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Potentiostatic and cyclic voltammetric deposition of nanostructured manganese oxide for supercapacitor applications

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ABSTRACT

Nanostructured manganese oxide was produced by potentiostatic and cyclic voltammetric deposition techniques from aqueous $KMnO_4$ solutions. Scanning electron microscopy (SEM) and X-ray diffraction were used to study the morphology and crystal structure of the deposited films. The electrochemical properties of deposited films, that obtained by two techniques, were investigated via performing the cyclic voltammetric tests. The results showed the higher specific capacitances of the nanostructured manganese oxide electrodes which have been produced via cyclic voltammetric deposition. The good retention was obtained for all synthesized electrode materials.

1. Introduction

The supercapacitors are the new kind of energy storage sources which are able to store greater amounts of energy in comparison with conventional capacitors. These energy sources charge quickly and deliver more power with respect to the batteries. Therefore, these can be used as complementary energy-storage devices along with batteries or fuels cells and exhibit improved power quality [1]. According to their charge storage mechanism, the supercapacitors are categorized in three main groups; Double-layer capacitors, Pseudocapacitors, and Hybrid capacitors. In electric double-layer capacitors (EDLCs), electrostatic storage of the electrical energy is achieved by nonfaradaic separation of charge in the Helmholtz double layer at the electrode/electrolyte interface. In the pseudocapacitors, the electrochemical storage of the electrical energy, establishes by performing redox reactions at the surface of the electrode or by specifically adsorbed ions that result in a reversible faradaic charge-transfer on the electrode surface. Hybrid capacitors are the capacitors with special electrodes that exhibit significant double-layer capacitance and pseudocapacitance [1,2]. RuO_2 with the highest specific capacitance and cycle life is the best material for pseudocapacitors [3]; but it is toxic and too expensive. Therefore, other metal oxides like MnO_2 [4], Co_2O_3 [5], NiO [6], SnO_2 [7], FeO [8], V_2O_5 [9], TiO_2 [10] have been widely investigated as pseudocapacitors materials. Among these oxides, MnO_2 has attracted more attention because of its low cost, high energy density, natural abundance and environmentally friendly nature.

The nanostructured manganese dioxide has been produced by different methods, like hydrothermal [11], sono chemical [12,13], sol-gel [14], electrophoretic [15] and solid-state reaction techniques [16]. The electrodeposition method has many advantages over other synthesis routes in terms of low cost, easy method, with the possibility of easier and better controlling the morphological and structural properties of the deposited metal oxide via simply adjusting the deposition parameters like bath composition, temperature, current density, applied voltage, and so on. The as prepared metal oxide films can also be used directly as an electrode without additional processing step as adding binder or using electric conductor [17].

The electrochemical deposition of MnO_2 could be carried out using two different techniques, the anodic oxidation of Mn^{2+} or cathodic reduction of Mn^{7+} species. Anodic deposition of nano MnO_2 has been performed by various techniques like galvanostatic [18], potentiostatic [19], potentiodynamic [20], cyclic voltammetric [21], pulsed potential, and pulsed current [22,23] deposition modes. Unlike the anodic deposition, there are lesser reports on the investigation of the cathodic deposition of nano MnO_2. The cathodic deposition gives us the opportunity to use different metals as substrate for electrodeposition without the probability of the anodic oxidation of base substrates; also it presents new ways to produce the composite films, with the possibility of codeposition of other materials with manganese oxide in order to improve the

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electrochemical properties of the manganese oxide [24]. This indicates the importance of cathodic electrodeposition and rationalizes the increasing interest in its developing. Cathodic deposition of MnO_2 has been done by galvanostatic [25,26], pulse and reverse pulse deposition modes [24]. Zhitomirsky et al. [27] have reported the high specific capacitance of 770 F g^{-1}, through deposition of Ag doped manganese oxide via galvanostatic deposition. Recently Cheney et al. [28] have produced electrolytic amorphous nano manganese oxides (EAMD) for battery application, with the finer particle sizes than anodically deposited ones via a potentiostatic route. Up to now cathodic deposition of manganese oxide has performed mainly via galvanostatic mode. Different synthesis modes results in the formation of different nanostructures with distinct electrochemical properties. In this regard and in order to more developing the cathodic deposition of manganese oxide, we have synthesized manganese oxide nanostructures cathodically via cyclic voltammetric and potentiostatic deposition techniques. Also we studied the influence of each synthesis mode on the physical and electrochemical properties of the obtained nanostructures. Manganese oxide nanostructures were produced through a simple method at room temperature and directly used as electrode material for the electrochemical supercapacitors. The prepared nanostructures in the present investigation have completely different morphology in comparison with the previously prepared samples via anodic and cathodic methods, and possess good capacitive behavior with long cycle life.

2. Experimental procedure

2.1. Preparation of manganese oxide

Cathodic deposition of manganese oxide was carried out in a three electrode system, in which two platinum plates (0.7 × 1.6 cm) acted as working and counter electrodes, and a mercury/mercurous sulfate electrode (MSE) used as a reference electrode. The electrochemical deposition was done under a constant voltage of −0.922 V in the potentiostatic mode (PS), and also cycling potential between −0.7 to −1 V with a scan rate of 250 mV/s at the cyclic voltammetric mode (CV). The deposited mass was limited to 1.6 mg/cm^2 in the both deposition methods. Prior to electrodeposition, the working and counter electrodes were cleaned with acetone and distilled water. The electrosynthesis was performed at room temperature using a deposition bath composed of 0.02 M $KMnO_4$ (AR, Merck), and 0.15 M K_2SO_4 (GR, Merck). The working electrodes were rinsed with distilled water and dried at room temperature for 12 h after electrodeposition.

2.2. Characterization

The morphology and crystallinity of the as prepared manganese oxide was studied by using a Philips XL30 scanning electron microscope (SEM), and a Philips X-ray diffractometer (XRD). The diffraction patterns were recorded in the 2θ range of 15–80°.

2.3. Electrochemical measurements

Supercapacitive behavior of prepared manganese oxide was investigated through performing cyclic voltammetric tests in 0.1 M Na_2SO_4 solution using a three-electrode configuration, including the deposited manganese oxide platinum plate as working electrode, a bare platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode. CVs were recorded between 0 and 1 V at various scan rates ranged from 5 to 100 mV/s using an AUTOLAB PGSTAT30 potentiostat/galvanostat.

3. Results and discussion

3.1. Electrodeposition procedure

The potential range for the cathodic deposition was assigned with respect to the peak zone in the linear voltammogram (Fig. 1). Two peaks can be seen at this voltammogram; one around −0.9 V vs. MSE (mercury/mercurous sulfate electrode), that is related to the reduction of Mn^{7+} to Mn^{4+}, and another small peak around 0.5 V vs. MSE which is attributed to the reduction of dissolved oxygen at the solution. The deposition mechanism can be described as the diffusion and cathodic reduction of MnO_4^- species, which is a complex process, and there is not sufficient information about it [29]. The potential and pH are of the influencing factors that affect the kinetic pathway of this reaction. The following reaction has been suggested for reduction of MnO_4^- species in neutral aqueous solutions [29]:

$$MnO_4^- + 2H_2O + 3e \rightarrow MnO_2 + 4\,OH^- \quad (1)$$

3.2. SEM

Fig. 2 shows the effect of synthesis route on the morphology of as prepared films. Manganese oxide which has been produced via cyclic voltammetry, Fig. 2(a and b) has composed of some blades with the thicknesses of about 35 nm, which have formed together sphere like structures. According to Fig. 2(c and d), potentiostatic synthesis resulted in the formation of thicker nanostructures with the thicknesses of about 46 nm.

3.3. XRD

The XRD patterns for manganese oxide specimens, Fig. 3(a and b), indicate the almost amorphous structure for the films produced via both methods, however, some poor and broaden peaks can be seen around 25°, 38°, and also a much poorer broadening around 65°, that may be attributed to rancieite or birnessite crystal structures [29]. This peak broadening may be due to the small particle size and more distorted structure of the deposited films.

3.4. FTIR

Fig. 4(a) and (b) shows the IR spectrum of deposited manganese oxide specimens prepared via cyclic voltammetry, and potentiostatic methods respectively. The IR bands in the region of 1000 to 400 cm^{-1} are attributed to the formation of MnO_6 octahedral structure, and confirm the formation of manganese oxide

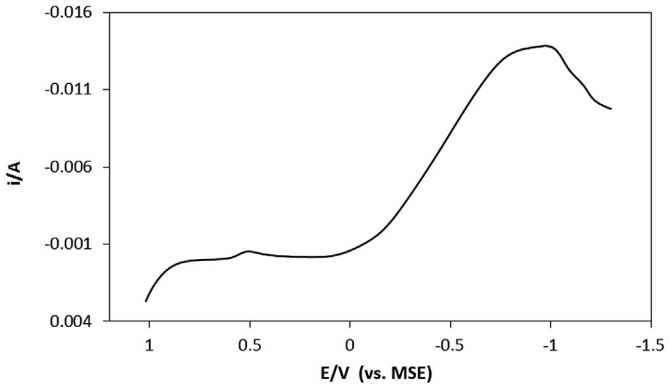

Fig. 1. Linear voltammogram in the 0.02 M $KMnO_4$, 0.02 M K_2SO_4 solution at a scan rate of 0.01 V/s, on Pt substrate.