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Catalytically Active Electrode Materials for Oxygen Electrodes Based on Molybdenum-Modified Carbon Nanotubes

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Abstract An electrochemical method for the application of molybdenum oxide on multiwalled carbon nanotubes as well as its procedure is adduced. The preparation of molybdenum oxide applied on multiwalled carbon nanotubes is proven by an X-ray phase analysis and by electron micrographs. The obtained nanocomposite was investigated as an electrode material for oxygen electrodes of low-temperature fuel elements working in alkaline electrolyte. The current-voltage characteristics of the oxygen electrodes made of these nanocomposites are given. It is shown that the obtained nanocomposites based on molybdenum oxide are highly competitive in electrochemical characteristics with the electrodes made of activated carbon supported with platinum.

Keywords: *carbon nanotubes, catalyst, fuel cells, oxygen electrodes, molybdenum oxide*

1. Introduction

Studies on energy-transforming processes are relevant nowadays, because the total energy capacity of distributed power generation exceeds the energy generated by nuclear, thermal and hydroelectric power plants combined. This fact accounts for the increasing interest in fuel cells and in electrode materials for them. The use of air or oxygen electrode in the devices generating electrical energy is very promising because it does not create environmental problems and saves natural resources such as oil and gas. Air and oxygen electrode is a three-phase electrode-electrolyte-gas system, where the generation of electric current is localized at the phase boundary. The current magnitude generated at such gas diffusion electrode depends on the triple contact zone of these three phases. In its turn, the electrode itself is composed of catalyst and carrier. The interaction between them determines the quantity of generated current, which depends on catalyst being used. It is known that nowadays platinum, which is a very expensive material, is the most effective catalyst for oxygen recovering. A great number of works is oriented towards the investigation of other effective but less costly catalysts. Another problem is catalytically active and stable carrier. A review article [1] displays the possibility of using multiwalled carbon nanotubes as electrode material for oxygen electrodes and also proves the stability of these materials over time for the various media. It was also noted that the use of multiwalled carbon nanotubes as a catalyst support enables no aggregation in contrasts to the use of activated carbons. In works [2,3,4,5] the benefits of carbon nanotubes used as the carrier are shown. The application of platinum on carbon nanotubes (CNT) enabled the characteristics of oxygen electrodes to be improved [4]. Carbon nanotubes are characterized by high conductivity and large specific surface area. They also can form mesoporous three-dimension structures, which makes them promising as carriers. Tubular carbonic structure enables the extension of triple electrode-electrolyte-oxygen contact zone, where the process of current flow generation takes place. This leads to an increase in operating current density as compared to activated carbon. The advantages of the material also include small specific density of carbon nanotubes as compared to activated carbon. It follows from the data given in [6] that molybdenum deposited from the gas phase has electrocatalytic characteristics in reactions of oxygen reduction. Molybdenum oxides have high melting point and high corrosion stability in alkaline and acidic media, in which the oxygen electrodes of power cells are working. Therefore, the investigation of the catalytic activity of molybdenum compounds deposited on carbon nanotubes by galvanic method was of special interest. This method of molybdenum electrodeposition on carbon nanotubes allows regulating the current density and the time of electrolysis and hence controlling the weight and size of the deposited catalyst particles. The purpose of this study was to investigate the electrocatalytic characteristics of carbon nanotubes, with molybdenum oxides applied on them by galvanic deposition, as the material of oxygen electrode for power cell.

2. Experimental

Multi-walled carbon nanotubes (MWCNT) [7] were investigated as carriers and electrode material. The product was a black powder with a bulk density of 25-

35g·dm^{-3}. The outer diameter of nanotubes was about 10-30nm, the specific surface area was 230m^2.g^{-1}, the weight of mineral impurities in crude product was 15-20%. MWCNTs were purified of catalyst by means of hydrofluoric acid treatment. Two-layer oxygen electrodes were prepared by pressing. Hydrophobic layer contained 0.07g·cm^{-2} acetylene black with 25% polytetrafluoroethylene. The active layer contained 0.02g cm^{-2} MWCNT, modified by the variety of molybdenum compounds with 5% polytetrafluoroethylene. The research was conducted on a power cell mock-up with zinc as the anode. The mock-up for gas diffusion electrodes testing is described in the works [8,9]. A solution of 5M potassium hydroxide with 1M lithium hydroxide was taken as an electrolyte. A silver chloride electrode connected via salt bridge was taken as the reference electrode. All potentials were measured with respect to standard silver chloride electrode. The characteristics were measured in the galvanostatic mode. The source of oxygen was a U-shaped electrolyzer with alkaline electrolyte. Oxygen was fed to the gas electrodes under surplus pressure of 0.01 MPa. Before the research the oxygen electrode was cleaned with oxygen during one hour. During the electrochemical research, the current at the electrolyzer exceeded by a factor of three the current generated at the gas electrode. The methods of applying molybdenum oxide are described in the work [10]. The electron micrographs were obtained with the help of electron microscope JEM-100 CXII. The X-ray phase analysis was carried out with the help of "DRON – 4" X-ray diffractometer (XRD) with the emission of CuK_α.

3. Results and Discussion

The deposition of molybdenum oxides was carried out by electrochemical method from solutions containing equal amount of ammonium molybdate four water reagent grade, 18 g dm^{-3} and different concentration of hydrofluoric acid of high purity, g dm^{-3}:1 (Sample 1); 2 (Sample 2) and 3 (Sample 3) Table 1.

Table 1. Characteristics of samples of nanocomposites based on multi-walled carbon nanotubes with deposited oxide compound of molybdenum

Sample number	Hydrofluoric acid concentrationin electrolyte, g/dm^3	Content of elemental Mo in a sample, mass %	Average size of catalyst particles, nm
1	1	5	3-5
2	2	4	
3	4	3.5	12-15

The conditions of electrolysis were the same: current density of 0.25 A dm^{-2}, the time of electrolysis of 0.5 hour and the temperature of 22 ℃. As a result, nanocomposites based on carbon nanotubes with deposited oxide molybdenum compounds were obtained by electrochemical method. The content of molybdenum in different samples was: 5, 4 and 3.5 mass %. As can be seen from the photographs Figure 1 and Figure 2, the size of obtained particles is growing simultaneously with the hydrofluoric acid concentration increase. We suppose that this is connected with the fact that, while the acid concentration in electrolyte is growing, the centers of molybdenum oxide crystallization on the surface of nanotubes are decreasing, and this leads to the increase in the average size of deposited particles.

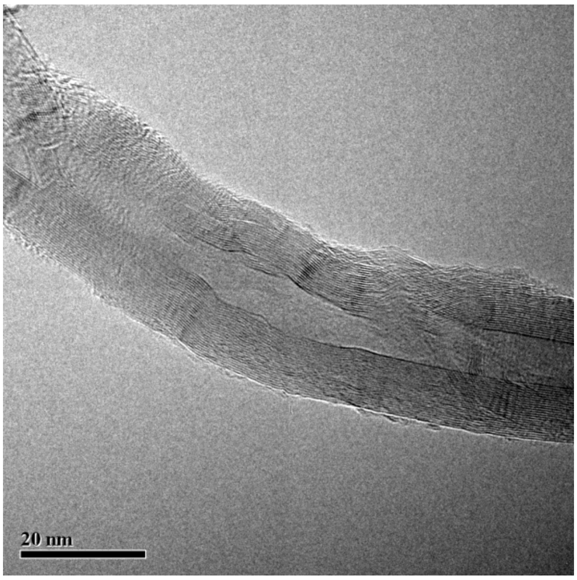

Figure 1. Electron micrograph of the sample No 1. Elemental molybdenum content 5 wt %

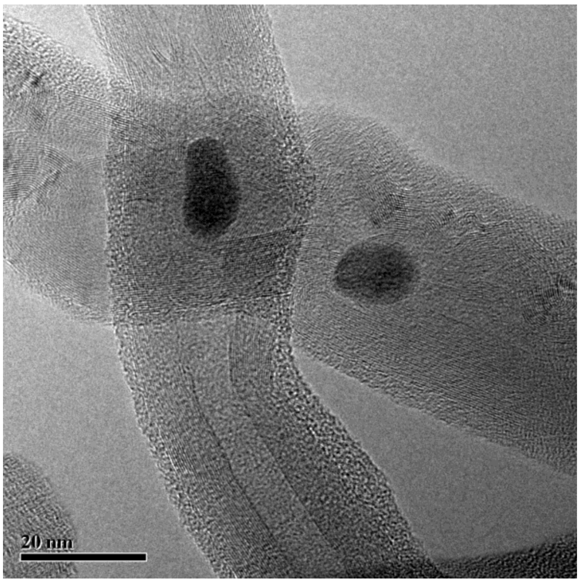

Figure 2. Electron micrograph of the sample No 3. Elemental molybdenum content 3.5 wt %

An X-ray phase analysis of obtained composites was carried out for the identification of deposited particles. Figure 3 displays the X-ray pattern of composites obtained from the solutions containing the hydrofluoric acid. Curve 1 corresponds to Sample 1 (Table 1) and curve 2, to Sample 3 (Table 1). The obtained apexes were identified as a molybdenum oxide at 2θ=26.04 degrees, by virtue of roentgen-amorphism of carbon nanotubes. However, the lines from synthesized oxide are marginally displaced from theoretical diffractogram. This points to the fact that the lattice constant doesn't correspond to oxide balanced state, for example, due to nonstoichiometric structure. The oxygen electrodes were made from the obtained composites. Figure 4 shows the plots of potential against current density for oxygen electrode based on nanostructured composites from the nanotubes with molybdenum oxide applied on them.

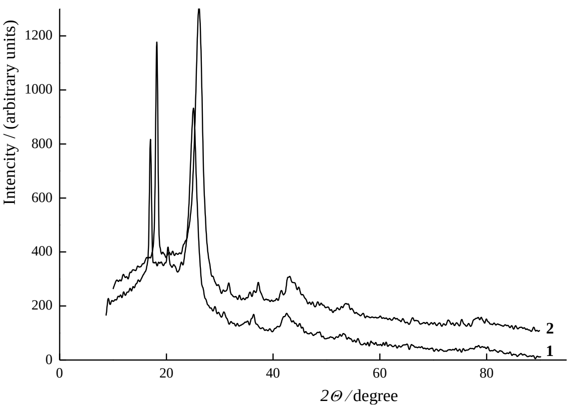

Figure 3. X-ray phase analysis of composites sample based on molybdenum oxide and carbon nanotubes containing elemental molybdenum with mass % of: (1) 5.0, (2) 3.5. An apex at 2θ=26.04 degrees corresponds to molybdenum oxide

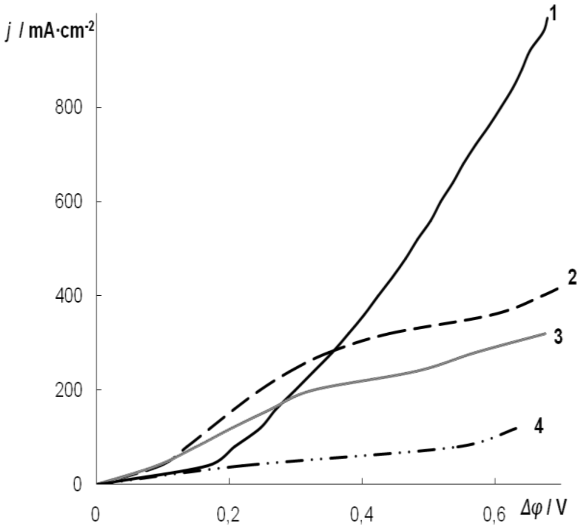

Figure 4. Dependence of potential on current density for an oxygen electrode based on 0.02 g/cm^2 nanostructured composites of nanotubes with deposited molybdenum oxide with an elemental molybdenum content of (wt %): (1) 5.0, (2) 4.0, (3) 3.5, (4) pure carbon nanotubes

It follows from the figure that the electrode which contains 5 mass % of elemental molybdenum has the best electrical characteristics of oxygen electrodes. Next to them, according to activity decrease, are the electrodes based on nanotubes composites with molybdenum oxide containing 4 and 3 mass % of molybdenum. For comparison, Figure 4 shows a curve for electrodes based on initial nanotubes. Such dependence of electrical characteristics of oxygen electrodes is determined by the decrease in particle size of deposited molybdenum oxide compounds. It is also confirmed by electron micrographs: Figure 1 for 5 mass % of molybdenum and Figure 2 for 3.5 mass % of molybdenum. It follows from the photographs that the average size of molybdenum oxide particles increases with the concentration of hydrofluoric acid in electrolyte. The studies of the electrical characteristics of the oxygen electrode proposed by us have been conducted during 6 months. They showed that the electrode materials based on synthesized nanocomposite of molybdenum oxide deposited on carbon nanotubes are stable over time. Electrical characteristics of various oxygen electrodes of pure carbon nanotubes coated with manganese dioxide [5], molybdenum oxide and platinum, are shown in Table 2.

Table 2. Comparative electrical characteristics of different oxygen electrodes basing equalized polarization of 250 mV

Primary MWCNT, mA/cm^2	Nanocomposite based on MWCNT and manganese dioxide of 15 mass %, mA/cm^2	Nanocomposite based on MWCNT and molybdenum oxide with the elementary molybdenum content of 5 mass %, mA/cm^2	Nanocomposite based on MWCNT and platinum of 15 mass % , mA/cm^2
40	150	300	350

Characteristics of the obtained oxygen electrodes are given at 250mV polarization relative to stationary potentials of these electrodes. Calculated electrochemical characteristics of the oxygen electrode of power cell based on molybdenum oxide compound deposit on multiwalled carbon nanotubes are 300mW cm^{-2} with the polarization of 250mV at room temperature.

4. Conclusions

An electrochemical method for the obtaining of nanostructured composites based on carbon nanotubes and molybdenum oxide of +4 oxidation state is proposed.

It is shown that the obtained electrode materials are promising catalysts for oxide electrodes of fuel elements which can replace commercial electrode materials containing platinum.

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