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Carbon nanotube-assisted electrodeposition. Part II: Superior pseudo-capacitive behavior of manganese oxide film electrodeposited at high current densities

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HIGHLIGHTS

- Changing the electrochemical synthesis by a small amount of carbon nanotube.
- Finding optimum conditions for battery or supercapacitor.
- Controlling the film morphology and properties by controllable factors.

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ABSTRACT

A practical approach for controlling the morphology and electrochemical properties of electroactive materials is proposed. In this study, manganese oxide films were galvanostatically deposited in the presence of a small amount of carbon nanotube (CNT). The resulting film cannot be considered as a CNT-based nanocomposite, as no CNT is detected by electron microscopy. However, the manganese oxide electrodeposited delivers an excellent pseudo-capacitive behavior to be used as a superior supercapacitor. The samples prepared by applying a current density of 3.0 mA cm^{-2} showed a specific capacitance of 280 F g^{-1}. As it seems that the capacitance of this electrode is related to the chemisorption of the alkali cation, an extremely high specific capacitance of 434 F g^{-1} was achieved in a saturated medium of Li electrolyte. This high specific capacitance can be attributed to a bulk process. The presence of carbon nanotubes results in the formation of nanostructured films which provide a better accessibility for capacitive behavior. Although the exact mechanism for this phenomenon is still vague, the presence of carbon nanotubes (probably as a solid charge carrier) close to the electrode surface is apparently responsible for a different pathway for the electrodeposition process.

1. Introduction

Metal oxides are the most promising materials for the fabrication of supercapacitors, due to their reversible faradaic reactions occurring at electrode surface, resulting in the charge-transfer pseudo-capacitance [1,2]. In this category, although ruthenium oxide provides a high specific capacitance of ca. 800 F g^{-1} [3,4], its high cost is a serious disadvantage for commercialization. Thus, it is necessary to find possible alternatives for this beneficial type of supercapacitors. Similar to the case of secondary batteries, manganese oxide is a promising material owing to its considerable advantages for commercialization. A considerable attention has been paid to nanostructured manganese oxide materials for the fabrication of supercapacitors [5–9]. For this purpose, chemical synthesis of manganese oxide is the dominant method, as it is possible to control the material morphology by changing different controllable parameters. Alternatively, manganese oxide can be synthesized electrochemically with the advantage of *in situ* attachment to substrate surface. However, less attention has been paid to electrodeposition of manganese oxide films for supercapacitor applications, as the specific capacitance of the manganese oxide prepared electrochemically is normally lower than that synthesized chemically [10]. This failure can be attributed to the dense structure formed during electrodeposition, as the electroactive film has a lower specific surface area in comparison with paste-based electrodes prepared by casting the manganese oxide chemically prepared. Nonetheless, various researchers have paid a particular attention to electrodeposition of manganese oxide films for supercapacitor applications [11–20].

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Here, we aim to emphasize on the usefulness of electrodeposition method for the preparation of manganese oxide-based supercapacitors. Due to the capability of CNTs to increase the specific surface area (i.e. a main requirement for supercapacitors) of their corresponding nanocomposites, manganese oxide/CNT nanocomposites have been recently investigated as a promising material for supercapacitors [21–25]. Casting CNTs with solid materials is easy; thus, these nanocomposites are also based on chemically prepared manganese oxide materials, and less attention has been paid to *in situ* incorporation of CNTs into depositing films of manganese oxide. The present study is based on a different strategy, as it is aimed to affect the electrochemical synthesis by adding only a small amount of CNT.

2. Experimental

Electrochemical synthesis of manganese oxide films was performed under galvanostatic condition by applying a constant current density. Although active metals are commonly employed for the electrodeposition of manganese oxide films, conventional Pt substrate electrode was employed to inspect the exact influence of the CNT by excluding the substrate effects. The working electrode was a Pt sheet with the geometrical area of 0.8 cm^2. A conventional aqueous electrolyte solution of 0.5 M $MnSO_4$ in 0.5 M H_2SO_4 (i.e. the most conventional electrolyte for this synthesis) was also used. For the electrodeposition in the presence of CNT, a small amount of CNT, e.g., 200 ± 5 μg was dispersed in a 10 ml of the electrolyte solution and sonicated for 30 min. The amount of CNT incorporated into the film was tiny as estimated by the losing CNT from the electrolyte solution.

The electrodeposition was performed galvanostatically by applying different current densities. Of course, the electrodeposition time was varied for different cases to equalize the charge passed through the cell, leading to the deposition of approximately a constant mass of the electroactive material. Although, the influence of the film thickness on pseudo-capacitive behavior is an important feature, it has been widely reported for manganese oxide films and the results are similar, independent of the synthesis route. Our investigation was also showed similar dependence on the film thickness, thus, such results were not reported here. A typical charge of 2.25 C was chosen for this study.

CNT was synthesized according to a method developed by our group [26]. The special feature of this method is to use a water-soluble catalyst support in catalytic chemical vapor deposition of CNT. As a result, the vital step of acid treatment after the CNT synthesis is not mandatory. By excluding this process, which oxidizes the CNT, it is possible to work with pristine CNT. On the other hand, high-yield of this synthesis route, e.g., 2000%, significantly weakens the effects of residual impurities of the metallic catalyst. This is of particular importance, as it is known that the incorporation of other metal oxide into manganese oxide can improve its pseudo-capacitive behavior, and it is necessary to inspect the mere influence of CNT.

The amounts of the active material electrodeposited were calculated by weighting the substrate electrode before and after electrodeposition. Due to the small amount of electrodeposited material, a light substrate electrode was used to increase the accuracy. The weighting was carried out with a micro-balance with instrumental error of less than 0.1 μg. All electrochemical experiments were performed using an Autolab PGSTAT 30 utilizing its corresponding software in a standard three-electrode cell utilizing an Ag/AgCl reference electrode and Pt counter electrode. The Scanning Electron Microscopic (SEM) images were taken using a Philips XL 30 scanning electron microscope at operating voltage of 25 kV.

3. Results and discussion

Fig. 1 shows the galvanostatic synthesis of the manganese oxide films at different current densities in the presence of a small amount of CNT dispersed within the electrolyte. Electrodeposition at lower current densities has been extensively reported in the preceding paper [27]. The existence of even such a small amount of CNT has significantly changed the general shape of chronopotentiograms (in comparison with similar electrodeposition of manganese oxide in the absence of CNT, e.g., Ref. [11]). Another observable feature is the appearance of potential fluctuations, which can be attributed to the local adsorption of the CNT to the substrate surface, changing the electrode active area. In such fluctuations, the potential temporarily decreases from its general steady-state line, suggesting temporal decrease of the applied current density due to an increase of the surface area. Unexpectedly, a sudden increase in the potential occurs upon applying a high current density (Fig. 1c). This is an inverse behavior in comparison with the aforementioned fluctuations, and is probably related to a fast process occurring at the electrode surface in the presence of CNT. In general, these chronopotentiograms suggest the significant influence of CNT on the electrochemical synthesis of manganese oxide, and are indicative of a different growth pathway in this electrosynthesis.

In agreement with the difference in the electrodeposition process observed in the presence of CNT, the morphology of the manganese oxide films is completely different when electrodeposited in the presence of a small amount of CNT. According to the SEM images (Fig. 2), instead of formation of a uniform surface, the existence of CNT results in the formation of sunflower-like microparticles (Fig. 2a, c and e) on the substrate surface for all cases, regardless of the value of applied current density. These sunflower-line microparticles have nanostructures consisted of nanoparticles closely packed. Indeed, the applied current density just controls the shape of these sunflower-like microparticles, and size of the individual nanoparticles decreases by increasing the applied current density (Fig. 2b, d and f). It is believed that the CNT available in the electrolyte just induces a different pathway for the growth of the electroactive films. In fact, they act as growth sites for the formation of such sunflower-like microparticles on an initial manganese oxide layer. The background in the SEM image illustrated in Fig. 2a is a relatively smooth manganese oxide film with thickness of ca. 2–5 μm (while the sun-flower particles are thicker than 10 μm).

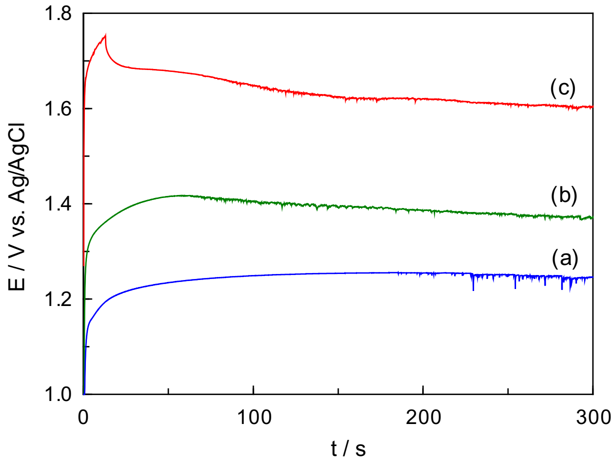

Fig. 1. Galvanostatic deposition of the manganese oxide films by applying the constant current densities of (a) 1.5, (b) 3.0, and (c) 7.5 mA cm^{-2}.

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