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Synthesis of manganese dioxide nanosheets and charge storage evaluation

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ABSTRACT

Manganese oxide nanostructures were synthesized by chemical–electrochemical process using controlled-current electrochemical methods and heat-treatment. Manganese hydroxide precursor was prepared by electrogeneration of hydroxide (OH^-) at electrode surface from nitrate solution. MnO_2 hexagonal nanostructures were then achieved by heat annealing of the obtained precursor. A variety of characterization methods have been applied to the samples including Fourier transform infrared spectrometry, energy dispersive X-ray analysis, X-ray diffraction and scanning electron microscopy. The scanning electron micrographs showed that the product consists of nanosized disc-like structures with average diameter of 800 nm and thickness of 50 nm. The electrochemical properties of MnO_2 nanostructures were investigated by Cyclic Voltammetry. The maximum specific capacitance achieved was 204 F g^{-1} at a scan rate of 1 mV s^{-1}.

1. Introduction

Since the introduction of Laclanche batteries in the late 1900s, manganese dioxide has attracted considerable attention because of its unique properties such as high availability, low toxicity and cost. Manganese dioxide is still a serious rival for other electrode materials, even after the replacement of Laclanche batteries by newer ones [1]. Electrochemical capacitors or pseudocapacitors have been considered to be promising devices for applications requiring a high power output and/or a high cycle capacity. Manganese dioxide as an active material in supercapacitors has an enormous theoric storage ability of 1450 F g^{-1} but the actual storage ability is a complex function of structural parameters. Hence, a great number of research works have been conducted to investigate the effect of structural parameters such as crystalinity, particle size, crystalline lattice defect and degree of stochiometric deviation on electrochemical behavior and storage ability of manganese dioxide [2].

Progress in energy conversion and storage technology has benefited greatly from moving from conventional to nanostructured energy materials. The large surface area and smaller diffusion length for the ions intercalation created by nanoscale structures significantly enhances the efficiency in utilizing the energy material and therefore improves the performance [4].

Nanostructured MnO_2 has attracted a lot of interest due to its unique physical and chemical properties. This is because many properties of materials, such as catalytic activity, sensitivity or conductivity, are closely related to surface area and particle size. Manganese dioxide nanostructures hold great potential for supercapacitors and other energy storage systems due to their large surface area and upper contact surface with the electrolyte.

Many efforts have been made to prepare nanostructured MnO_2 with special morphology, such as nanowire [5],

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porous and hollow structures [6] by using a variety of methods including template-directing [7] and self-assembly technique.

The three (3D) and two (2D) dimensional nanostructured MnO_2 are promising as electrode materials for supercapacitors due to their porous structure, large surface area and short diffusion length for protons or alkali cations [8].

Two-dimensional (2D) nanostructures have two dimensions inside the nanometric size range. In recent years, synthesis of 2D nanostructures has become a focal point in materials research, owing to their low dimensional characteristics different from the bulk properties. In the quest of 2D nanostructures, considerable research attention has been focused over the past few years on the development of 2D nanostructures. 2D nanostructures with certain geometries exhibit unique shape-dependent characteristics and subsequent utilization as building blocks for the key components of nanodevices [9]. In addition, 2D nanostructures are particularly interesting not only for basic understanding of the mechanism of nanostructure growth, but also for the investigation and development of novel applications in sensors, supercapacitors, photocatalysts, nanocontainers, nanoreactors, and templates for 2D structures of other materials [10].

In this work, a novel nanostructure of MnO_2 with a large surface area and uniform size has been synthesized by a facile method. The sample is investigated by means of Scanning Electron Microscopy (SEM), Fourier transform Infrared spectrometry (FTIR), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction. The electrochemical characterization of the sample for supercapacitors has been also investigated.

2. Experimental

2.1. Preparation of MnO_2

A solution of Mn^{2+} at a concentration of 10^{-2} M was freshly prepared by dissolving appropriate amounts of $Mn(NO_3)_2 \cdot 4H_2O$ in deionized water. Electrodeposition reactions were triggered at a constant current density of 0.5 mA cm^{-2} in a 1 L cubic glass container. A piece of steel 316 L with $100 \times 100 \times 0.5$ mm^3 dimension and two parallel planar graphite electrodes of the same dimensions were hung from the top working as the cathode and counter anodes respectively. The reaction was continued until the passage of 3.5 C per square centimeter of electrode surface. Then, the steel electrode with the deposited layer was removed from the solution and immediately washed with water and acetone. The deposited $Mn(OH)_x$ layer was scrapped after 12 h and subjected to heat treatment. The annealing step was done between 25 and 300 °C at a heating rate of 15 °C min^{-1}.

2.2. Characterization

A BOMEM MB-series FTIR spectrometer was used to record Infrared spectra within the range of 250–4000 cm^{-1} wave numbers after pelleting with KBr. The surface morphology and chemical composition of the sample were examined by means of a TESCAN VEGA3 SB scanning electron microscope equipped with an energy dispersive X-ray (EDX) detector. The crystal structure of the sample was characterized by CuKα line ($\lambda = 1.5406$ nm) from a STOE XD-3A X-ray diffractometer.

2.3. Electrochemical measurements

Electrochemical studies were performed using an Autolab 302N potentiostat/galvanostat. Cyclic voltammetric measurements were carried out by means of a standard three electrode cell configuration with a platinum wire, an Ag/AgCl and a glassy carbon (with 0.071 cm^2 area) as counter, reference and working electrodes respectively. In order to investigate the storage ability of the sample, cyclic voltammetry was performed in Na_2SO_4 (0.5 M) aqueous solution within a potential range from −0.1 to +0.9 v vs Ag/AgCl at different scan rates ranging from 1 to 100 mV s^{-1}. The Specific Capacitance (SC) was calculated by integration of current over the whole range of applied cyclic potential according to the following equation:

$$SC = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V)dV \quad (1)$$

where I is the measured current (A), $(V_a - V_c)$ is the sweep potential range (V), m is the mass of electrochemically active material (g) and v is the sweep rate (V s^{-1}).

3. Results and discussion

3.1. XRD study

In order to study crystalline nature of the product, the XRD analysis was performed. Fig. 1 shows the XRD pattern of the sample. As indicated on the top of the figure, all of the peaks can be ascribed to diffraction peaks of MnO_2 in α (JCPDS Card no. 44–0141) and γ (JCPDS Card no. 14–0644) crystalline forms [1]. The structure of α-MnO_2 is composed of double chains of edge-sharing octahedral units that share corners to form 2×2 and 1×1 channels. The structure of γ-MnO_2 is composed of a random intergrowth of 2×1 and 1×1 channels. More electroactive γ form is dominant according to the higher intensity of corresponding peaks. The small size of the particles cause the widening of diffraction peaks.

3.2. Electrodeposition mechanism

Fundamental aspects and mechanism of cathodic electrodeposition of oxides and hydroxides have been reviewed in the literature [2,3]. In this method, cathodic reduction of water, dissolved oxygen or nitrate ions bring about a local increase in pH at the electrode surface according to the following reactions [11]:

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^0 = -1.05 \text{ V vs. Ag/AgCl} \quad (2)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad E^0 = +0.18 \text{ V vs. Ag/AgCl} \quad (3)$$

$$NO^{3-} + H_2O + 2e^- \rightarrow NO^{2-} + 2OH^- \qquad E^0 = -0.21 \text{ V vs. Ag/AgCl} \quad (4)$$