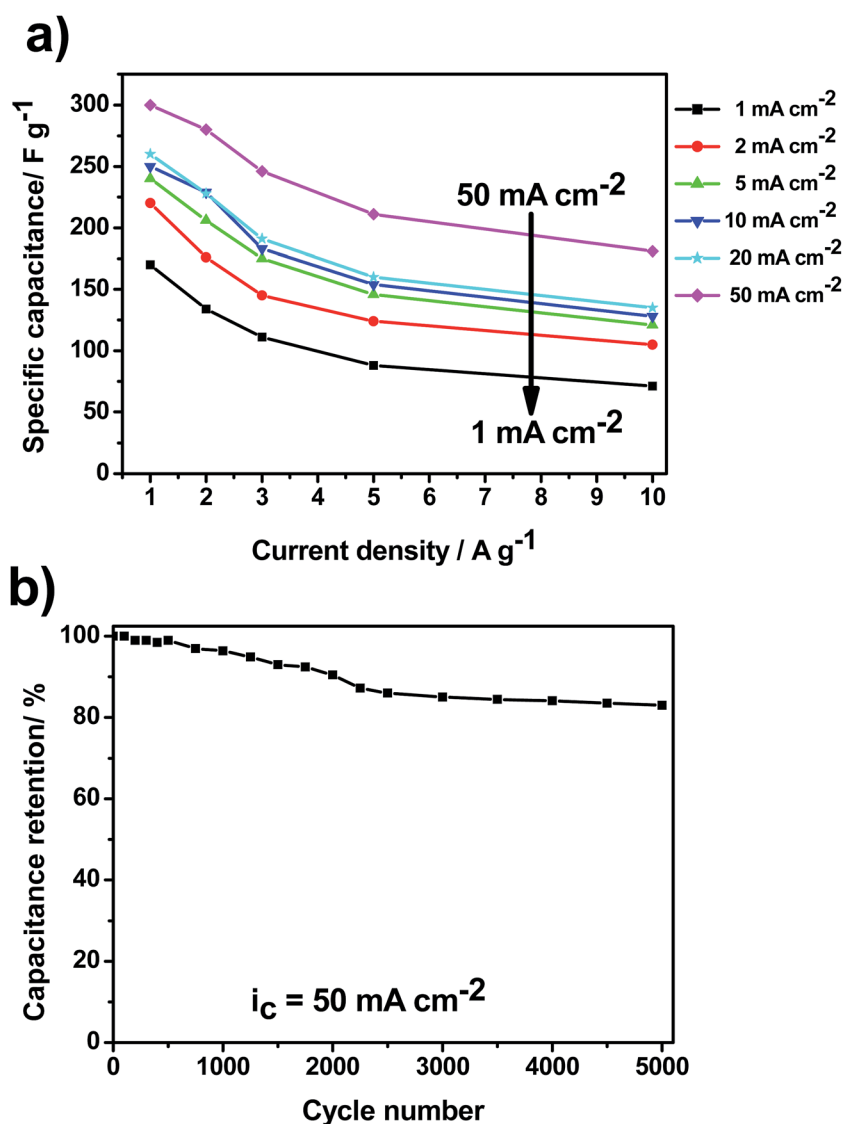


Fig. 6 Rate capability at various current densities for all prepared MnO_2/SS electrodes (a). Capacitance retention as a function of cycle number for the MnO_2/SS electrode prepared at 50 mA cm^{-2} by applying 5 A g^{-1} (b).



performance EC materials, three well-established strategies might be used:⁶ (1) production of mixed oxides: transition metal elements, such as Ni, Cu, Fe, V, Co, Mo and Ru, can be incorporated to MnO₂ enhancing the electrical conductivity and charge-storage capability of the resulting mixed oxide, (2) MnO₂ doping: MnO₂ modified electrodes can be doped with small amount of other metallic elements, e.g., Al, Sn and Pb which leads to a significant increase on the electronic conductivity and, consequently, on the specific capacitance and rate capacity, and (3) formation of composite electrodes: utilization of porous architectures such as carbon nanofoams, templated mesoporous carbon and nanographite, to form MnO₂/carbon-based composite electrodes. In this approach, carbon not only acts as the physical support of MnO₂ but also gives rise to channels for charge transport. Its high electronic conductivity enhances the rate capability and power density at large charge/discharge currents.²⁹ With regard to MnO₂/SS electrodes cyclability, a long-term test performing 5000 cycles at 5 A g⁻¹ has been carried out in 1 M Na₂SO₄ solution. Fig. 6b shows the capacitance retention as a function of cycle number for the sample obtained at 50 mA cm⁻². Capacitance retention of ca. 83% is noticed after 5000 cycles indicating an excellent cycle life under the proposed experimental conditions.

4. Conclusions

In summary, the use of room temperature cathodic electrodeposition to produce MnO₂ electrochemical capacitor electrodes has been demonstrated. By employing a permanganate-based bath, birnessite-type MnO₂ electrodes are directly obtained with no further heat treatment. In addition, the influence of applied current density (*i*_c) on the structure and capacitive performance of MnO₂ electrodes has been studied. By simply modulating *i*_c, either crystalline (δ -phase) or amorphous MnO₂ electrodes are obtained. Specific capacitance values ranging from 170 up to 300 F g⁻¹ at 1 A g⁻¹ are achieved depending on *i*_c. Electrodeposition has shown to be a versatile (thin or thick), efficient (high current efficiencies can be obtained), binder-free and room-temperature technique to produce MnO₂ electrochemical capacitor electrodes.

Acknowledgements

The authors would like to acknowledge FCT for financial support under the projects M-ERA.NET/0002/2012, M-ERA.NET/0004/2014 and PEst-OE/UI0100/2013. We also thank Prof. Teresa Duarte and Prof. Luis Santos (CQE/IST) for XRD and Raman facilities, respectively. We are indebted to Professor John Miller (JME, Inc., USA) that kindly reviewed the manuscript.

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