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NANOSTRUCTURED AND DISORDERED OXIDES OF MANGANESE OBTAINED BY ELECTROCHEMICAL DOPING TECHNIQUE

Disordered and semi-amorphous oxides of manganese have been prepared by the anode electrodeposition from fluoride containing electrolytes of manganese sulfate at the presence of additives of cobalt(II), copper(II), lithium ions. Materials obtained were characterized with XRD, TGA, TEM, Fourier spectroscopy. The low doping by ions of cobalt, copper, and lithium have also been studied. It has been shown that the latter additives allow varying the phase composition, defects concentration and size of crystallites of the anode product. The heavier doping leads to the formation of X-ray amorphous products.

Розглянуто невпорядковані і напіваморфні оксиди мангану, які були отримані методом анодного електроосадження з фторвмісних електролітів на основі сульфату мангану в присутності добавок іонів двовалентних кобальту, міді, літію. Отримані продукти характеризувалися методами РФА, ТГА, ТЕМ, Фур'є спектроскопії. Досліджувано низький вміст домішок іонів кобальту, міді, літію. Показано, що згадані домішки дозволяють направлено змінювати склад, дефектну концентрацію і розмір кристалітів анодного продукту. При високому вмісті домішок утворюються рентгеноаморфні продукти.

Introduction

Nanoscience and nanotechnology have become a new frontier of science and promising area with political, economic, and social context during the last decades. There are three important features of science and technology on the nanometer scale. One is that surface effects are accentuated. A second is that scaling laws can break down. The third is that quantum effects can appear.

Electrochemistry as a branch of chemistry should play a key role in synthesis and application of next-generation of nanostructures including oxide-based materials. For instance, electrodeposition is known to be a prospective method of nanopowders and nanofilms preparation. It allows fine control over the thickness of the films. Adjustment of the structure ordering and composition of the electrodeposition products can be achieved due to the wide range of synthesis conditions. On the other hand, the reproducibility of results is often very difficult to achieve. First of all, non-equilibrium conditions of a nanostate and high chemical energy explains strong tendency of nanoparticles to agglomeration and usually we have to do with aggregated electrochemical nanostructured materials instead of nanomaterials on the whole [1]. The further investigations are necessary to develop more selective conditions and methods of preparation of functional electrochemical nanomaterials.

The electrochemical synthesis from fluoride containing electrolytes has many advantages comparing with the state-of-the-art electrolytic methods including the realisation of higher rates of electrodeposition. Fluoride containing electrolytes allow to produce electrolysis products with significant concentration of defects by changing the fluoride-ligand concentration in electrolyte [2; 3]. Changing the concentration of fluoride, the nonstoichiometry of the product can be varied as well as its electrochemical and catalytic activity.

We suppose addition of dopant ions at electrochemical synthesis to be the next step of adjustment of phase and chemical composition, channels and layers, and also defects in nanostructured samples. Heavy doping would lead eventually to the formation of composite oxide materials [4]. Both the low doping and mixed oxide approaches have some merit. For instance, the electrocatalytic activity of electrodes, as well as their stability, can often be considerably enhanced by the incorporation of some foreign ions added to the electrodeposition solution [4; 5]. Among these, Bi^{3+}, Fe^{3+}, Co^{2+} and F^- gave very good PbO_2 electrodes for oxygen transfer reactions, including formation of ozone [6].

The purpose of this paper is to investigate the influence of dopant ions of lithium, copper, and cobalt (II) on the nanostructured manganese dioxide electrodeposited from fluoride containing electrolytes.

Experimental

The products of anode oxidation of manganese(II) ions at the presence of additives of lithium, copper and cobalt ions were synthesized in the electrochemical method from fluoride containing electrolytes [3]. The concentration ranges for dopants used in the electrolyte were chosen on the basis of the solubility of the corresponding compounds and some preliminary results of chemical analysis.

The electrodeposition of the doped manganese dioxide was studied on a Pt anode in 0.5 M HF containing 0.7 M $MnSO_4$.

For doping with cations, the corresponding salts introduced by the addition of 0.001–0.02 mole·L^{-1} $CuSO_4$ or 0.025–0.15 mole·L^{-1} LiOH. A constant current density range was 1–6 A·dm^{-2} at room temperature. A plate of steel of 1CH18N10T grade served as a cathode. Deposits were mechanically removed from the anode and rinsed with distilled water onto vacuum filter, dried in air without heating.

Some samples were prepared using trinary electrolytes by ions of metals. They contained besides manganese sulfate and hydrofluoric acid HF additives of cobalt sulfate and lithium hydroxide. The dopant ions were introduced by the addition of 0.03–1 mole·L^{-1} of $CoSO_4$ and 0.1–4 mole·L^{-1} LiOH.

The content of Mn^{3+} and Mn^{4+} ions in the samples was determined by chemical analysis. The total manganese in the samples was determined by titrating with $KMnO_4$, the Mn^{4+} content being estimated using oxalic acid. The difference between the total manganese and Mn^{4+} content after correction for the actual Mn^{2+} content corresponds to the experimentally determined value of Mn^{3+}. The content of cobalt and lithium in the doped samples was determined by Atomic Absorption Spectroscopy.

X-ray powder diffraction (XRD) analyses of the products were carried out on a DRON-3 X-ray diffractometers with Cu Kα radiation (λ = 0.15406 nm). The phase composition and grain size of the samples was investigated by the program Powder Cell for Windows v 2.3 (http://www.iucr.ac.uk). The Fourier Transmission Infrared (FTIR) spectra were taken on a FSM-1201 Fourier spectrometer, using standard KBr pellet methods.

Transmission Electron Microscopy (TEM) images were obtained at 100 kV with a JEM-100CX II electron microscope.

Samples for TEM were prepared by placing a drop of 10^{-2}–10^{-3} mol L^{-1} manganese sols/colloids on carbon coated copper grids and allowing the water to evaporate at ambient temperature.

Thermogravimetric Analysis (TGA) data were collected with a derivatograph of Paulic-Paulic-Erdey (Hungary). The temperature was increased from ambient to 900 °C at a rate of 10 °C/min.

Results and discussion

Fig. 1 illustrates the X-ray diffraction patterns of manganese dioxide anodically deposited in 0.7 M $MnSO_4$ + 0.25 M HF doped by LiOH.

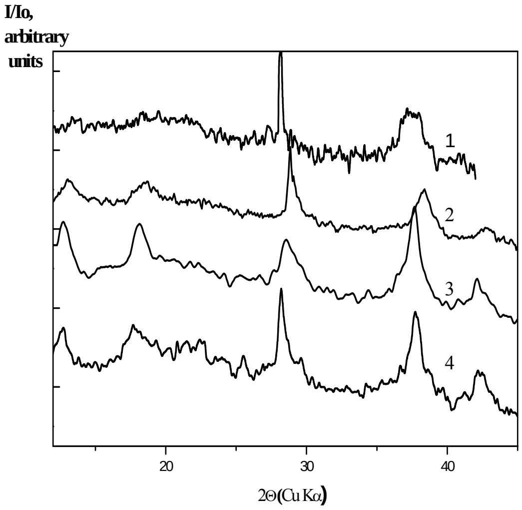

Fig. 1. XRD patterns of undoped MnO_2 sample (*1*) and doped by 0.025 M (*2*), 0.1 M (*3*), 0.15 M (*4*) solutions of LiOH, respectively

These patterns show reflections of a main component identified as α-MnO_2. The growth of dopant ion of lithium concentration causes shifts of XRD pattern peaks and increases the structure ordering comparing with undoped manganese dioxide obtained from the same electrolyte.

Lithium as a dopant stabilizes more opened α-polymorph of manganese dioxide with the structure type of hollandite (I4/m space group) where ions of lithium occupy the blank space of structure channels. The growth of the lithium content causes the expansion of the unit cell (fig. 2). To a certain extent the similar mechanism is observed in manganese dioxide doped by copper. However, the main phase at the presence of copper ions is γ-polymorph of MnO_2.

The choice of fluoride containing electrolytes was by no means accidental. The fluoride containing complexes such as $[Mn(H_2O)_6(SO_4)_2(NH_4)F]^{2-}$ in electrolyte of manganese have higher mobility at electrodeposition of manganese dioxide [7].

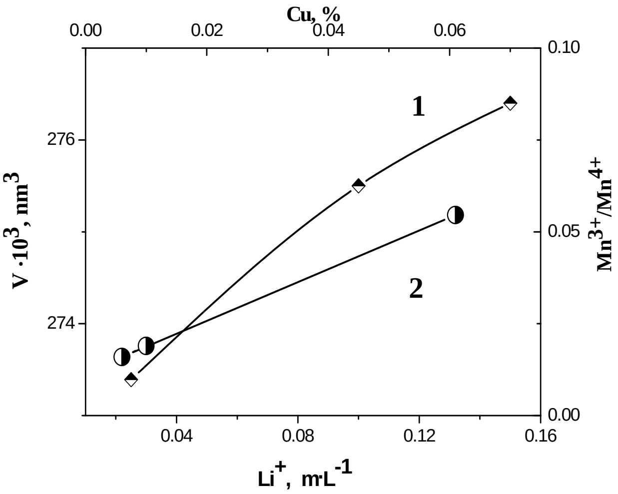

Fig. 2. The correlation of lithium content in electrolyte with the unit cell volume (*1*) and copper content in the doped samples with the Mn^{3+}/Mn^{4+} ratio in the anode products (*2*)

Moreover, the presence of fluoride increases markedly content of incorporated cobalt at anode deposition of lead dioxide [4]. Authors of this paper supposed that formation of F-containing complexes, probably bearing a partial negative charge, such as $[Co(OH)_xF_y]^{(2-x-y)}$, are responsible for an increase of Co surface concentration due to more favourable adsorption. The maximal content of incorporated cobalt in our experiments made up about 3 % at minimal concentration of manganese ions.

It is known that manganese dioxide form family of tunnelled polymorphs capable of intergrowth of their tunnels [8]. Manganese dioxide exists in five polymorphic modifications: α-, β-, γ-, ε-, δ-, and λ-MnO_2.

The multiphase composition and the grain size of the samples obtained were analyzed by the program Powder Cell v. 2.4. The evaluation of the latter showed anomalous dispersity of the samples (2–10 nm). For instance, the typical multiphase sample doped by Cu^{2+} (0.02 mole·L^{-1}) showed the presence of 85 % of γ- 15 % of α- and 5 % of ε- polymorphs of manganese dioxide, respectively.

Based on different phase compositions and the peaks shifts of X-ray diffraction patterns in samples doped by copper or lithium it is concluded that ions of copper have another mechanism of incorporation in the framework of manganese dioxide. The substitution of framework cations by divalent inorganic cations such as Cu^{2+} changes the average manganese oxidation state. Subsequently, the content of copper in samples correlates with the ratio Mn^{3+}/Mn^{4+} (fig. 2).

In accordance with the model recently proposed by Ruetschi [9], it is now widely believed that the reason of nonstoichiometry of manganese dioxide is the presence of cation vacancies in the crystallographic structure.

Thus we are fully justified in observing that incorporation of the foreign species such as ions of copper and probably cobalt in manganese dioxide occurs at defect sites. This conclusion conforms to the results reported earlier by A. Velichenko [6].

The simultaneous presence of ions of Li and Co(II) in fluoride containing electrolytes and growth of their concentrations showed the following peculiarities: decrease of crystallinity of samples and X-ray amorphous behaviour, the length and perfection of nanorods of the main phase of manganese dioxide. The results of chemical analysis, TEM and FTIR-spectroscopy investigations of such products showed that these samples belong to nanostructured crystallites of manganese dioxide of 5-10 nm diameter and length to width ratio below 50.

Comparison of TEM images confirmed an assumption concerning the change of samples dispersity and crystallinity at doping. The needle-like crystallites of manganese dioxide sample doped by ions of lithium lose their perfection and decrease their size at maximal content of additives.

Results of thermogravimetric and XRD analysis examine that doped samples of manganese dioxide are semiamorphous or X-Ray amorphous in accordance with the XRD patterns and the amount of physically sorbed water. Thermogravimetric analysis of the sample with maximal content of dopant ions of cobalt and lithium used in this work the content of physically sorbed water makes up about 20%. This endothermic heat effect is observed at 120°C. Exothermic heat effect at 320 °C characterizes phase transition in more regular polymorph of β-manganese dioxide. The endoeffect of transformation MnO_2–Mn_2O_3 is observed at lower temperature (478 °C) in comparison with crystalline undoped samples of manganese dioxide (520–560 °C).

Conclusion

In summary, disordered and semi-amorphous oxides of manganese have been prepared by the anode electrodeposition from fluoride containing electrolytes of manganese sulfate at the presence of additives of cobalt(II), copper(II), lithium ions. Their further potential as electrode materials in power sources and as catalysts is currently under investigation.

It is shown by XRD method that in spite of general ability of transition metal ions to substitute manganese (IV) ions in the framework of the host structure the mechanism of extraframework substitution or the formation of more opened polymorphs of manganese dioxide with larger tunnels takes place during electrodeposition at the low doping by ions of copper, cobalt, and also lithium. Lithium as a dopant stabilizes more opened α-polymorph of manganese dioxide with the structure type of hollandite (I4/m space group) where ions of lithium occupy the blank space of structure channels. The growth of the lithium content causes the expansion of the unit cell. Based on different phase compositions and the peaks shifts of X-ray diffraction patterns in samples doped by copper or lithium it is concluded that ions of copper have also another mechanism of incorporation in the framework of manganese dioxide. Thus we are fully justified in observing that incorporation of the foreign species such as ions of copper and probably cobalt in manganese dioxide occurs at defect sites.

The heavier doping leads to the formation of X-ray amorphous products. The results of chemical analysis, TEM and FTIR-spectroscopy investigations of such products showed that these samples belong to nanostructured dioxide of manganese consisting of nanorods of 5-10 nm diameter and length to width ratio below 50.

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