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Synthesis 2D nanocrystals of Co-doped manganese oxide as cathode materials of zinc-ion hybrid supercapacitor

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ABSTRACT In the present work, we propose a novel promising route for synthesis of Co-doped manganese oxide nanostructure via successive ionic layer deposition method as cathode material of zinc-ion hybrid supercapacitor. The synthesized nanolayers were analyzed by SEM, EDX and XRD. It was shown that the synthesized nanolayers were formed from ultrathin (6–8 nm) two-dimensional nanocrystals containing birnessite MnO_2 and hausmannite Mn_3O_4 crystal phases and having the morphology of "nanosheets". Electrode based on nickel foam and Co-doped manganese oxide nanolayers exhibited a high specific capacity (514.5 F/g at 0.1 A/g) and excellent cycling stability (99 % capacity retention after 1000 charge-discharge cycles). Obtained results demonstrate that the 2D Co-doped manganese oxide is a promising material for effective zinc-ion hybrid supercapacitor.

KEYWORDS nanocrystals, manganese oxides, electrode materials, cathodes, zn-ion hybrid supercapacitor.

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1. Introduction

Rechargeable zinc-ion batteries are one of the most promising candidates for replacing lithium-ion batteries which meet the future requirements for promising electrical energy storage devices due to the greater availability of zinc-containing raw materials, low cost and high theoretical specific capacity (820 mAh/g) [1, 2]. Zinc-ion hybrid supercapacitors are of particular interest, because they combine the advantages of zinc-ion batteries (high energy density) and supercapacitors (power density and long cycling life) [3–5]. Recently, some progress has been achieved in improving the electrochemical characteristics of electrode materials for such devices, but there are still problems associated with the lack of suitable cathode materials that can withstand multiple intercalation/deintercalation of zinc-ions [6]. To meet these requirements, layered and tunnel structured compounds with redox components are often chosen [7]. The set of materials that meet the presented requirements includes analogues of Prussian blue, manganese and cobalt oxides, vanadium oxides, as well as organic compounds [8]. Among these materials, manganese oxides are of the greatest interest from the point of view of their further commercialization, since they have a high specific capacity and a wide working potential window, while they can be synthesized from relatively inexpensive and affordable precursors [9–11]. Recently published works [12, 13] have shown the high efficiency of using manganese oxides as cathode materials for zinc-ion hybrid supercapacitors, which have shown high energy density and ultra-long cycling life. However, these cathode materials have low electronic conductivity, which does not allow them to achieve the theoretical values of the specific capacitance.

One of the solutions to this problem is to obtain oxide materials with a two-dimensional structure. The key characteristic of 2D materials is ultrathickness (about few nanometers) so charge carriers can travel extremely short distances from the volume to the surface, while significantly improving electronic conductivity [14, 15]. The main problem in the creation of cathode materials for zinc-ion hybrid supercapacitors at the moment is the complexity of obtaining, by existing synthesis methods, ultrathin oxide nanocrystals with a graphene-like morphology of "nanosheets", which would significantly reduce the degradation of the electroactive material and improve electronic conductivity.

The successive ionic layer deposition method (SILD) has a number of unique features and advantages for obtaining nanoscale capacity electrode materials. In particular, it allows the formation of nanolayers on the surface of substrates with a developed morphology and a large specific surface area, as well as the possibility of controlling a variety of synthesis parameters (concentration and ratio of reagents, pH value, processing time, number of deposition cycles, etc.) [16, 17]. In addition, due to the ability to regulate the flow of ionic reactions at the substrate-solution interface, it is possible to set the preferred crystallographic orientation and grain structure, thus controlling the growth of crystals. Previously, oxides and hydroxides of transition metals with various morphologies were successfully synthesized by this method [18–20]. The obtained nanomaterials showed excellent capacitive and electrocatalytic characteristics.

In this research, we propose a novel facile route synthesis of ultrathin two-dimensional nanocrystals of Co-doped manganese oxide via successive ionic layer deposition method from aqueous solutions of manganese and cobalt salts. We investigate its application as effective electrode materials for zinc-ion hybrid supercapacitor.

2. Experiment

2.1. Fabrication of the Co-doped manganese oxide via successive ionic layer deposition technique

Beforehand, nickel foam (NF) was cleaned in acetone, ethanol and distilled water sonication of 15 min to remove the impurities, then treated with 6 M HCl solution for 15 min to remove the oxidation layer and dried on air at 80°C for 30 min. The Co-doped manganese nanolayers were fabricated by SILD technique used for obtaining Co-doped manganese oxide nanolayers. Aqueous solutions of mixed analytical grade salts $MnSO_4$ (C = 0.01 M) and $CoSO_4$ (C = 0.005 M) were used as a precursor for synthesis and aqueous solution of $KMnO_4$ (C = 0.01 M, pH = 11) plays the role of oxidizer. The precleaned NF substrates were first dipped in the solutions of mixed salts $MnSO_4$ and $CoSO_4$ for 30 s and then were washed from excess reagent in distilled water for 15 s. On second step, substrates were dipped in solution of $KMnO_4$ for 30 s and again were washed in water. After repeating 50 SILD cycles, insoluble film of synthesized product was formed on the surface. Finally, the as-prepared nanolayers were annealed at 300°C in argon atmosphere for 3 hours to obtain oxide thin films.

2.2. Characterization and electrochemical measurement

The morphology and nanostructure of synthesized nanocrystals were analyzed by SEM (Zeiss Merlin microscope and Tescan Vega 3 SBH microscope) and XRD (Rigaku Miniflex II X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154056$ nm)) technique. The chemical composition of the samples was characterized by EDX (Oxford INCA x-act X-ray). The electrochemical experiment was carried out using Elins P45-X potentiostat with two-electrode electrochemical cell. The working electrode was obtained in the form of Co-doped manganese oxide nanolayers modified nickel foam. Carbon rod serves as an anode and 1M $ZnSO_4$ aqueous solution is the electrolyte. Electrochemical characterization was performed by cyclic voltammetry (CVA) and galvanostatic charge-discharge (GCD) and also electrochemical impedance spectroscopy (EIS) techniques. The specific capacitance C (F/g) can be calculated via eq. (1):

$$C = \frac{Idt}{dVm}, \tag{1}$$

where I (mA) is a galvanostatic current, dV (mV) is the potential window, dt (s) is the discharge time and m (g) is the mass of the active material in the film electrode. The mass of the electroactive material of the working electrode was measured using a microbalance.

3. Result and discussion

Figure 1(a,b,c) shows SEM images of Co-doped manganese oxide nanolayers synthesized as a result of 15, 25 and 50 treatment SILD cycles. As can be seen from the presented SEM images, in the process of increasing the number of treatment cycles, the surface of the foam nickel is gradually overgrown with a layer of the synthesized compound. The nanolayer is formed by spherical agglomerates. Moreover, as can be seen from the image with a large magnification, the agglomerates, in turn, consist of a set of ultrathin (6–8 nm) manganese oxide nanosheets (Fig. 1d). The EDX spectrum (Fig. 2) data demonstrate the presence of Mn, Co, O, Na, K and Ni (from substrate) atoms in synthesized nanolayers, the Co:Mn atomic ratio is 0.27:1.00 (Na and K amounts are less than 10 %).

According to XRD data analysis, the prepared sample is crystalline one. XRD pattern (Fig. 3) shows evidance of well crystallized sample containing crystalline phases of hausmannite (Mn_3O_4, $I4_1/amd$) (AMCSD #0002024) and birnessite (δ–MnO_2) (AMCSD #0004947). The peaks of the metallic cobalt and cobalt oxide phase were not observed.

Analyzing the results obtained via SEM, EDX and XRD technique, we can assume that the obtained nanolayers are formed by Co-doped manganese oxide ultrathin nanocrystals with nanosheets morphology containing both crystalline phases of hausmannite (Mn_3O_4) and birnessite (δ–MnO_2).

Electrochemical characteristics of synthesized nanolayers as cathode material for zinc-ion hybrid supercapacitors were carrying out by cyclic voltammetry (CVA) and galvanostatic charge-discharge (GCD) techniques. The cyclic voltammograms of the nickel foil electrode with Co-doped manganese oxide nanolayers were recorded in a potential window from 0.5 to 2 V vs. Zn/Zn^{2+} electrode in 1M $ZnSO_4$ electrolyte at scanning rates of 10 mV/s (Fig. 4a). At a scan rate of 10 mV/s, two electrochemical processes take place in the layer, including the intercalation of zinc-ions at and their de-intercalation, indicating that Co-doped manganese oxide is the battery-type electrode material. It is noted that, after the first cycle, subsequent cycles are almost overlapped, demonstrating the excellent reversibility of the Zn^{2+} intercalation/deintercalation and dual-ion reaction process. Fig. 4b shows the galvanostatic charge/discharge curves of the Co-doped manganese oxide/NF electrode at different current density (0.1, 0.2, 0.5 and 1 A/g). The specific capacitance of Co-doped manganese oxide/NF electrode was calculated by eq. (1) is 514.5 F/g at a current density of 0.1 A/g.

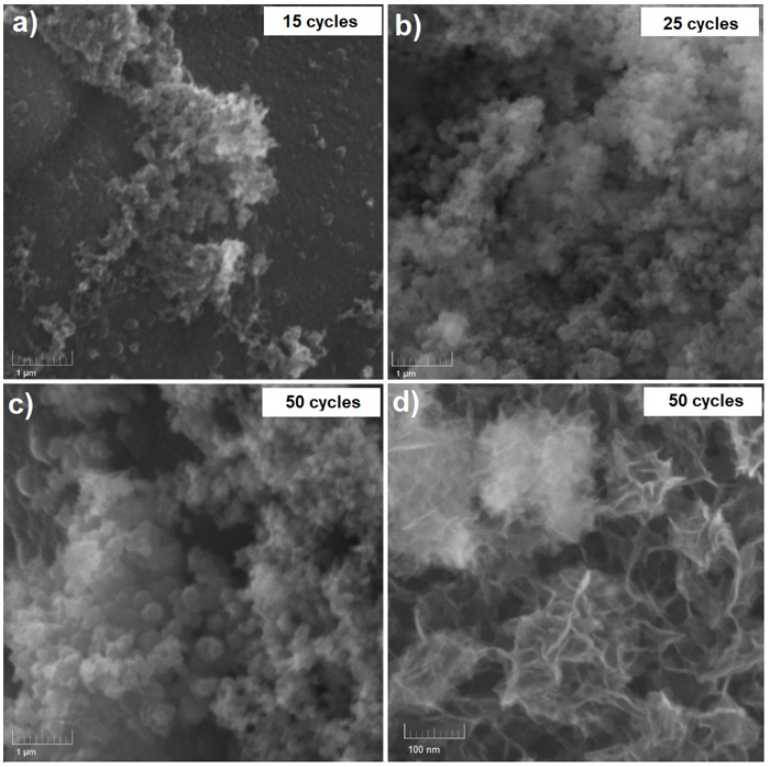

FIG. 1. SEM images of Co-doped manganese oxide nanolayers obtained after 15 (a); 25 (b); 50 (c) treatment SILD cycles and images of nanolayers after 50 (d) treatment cycles obtained at a higher magnification (d)

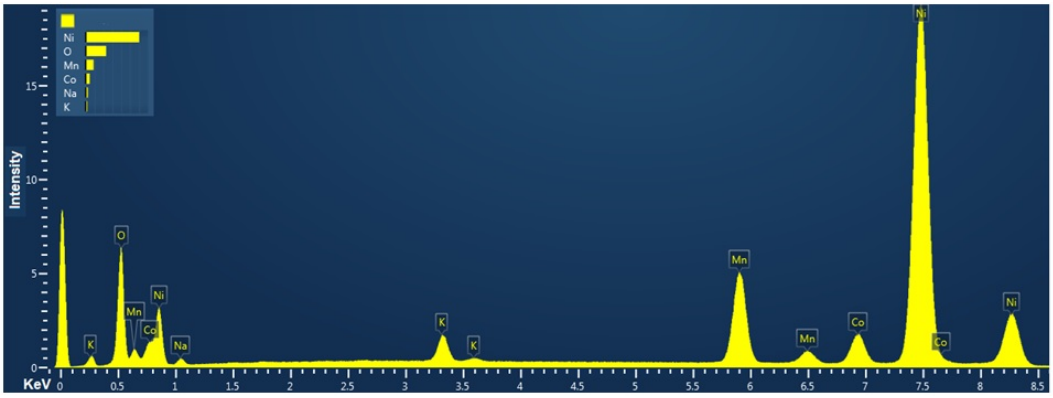

FIG. 2. EDX spectrum of Co-doped manganese oxide nanolayers

The EIS characterization of the electrode obtained at the frequency range from 100 kHz to 10 mHz (is not shown on figure). The Nyquist plot displays a linear part in the low-frequency region and an absence of semicircle in the high-frequency region which indicates very small transfer resistance and fast electrochemical reactions. The internal resistance was calculated from Nyquist plot and is equal to 1.9 Ω. Cycling performance is also important in the practical application of zinc-ion hybrid supercapacitor. It is important to note, that the electrode based on Co-doped manganese oxide exhibits a high cycling stability after 1000 cycles with high capacity retention of 99 %. Such high electrochemical performance, in our opinion, can be explained by a "synergy effect" of unique morphology ultrathickness nanocrystals and layered crystal structure of Co-doped manganese oxide, which enlarges the electroactive surface area of the electrode and the smaller size of nanocrystals brings about good intercalation/deintercalation of zinc-ions on the electrode surface on the frontier of the electrode/electrolyte and hence affects positively on the electrochemical stability.

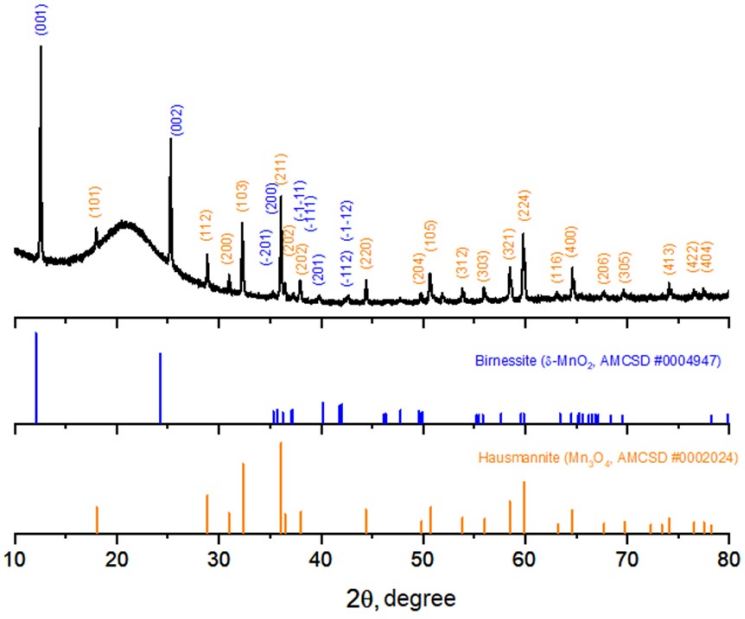

FIG. 3. XRD patterns of Co-doped manganese oxide nanolayers

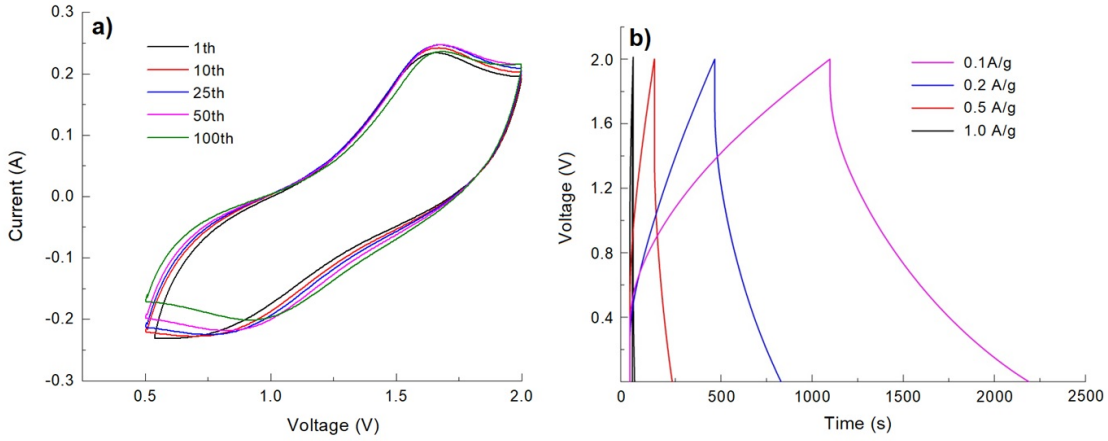

FIG. 4. CVA cycling stability after 100 cycles (at 10 mV/s) (a) and galvanostatic charge–discharge curves at different current density (b) of the electrode based on nickel foam and Co-doped manganese oxide nanolayers

4. Conclusion

To conclude, we can remark that the possibility for direct synthesis of two-dimensional nanocrystals of Co-doped manganese oxide was shown for the first time. The obtained nanomaterial were formed from ultrathin (6–8 nm) two-dimensional nanocrystals of Co-doped manganese oxide with the "nanosheets" morphology which contains birnessite and hausmannite crystal phases. The electrochemical study of Co-doped manganese oxide nanolayers modified nickel foam electrodes, prepared as result 50 treatment SILD cycles, demonstrate that the specific capacitance is 514.5 F/g at a current density of 0.1 A/g. Repeated cycling for 1000 charge-discharge cycles demonstrates a relatively small 1 % capacitance fade.

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