



Hydrogen bubbling-induced micro/nano porous MnO₂ films prepared by electrodeposition for pseudocapacitor electrodes



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ABSTRACT

Micro/nano porous manganese oxide MnO₂ electrodes for electrochemical energy storage were prepared by cathodic electrodeposition over stainless steel collectors using hydrogen bubbling as dynamic template. The morphology of the resulting film consisted of nanoporous MnO₂ crumpled nanosheets and homogeneously distributed micro-holes. The electrochemical studies revealed that the micro/nano porous MnO₂ electrodes displayed good pseudocapacitive response. The specific capacitance of the electrode was 305 F g⁻¹ at 1 A g⁻¹ in a potential window of 1 V, and the rate capability was 61% when the current density increased from 1 A g⁻¹ to 10 A g⁻¹.

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1. Introduction

Manganese oxides are being considered as prospective materials for fabricating electrodes for electrochemical energy storage because they show good pseudocapacitive performance (which results in increased energy density in aqueous electrolytes), low cost, natural abundance and environmental friendliness [1]. The electrochemical response of manganese oxide-based electrodes is characterized by nearly rectangular cyclic voltammograms in a potential window of approximately 1 V, in neutral aqueous electrolytes, as consequence of the Mn multi-valence states [2]. The growth of nanostructured morphologies with high surface area and porosity has been considered an important parameter for enhanced pseudocapacitive performance due to increased reactive sites for redox reactions [3]. Therefore, rational design of porous nanostructured manganese oxide electrodes is crucial for optimizing their pseudocapacitive performance [4,5]. Moreover, due to its extensive application in other areas such as batteries, catalysts and magnetism, the routes for growth of manganese oxides have received considerable attention in the research community [6–8].

Electrodeposition has been widely used to prepare porous manganese oxide films for electrochemical energy storage

electrodes in supercapacitors due to the ability to control the surface morphology by varying the deposition parameters [2,9]. Moreover, this method allows growing the active electrodes directly on current collectors without using binders, which are commonly required to prepare electrodes from manganese oxides synthesized by various chemical routes such as precipitation [10], microwave synthesis [11] and sol-gel [12]. Thus, electrodeposition excludes unreactive additives that increased the electrical series resistance of the material and results in electrodes that display increased electrochemical activity.

Electrodeposition in the anodic regime allows growing films formed by oxidation of Mn²⁺ to Mn⁴⁺ [13,14]. In the cathodic regime, the oxides can be formed either by reaction of Mn²⁺ with generated OH⁻ and post oxidation or by the reduction of Mn⁷⁺ to Mn⁴⁺ [15–17]. Nanostructured manganese oxides films composed of nanosheets [18], nanorods [19], nanoflowers [20] and nanowires arrays/networks [21] have been prepared by electrodeposition. Hard templates, such as anodic aluminum membranes, were also used to electrodeposit porous manganese oxide nanowire arrays [22]. These reported materials displayed good pseudocapacitive performance.

Cathodic electrodeposition, involving hydrogen evolution, has been often used to create metallic foams of Ni, Cu, Pd, Ag, Pt, and Au [23,24]. The hydrogen bubbles that continuously evolve from the substrate prevent the deposition of the metal on these sites, therefore acting as a dynamic negative template that leads to the formation of porous metallic foams with controlled micro-scale

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pores [25]. Metallic foams with micro pore size induced by hydrogen bubbling have been widely reported for application in various fields such as electrocatalysis; however the possibility of using this route to deposit oxides for application as electrodes for redox supercapacitors is still an open discussion. Generally, it is expected that hierarchical structures of metal oxides in general, and of manganese oxides in particular, characterized by well-defined porosity, will provide superior pseudocapacitive performance [20–22]. Additionally, the micro sized pores created by hydrogen bubbling together with other nanostructured features of oxide films formed by electrodeposition can result in a novel hierarchical electrode, displaying improved pseudocapacitive performance.

Thus, this work aims at using the hydrogen bubbling as dynamic template to electrodeposit micro/nano porous manganese oxide films to be used as electrochemical energy storage electrodes. Results on the formation and physico-chemical characterization of the multi-scale porous oxide films, and on the electrochemical response will be presented.

2. Experimental

The potentiostatic electrodeposition was performed in a conventional three-electrode electrochemical cell, at room temperature, using Radiometer Voltalab PGZ 100 Potentiostat with stainless steel (AISI 304, Goodfellow) as a substrate (working electrode), platinum foil as counter electrode and the saturated calomel electrode (SCE) as reference electrode. The electrolytes were 0.1 M MnSO_4 + 0.1 M Na_2SO_4 . Deposition potentials and

applied charges were varied to control the surface morphology of the electrodeposited films. All the potentials referred in this work are vs. SCE. After the electrodeposition process, the films were stabilized by potential cycling in 0.1 M Na_2SO_4 for 10 cycles. The mass of the deposited films was estimated by carefully weighting substrates before and after electrodeposition using Sartorius micro-balance with precision of 0.01 mg.

Field emission gun scanning electron microscopy (FEG-SEM, JEOL 7001F microscope) was used for studying the surface morphology of the deposited films. Topographic images were obtained with an atomic force microscope (AFM, Nanosurf Easyscan microscope) working in tapping mode. Film thickness was determined by performing FEG-SEM observation with a sample holder tilted at 70° . X-ray diffraction (XRD, Bruker AXS D8 Advance diffractometer) in Bragg-Brentano configuration with $\text{Cu K}\alpha$ radiation was used for phase identification. Raman spectroscopy (Horiba/Jobin Yvon LabRam spectrometer) was carried out for studying the structural characteristics of the formed films, using 632.8 nm He-Ne laser exciting over an area of $1\ \mu\text{m}^2$. The structural details of the films were studied by transmission electron microscopy (TEM, JEOL JEM-2010 microscope) working at an acceleration voltage of 200 kV with point to point resolution of 0.19 nm.

The electrochemical performance of the electrodes was determined by cyclic voltammetry (CV) and charge-discharge (CD) in 1 M Na_2SO_4 electrolytes. Electrochemical impedance spectroscopy (EIS, Solartron Potentiostat) was performed with applied voltage amplitude of 10 mV and frequency scanning from 5 mHz to 10 kHz at an open circuit potential. All the

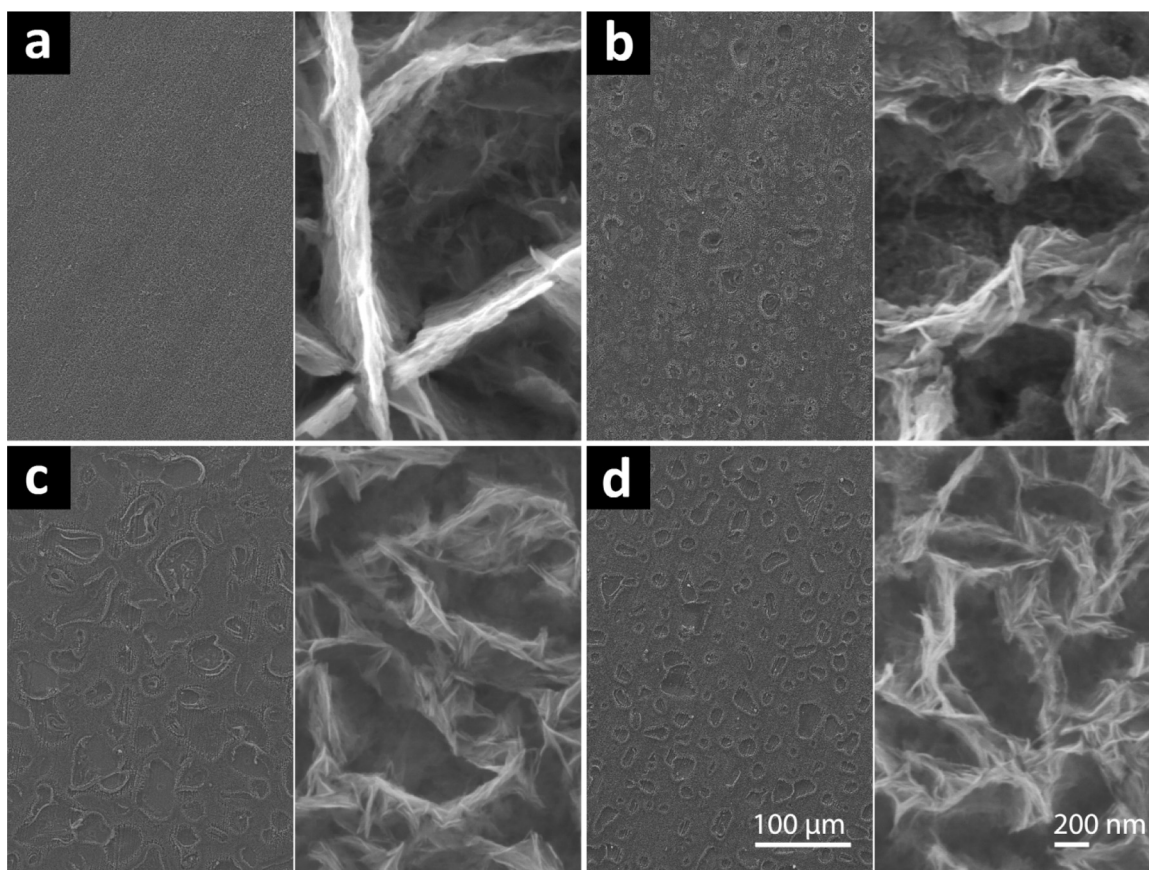


Fig. 1. FEG-SEM images of the films deposited at different potentials of (a) $-1.1\ \text{V}$, (b) $-1.3\ \text{V}$, (c) $-1.5\ \text{V}$ under a total applied charge of $-1.1\ \text{C cm}^{-2}$, and (d) deposited at potential of $-1.5\ \text{V}$ under a total applied charge of $-0.55\ \text{C cm}^{-2}$. Left and right parts of each image in the figure correspond to images magnified 200 and 35 000 times, respectively. The scale bars on the bottom of the figure are applied for all images with the same magnification.

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