Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Synthesis of γ-MnOOH nanorods by successive ionic layer deposition method and their capacitive performance

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ARTICLE INFO

Article history:
Received 15 December 2016
Revised 8 April 2017
Accepted 10 April 2017
Available online xxx

Keywords:
Manganite
Nanolayers
SILD
Supercapacitor

ABSTRACT

It was first shown in the present study that layers of manganite γ-MnOOH can be deposited on the surface of a substrate by its multiple successive treatment by the solutions of $MnSO_4$ and $K_2S_2O_8$ using the successive ionic layer deposition (SILD) technique. Their analysis was carried out by the XRD, XPS, FT-IR, SEM and EDX methods. It has shown that the synthesized layers are formed by aggregates of nanorods up to 80–100 nm in length and approximately 8–10 nm in diameter. A probable sequence of chemical reactions leading to the formation of a layer of the given morphology is suggested. Testing of performance of supercapacitors with nickel foam electrodes incorporating the γ-MnOOH layers in the 0.1 M KOH electrolyte at 1 A/g indicated the specific capacitance equal to 1120 F/g. After 1000 work cycles the observed degradation of this value was less than 3%.

1. Introduction

Manganese oxides MnO, Mn_3O_4, Mn_2O_3 and MnO_2 deserve special attention among the electrode materials for supercapacitors and there is a lot of studies devoted to investigation of their electrochemical properties [1–9]. The interest is stimulated by relatively high capacitance of these oxides and stability of their properties, their ecological friendliness and low cost of production. Besides the metal oxides mentioned above much attention is paid lately to the development of supercapacitor electrodes based on manganese (III) oxide-hydroxide, γ-MnOOH, with manganite monoclinic crystal structure [10–13]. Usually nanosize manganite crystals are observed in the morphology of wickers or nanorods, which allows to construct electrodes with relatively high specific surface area and thereby supercapacitors of high performance.

In addition, manganite is an active catalyst for water oxidation [14], a sorbate removing arsenic from water solutions [15], an electrode material for lithium accumulators [16] and electrochemical sensors for the determination of hydrazine [17] and H_2O_2 [18], and other.

The techniques used for its production include hydrothermal method [19–21], methods using oxidation of $Mn(OAc)_2$ solution by oxygen of the air [22], reduction of $KMnO_4$ solution by $MnSO_4$ solution in an acidic medium [23], treatment of suspension of manganese oxide with birnessite crystal structure in a solution of manganese(II) salt [24], and some others.

The purpose of the present study was to explore the feasibility of synthesis of the manganite layers by SILD method [25], also called the successive ionic layer adsorption and reaction (SILAR) [26,27]. The method is based on multiple and successive treatment of substrate by solutions of reagents which enter into reaction at its surface and form a layer of poorly soluble substance. The method is known to be used previously for the synthesis of sparingly soluble layers of oxides [28], oxyfluorides [29], fluorides [30], sulfides [31], as well as silver [32], gold [33], and their nanocomposites with metal oxides [34]. The distinctive features of this method are its capability of deposition of the layers of controlled thickness on the surface of parts of any shape, which are exactly the requirements to the methods of synthesis of the layers on the surface of electrodes for supercapacitors. These particular features allowed to attain relatively high values of capacitance with supercapacitor electrodes based on $NiO_{1+x}\cdot nH_2O$ and $Co_2Al(OH)_{7-2x}(CO_3)_x\cdot nH_2O$ reported in Refs. [35] and [36], respectively.

2. Experimental

As a substrate were used 5×30 mm polycrystalline nickel foam (NF) plates (porosity 110 PPI) for electrochemical experiments, and also $10 \times 20 \times 0.35$ mm single-crystal silicon plates with $<100>$ orientation used for physical characterization. Extra pure water (Mili-Q) was used in all experiments. Substrates of silicon were cleaned in an ultrasonic bath filled with acetone for 10 min. Than plates were sequentially treated for 10 min in concentrated HF, water, 70% HNO_3, water, 0.01 M KOH and then flushed out by water.

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http://dx.doi.org/10.1016/j.jechem.2017.04.015
2095-4956/

NF plates were treated according to the technique described in Refs. [37] for 15 min in 6M HCl solution, then several times rinsed by water and dried on air at 120 °C for 30 min.

Aqueous 0.01 M solutions of analytical grade $MnSO_4$ (pH = 7.2) and $K_2S_2O_8$ (pH = 9.5) were used. pH of these solutions was controlled by addition of 0.5 M KOH solution.

For synthesis of γ-MnOOH nanolayers substrate plates were sequential immersed for 30 s into solution of manganese salt, water, solution of potassium persulfate and again water. The sequence corresponds to one SILD cycle, which is repeated 30 times to obtain desired film thickness. Then samples were calcined on air at 150 °C for 10 min at a heating rate of 5 °C/min.

FT-IR transmission spectra of synthesized films on silicon surface were registered by FCM−2201 spectrophotometer using differential technique with respect to spectra of bare silicon plate.

XRD patterns were obtained using a Rigaku Miniflex II X-ray diffractometer with Cu K_α radiation ($\lambda = 0.154056$ nm).

The morphology and composition of synthesized films was investigated by SEM at accelerating voltage 1–10 kV on Zeiss Merlin microscope and EDX used detector Oxford INCAx-act. X-ray photoelectron spectroscopy (XPS) was obtained used ESCALAB 250Xi electron spectrometer, with Al K_α radiation (14,866 eV).

Electrochemical properties of the films were characterized by cyclic voltammetry (CVA), galvanostatic charge-discharge techniques and electrochemical impedance spectroscopy (EIS). Measurements of CVA and galvanostatic charge–discharge were made by Elins P-30I potentiostat and EIS were performed on Elins P-45X potentiostat with the module of the impedance measurements. All measurements carried out in a three-electrode cell with a platinum plate as counter electrode and Ag/AgCl (aq. KCl sat.) reference electrode with 0.1 M KOH aqueous solution as an electrolyte. Cyclic voltammogramms were recorded at different scan rates of 5, 10 and 20 mV/s with a potential sweep range between 0 and 0.6 V. EIS measurements were performed from 100 kHz to 10 mHz.

Specific capacitance (C) of a nickel foam electrode with LDH layer was determined according to Ref. [38] as:

$$C = I/(\Delta V/\Delta t) \times m,$$

where I (mA) is a galvanostatic current, ΔV (mV) is the potential window, Δt (s) is the discharge time of a cycle and m (g) is the mass of the active material in the film electrode. The mass active material on nickel surface was controlled by OHAUS Pioneer™ PA54C precise balance.

3. Results and discussion

Morphological characteristics of the sample are shown in the SEM images in Fig. 1, which show that the layer, synthesized on the nickel foam by the SILD method by 15 cycles of treatment, form of the germ on initial stage of the nanocrystals (Fig. 1(a)), and after 30 cycles of treatment is from nanorods with size approximately to 80-100 nm in length and approximately 8-10 nm in diameter (Fig. 1(b)).

The results of EDX indicate the presence of Mn, O and C atoms and some admixture of K and S atoms in the layer where the ratio of atomic concentrations of K, Mn and S was equal to 0.05, 1.0, and 0.02, respectively.

On the X-ray diffraction pattern of the synthesized sample (Fig. 2) the planes(−111), (002), (−121), (210), (220), (−302) and (−311) are corresponding to monoclinic crystal phase of γ-MnOOH (JCPDS 88-0649) [39]. In the FT-IR spectrum (Fig. 3) one can observe absorption bands with maximums at 3390 and 3150 cm^{-1} referring to valence oscillations of O–H groups in the molecules of water and HO–H_2O associates [40] of manganese oxide-hydroxide and also a band with maximum at 1580 cm^{-1} corresponding to deformation oscillation of O–H bonds in the Mn–OH groups and

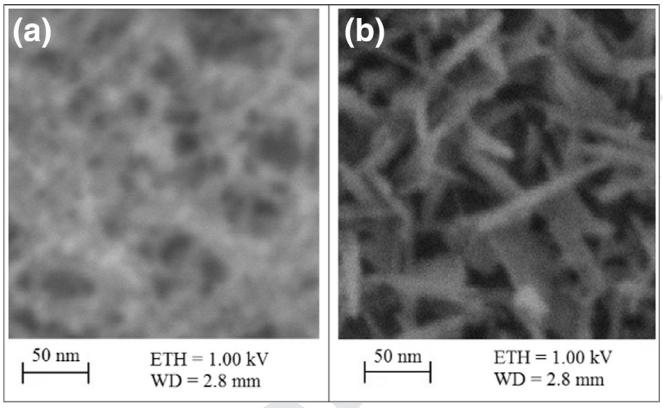

Fig. 1. SEM images of a layer synthesized on the nickel foam by the SILD method by different cycles of treatment using $MnSO_4$ and $K_2S_2O_8$ solutions: (a) 15 cycles and (b) 30 cycles.

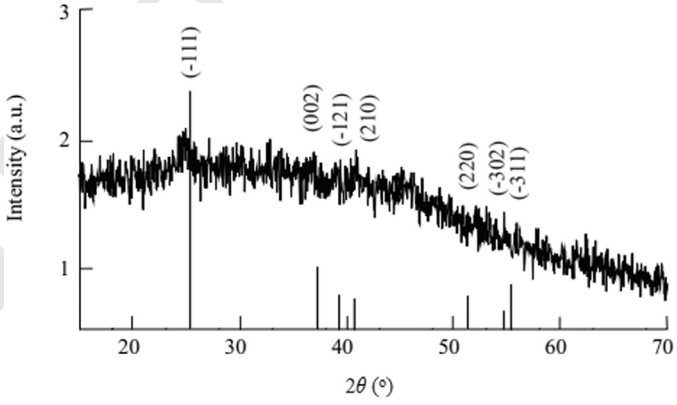

Fig. 2. X-ray diffraction pattern of a layer synthesized by SILD method by 30 cycles of treatment in the solutions of $MnSO_4$ and $K_2S_2O_8$.

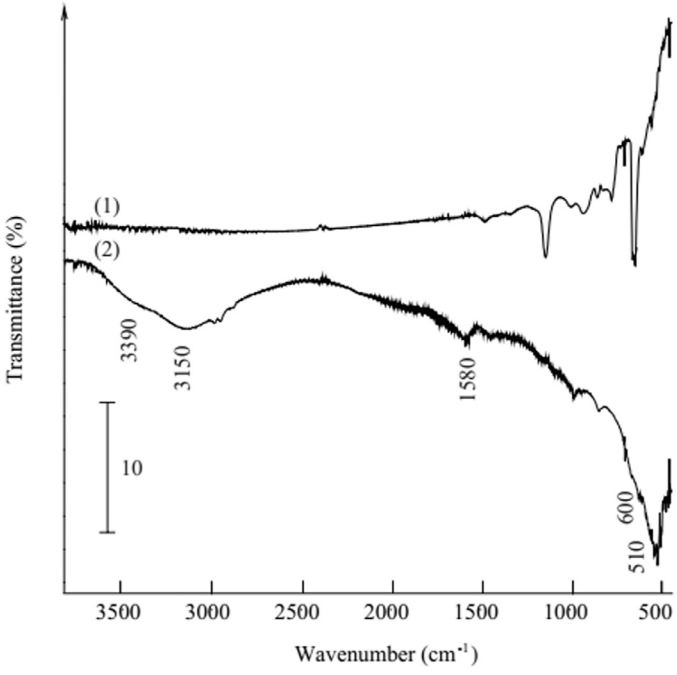

Fig. 3. FT-IR transmittance spectrum of: (1) – pure silicon substrate, (2) – layer synthesized by the SILD method on the surface of a silicon substrate by 30 cycles of treatment in the solutions of $MnSO_4$ and $K_2S_2O_8$.

Please cite this article as: A.A. Lobinsky, V.P. Tolstoy, Synthesis of γ-MnOOH nanorods by successive ionic layer deposition method and their capacitive performance, Journal of Energy Chemistry (2017), http://dx.doi.org/10.1016/j.jechem.2017.04.015