Liquid-phase synthesis, surface morphology and properties of the electrode materials based on MnO2 for electrochemical devices

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Abstract. The article focuses on the problems of development of electrochemical devices. The effect of a synthesis method and fabrication technology on the electrochemical performance of a MnO2-based electrode is discussed.

1. Introduction

Transition metal oxides, especially manganese (IV) oxide, are promising electrode materials for electrochemical devices such as pseudocapacitors (PCs) and microbiological fuel cells (MFCs) [1-9]. As a rule, properties of a material reveal its prospects. Manganese dioxide is prospective owing to a number of excellent electrochemical characteristics (a wide potential window – up to 0.9V in aqueous electrolytes, high specific capacity and charge-discharge rate), high catalytic activity, cheapness and facility of its manufacturing process.

Nevertheless, electrodes based on MnO2, as well as a number of other transition metal oxides (Fe2O3, Ni2O3, WO3-x, V2O5, Co3O4, etc.) lose in stability of electrochemical characteristics. They have low electrochemical reversibility and a high degree of self-discharge which is one of the most important electrical parameters of PCs. Moreover, low electronic conductivity of about 10^{-5}–10^{-6} S/cm is another significant drawback of MnO2 which limits its practical application [10]. Meanwhile, selection of an appropriate synthesis method and conditions may affect electroactivity and electrochemical stability of the electrode material.

In this paper, we report on the effect of a synthesis method and fabrication technology on the electrochemical characteristics of a MnO2-based electrode for a model electrochemical device.

2. Materials and methods

Manganese (IV) oxide was obtained by the following methods of liquid-phase synthesis: electrochemical deposition (ED) and chemical deposition (CD).

The ED on a conductive support (steel mesh) was carried out in a solution of manganese sulfate (II) at the constant current of 15 mA and the deposition time of 170 s. After the synthesis, the support was washed several times in distilled water and dried at room temperature until it reached a constant weight.
Chemical deposition of MnO$_2$ was a result of a 6-hour reaction between 0.15 M manganese sulfate (II) and 0.1 M potassium permanganate under constant stirring at the temperature of 25 °C. Then, the precipitate was filtered off, washed with distilled water and ethyl alcohol, and dried at 60 °C in the oven for 3 hours.

The MnO$_2$ obtained by ED is the final electrode material because it is deposited on a steel mesh as a homogeneous film with thickness of about 200-300 nm, and does not require additional processing. In this regard, the developed electrode – "MnO$_2$/steel mesh" was tested in a model electrochemical device as a working one.

Whereas MnO$_2$ obtained by CD is a ceramic non-conductive powder, it was first necessary to prepare an electroactive composite paste for covering the electrode (steel mesh). For this purpose, the following components were taken: electroactive material - MnO$_2$ (75 wt.%); conductive material - superconducting carbon black (20 wt.%) and binding material – fluoroplastics (5 wt.%). These components were ground to pasty state after addition of a few drops of n-propyl alcohol.

The resulting paste was ultrasonically processed (22 kHz) for 1 hour and then applied to a conductive support (steel mesh). Thus, composite electrodes were fabricated and further examined in electrochemical tests.

3. Results
Regardless of synthesis method, the obtained oxides are X-ray amorphous. Analysis of IR spectra indirectly confirmed the composition of manganese (IV) oxide by the absorption band in the 600 cm$^{-1}$ region reflecting the Mn-O bond vibration. Surface morphologies of the obtained oxides are significantly different. MnO$_2$ (ED) forms agglomerates with the length of 2 μm and thickness of 0.5 μm whereas MnO$_2$ (CD) forms spheres of about 100 nm in diameter.

Results of electrochemical tests of the composite electrodes are shown in Table 1.

| Type of electrode                | Specific capacity*, C/m, F/g | The equilibrium electrode potential**, U, mV | Electrochemical reversibility***, % | Self-discharge rate****, % |
|---------------------------------|------------------------------|---------------------------------------------|-----------------------------------|--------------------------|
| MnO$_2$/steel mesh              | 200                     | 245                                          | 13                                | 87                       |
| Electroactive paste/steel mesh  | 70                       | 170                                          | 35                                | 65                       |

* C/m, where C - capacitance (F), m - mass of electroactive film consisting of MnO$_2$ or mass of electroactive paste, (g);
**The equilibrium potential of the electrode was measured in a three-electrode cell in the voltmeter mode;
***Electrochemical reversibility was determined by the cyclic voltammetry method from the ratio of the values of -Q and +Q per a cycle;
****Self-discharge rate was determined by the previously developed method [11].

As seen from the table, the electrochemical parameters of the developed electrodes depend on the method of synthesis and fabrication. It should be noted that although capacity of the second type of electrodes (electroactive paste/steel mesh) is inferior to the specific capacity of the electrodes of the first type, their electrochemical stability is significantly better (based on the values of reversibility and self-discharge rate). This is probably due to the fact that composite paste stabilizes electrochemical parameters of pseudocapacitive electrodes.

4. Conclusions
Thus, electrodes of the "electroactive paste/steel mesh" type based on manganese dioxide obtained by chemical deposition, possess higher electrochemical stability compared to electrodes of "MnO$_2$/steel
mesh” type, where MnO₂ is obtained by electrochemical deposition. In the nearest future, we expect to improve the technology of manganese (IV) oxide synthesis and fabrication of electrodes for PCs as well as approbate the developed electrode materials not only in experimental PCs, but also in experimental MFCs in presence of the bacterium Geobacter sulfurreducens.

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