

Short communication

# Carbon nanotubes modified with catalyst—Promising material for fuel cells

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## Abstract

Carbon nanotubes (CNTs), modified with manganese dioxide, were synthesized. Manganese dioxide was obtained by reduction of solution of potassium permanganate with formic acid solution or with carbon of nanotubes. Electrochemical characteristics of the oxygen electrodes containing manganese dioxide modified nanotubes in active layer were investigated. It was shown, that deposition of manganese dioxide on surface of carbon nanotubes results in improvement of electrochemical characteristics in comparison with manganese dioxide as a separate phase. The optimum mass content of manganese dioxide is 50% from the sum (carbon nanotubes + MnO<sub>2</sub>).

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## 1. Introduction

Application of oxygen or air electrodes in chemical sources of current is very promising. These electrodes can be applied in fuel cells and in metal—air sources of current. They do not cause ecological problems, save critical materials, and have high specific energy.

The process of electrochemical reduction of oxygen was studied by many scientists [1–5]. Catalysts essentially influence this process. A great number of catalysts for electrochemical reduction of oxygen were offered. These are platinum, rhodium, iridium, silver, La<sub>x</sub>MnO<sub>3</sub>, MnO<sub>2</sub>, activated carbon, nickel and cobalt oxides, spinels (NiCo<sub>2</sub>O<sub>4</sub>, MnCo<sub>2</sub>O<sub>4</sub>, CoAl<sub>2</sub>O<sub>4</sub>), perovskites (LaCoO<sub>3</sub>, La<sub>1-x</sub>SrCoO<sub>3</sub>, La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub>, La<sub>1-x</sub>CaCoO<sub>3</sub>, etc.), macrocyclic complexes, their polymers and pyropolymers [6].

Along with development of carbon nanomaterials, particularly nanotubes, new possibilities of creation of new catalysts appeared. Such catalytic systems can be created by deposition

of known catalysts on surface of carbon nanotubes (CNTs). Synergetic interaction of the catalyst particles with carbon nanostructures can provide better catalytic parameters than application of carbonaceous materials and metal-containing catalysts separately [7,8]. It is known that activated carbons can interact with ions of some metals with deposition of the metals on surface of carbon [9]. In these reactions metal ions act as oxidant and carbon as a reducing agent. Metal–carbon composites, so obtained, can be good catalysts.

Carbon nanotubes have high electroconductivity and high specific surface area and can form mesoporous spatial structures. These factors are favorable for use of carbon nanotubes as catalysts supports. Highly efficient fuel cell electrode based on carbon nanotubes was demonstrated. The CNTs were grown on carbon paper by chemical vapor deposition (CVD) using electrodeposited Co/Ni catalyst [10]. Valuable advantage of this method is the possibility of growing of CNTs on a porous electroconducting support like carbon paper. The brush-like structure formed is favorable for creation of thin electrodes for fuel cells. Pt was subsequently deposited by spraying of Pt precursor on CNTs followed by in situ reduction with hydrogen. Cyclic voltammograms show a significant improvement of the Pt utilization in the CNT-based electrode compared to traditional electrodes. High performance was observed for CNT-based electrode (Pt loading of

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0.15 mg cm<sup>-2</sup>) with maximum power density of 623 mW cm<sup>-2</sup> at 70 °C and 0.3 MPa [10].

Today the cost of multiwalled CNT (MWNT) amounts nearly one to several thousands US\$ per kilogram, as it follows from data available in price lists of different producers. However, the cost tends to decrease. For instance, one of the largest producers of nanocarbon materials—NTP (China) have declared that in nearest future the cost of MWNT will be nearly US\$ 250 kg<sup>-1</sup>. It should be noted that the cost of raw materials used for CNT production (methane, ethylene, propylene) is low. The catalysts which are used in CVD process do not contain rare or noble metals. Their cost today is relatively high because of complicated technology needed for creation of nanodimensional structure with prescribed size and structure of catalytically active sites. However, technologies of both CNT CVD process and catalyst production process are being continuously improved. So, we think that in near future the cost of MWNT may be US\$ 50–100 kg<sup>-1</sup>. At that, in different applications CNTs have better performance than traditional carbon blacks. We believe that CNTs will replace carbon blacks in many applications.

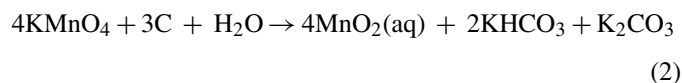
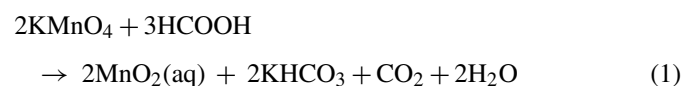
As is known, when carbon nanotubes are oxidized by various reagents in water solution, disordered carbon burns out first [11]. Thus, in the oxidizing medium it is possible to perform deposition of metal compounds on carbon nanotubes simultaneously with purifying the last of impurity of disordered carbon.

So, one may suppose that CNT, similarly to active carbons, can reduce ions of electropositive metals at the expense of easily oxidizable disordered carbon admixture. We have studied reduction of potassium permanganate to manganese dioxide as a model reaction demonstrating a possibility of nanodimensional catalytically active particles formation in such a way.

The purpose of the present work is research of influence of interaction of manganese dioxide catalyst with carbon nanotubes support on electrochemical characteristics of oxygen electrodes for fuel cells composed of these materials.

## 2. Experimental

Multiwalled carbon nanotubes were used as a support, and manganese dioxide as catalyst. Manganese dioxide was obtained by reduction of potassium permanganate solution with formic acid or carbon of MWNT according to the reactions:



It should be noted that the reactions equations listed above do not take into account an opportunity of formation of hydroxyl and carboxyl groups attached to nanotubes. In view of this the loss of nanotubes carbon at deposition of manganese dioxide should be less than at complete oxidation of carbon to carbonate according to the reaction (2).

MWNT were obtained by chemical vapor deposition method with use of ethylene as a source of carbon. Mixed iron-molybdenum-aluminum oxide was used as a catalyst for MWNT growth. The catalysts were obtained by co-precipitation of metal hydroxides with ammonia from solution containing aluminum nitrate, iron formicate–acetate, and ammonium molybdate at atomic ratio Al:Fe:Mo = 1:1:0.07. For decreasing of MWNT agglomeration aerosil A-300 was added into reactor [12]. The crude product was obtained as a black powder with bulk density of 25–30 g dm<sup>-3</sup>. External diameter of nanotubes was near 10–30 nm, specific surface area –230 m<sup>2</sup> g<sup>-1</sup>, mass content of minerals in the crude product was 15–20%. The crude product was purified of mineral impurity (catalyst and aerosil) by treatment with HF solution and further used as a water paste without drying.

For deposition of manganese dioxide on MWNT amount of potassium permanganate was calculated so that the mass content of anhydrous manganese dioxide in sum (MWNT + MnO<sub>2</sub>) was 9, 16.7, 50, and 80%. Actually, in conditions of our experiments hydrated manganese dioxide was precipitated.

Deposition of manganese dioxide on MWNT was performed by two methods.

The first one included reduction of potassium permanganate with formic acid in presence of suspended MWNT according to Eq. (1). It was found that at mixing an aqueous solution of potassium permanganate with MWNT suspension without heating first time reaction (2) proceeded in a small extent, but then the rate of this reaction strongly decreased. With increasing of quantity of permanganate the share of permanganate, consumed in reaction (2) with MWNT without heating, decreased. Probably, at first only low-ordered MWNT fragments react with permanganate. For complete reduction of permanganate formic acid was added into solution. So, 73.5 g of water paste of purified MWNT (mass content of dry substance 6.8%) was placed into a glass and diluted with 430 ml water at stirring. Separately 1.82 g of potassium permanganate was dissolved in 50 ml of water. Solution of permanganate was poured at stirring into MWNT suspension. The mixture was stirred with a mechanical stirrer during 1 h at room temperature. Then during 20 min at continuous stirring formic acid was added to the reaction mixture. Formic acid was taken 64% from stoichiometric amount calculated according to Eq. (2). Color of permanganate completely disappeared during 50 min after addition of formic acid. The reaction mixture consisted of large flakes of MWNT agglomerates and brown colloidal suspension of hydrated manganese dioxide. After boiling of this mixture within 1 h colloidal particles of manganese dioxide were completely adsorbed on nanotubes. The reaction mixture after coagulation represented black flakes in a transparent colorless liquid. The product was filtered, washed with water, and dried in a drying box at 120 °C. Weight of the black product (sample M-16.7form) was 6.1 g. The calculated content of anhydrous manganese dioxide was 16.7% from the sum (MWNT + MnO<sub>2</sub>).

Experiments with obtaining of materials with other content of manganese dioxide (50 and 80% from MWNT + MnO<sub>2</sub>, samples M-50form and M-80form) were carried out in a similar way. In these experiments calculated amount of potassium per-

manganate was increased to obtain specified content of  $\text{MnO}_2$ . At this the quantity of formic acid necessary for full reduction of permanganate (disappearance of a pink aura around of drop test on a filtering paper), was 80% from stoichiometric for sample M-50form and 89% for sample M-80form. Thus, small amount of permanganate was reduced by MWNT before addition of formic acid. In these experiments complete adsorption of manganese dioxide particles on MWNT (after reduction of all permanganate with formic acid) was not achieved after boiling of the reaction mixtures. The products represented mechanical mixture of MWNT, covered with uncertain amount  $\text{MnO}_2$ , and superfluous  $\text{MnO}_2$  as a separate phase.

The second method of obtaining of MWNT modified with manganese dioxide was based on reaction of reduction of permanganate solution with disordered carbon admixture in MWNT (2) at boiling. As follows from the equation of reaction (2), for deposition of 1 g anhydrous manganese dioxide combustion of 0.1036 g of carbon is necessary. Thus, burning relatively small amount of MWNT, predominantly disordered carbon, it is possible to deposit relatively great amount of manganese dioxide. In these experiments solution of potassium permanganate was added to MWNT suspension and the mixture was boiled at stirring up to disappearance of permanganate color. So, into a glass 40.6 g of purified MWNT aqueous paste was placed. Mass content of dry substance in this paste was 6.8%. The paste was diluted at stirring with 250 ml water. Separately 4.55 g potassium permanganate was dissolved in 250 ml of water. Solution of permanganate was poured at stirring into suspension of nanotubes. Then the suspension was heated up to boiling. For disappearance of permanganate color it required 40 min boiling at continuous stirring. The reaction mixture represented black flakes in transparent very slightly brownish liquid (probably, insignificant amount of manganese dioxide sol). To prevent coagulation of the precipitated manganese dioxide into sol, washing of the product was carried out with 2% solution of ammonium bicarbonate. At washing with ammonium bicarbonate solution coagulation of manganese dioxide was not observed (washing liquid was colorless). The product was dried in a drying box at 120 °C. Weight of the black product (sample M-50carb) was 5.20 g. Calculated content of anhydrous manganese dioxide in MWNT +  $\text{MnO}_2$  makes 50%. This content was calculated taking into account that a little part of carbon burned out according to Eq. (2).

Similarly samples with other mass content of manganese dioxide were synthesized (samples M-9carb, M-16.7carb, and M-80carb). The duration of boiling, necessary for complete reduction of permanganate by carbon nanotubes, amounted correspondingly 5, 20, 40, and 75 min for the samples M-9carb, M-16.7carb, M-50carb, and M-80carb, respectively. Permanganate reacts more quickly with admixture of disordered carbon than with well-ordered graphene layers of MWNT walls, so this results in great increase of time needed for reaction with potassium permanganate as its amount increases.

Two-layered oxygen electrodes were used, composed of hydrophobic layer, containing hydrophobic acetylene soot and 25% of polytetrafluoroethylene (PTFE), and active layer, containing MWNT, manganese dioxide, and 5% of PTFE. Elec-

trodes were made by pressing in a press mold with 30 mm diameter die at pressure of 20 MPa.

Experiments were carried out with use of fuel cell oxygen electrode described in Ref. [13] at 20 °C and pressure of oxygen gas, 0.1 MPa. 5 M KOH solution was used as electrolyte, and zinc as auxiliary electrode. Potentials were measured compared to silver-chloride electrode connected through a salt bridge. Electrochemical characteristics were recorded in galvanostatic mode. U-shaped electrolytic cell with alkaline electrolyte was used as a source of oxygen. Current through electrolytic cell three times exceeded the current generated in oxygen electrode. Oxygen was fed to the oxygen electrode at superfluous pressure of 0.01 MPa. Before measurements oxygen was passed during 1 h at open circuit of fuel cell.

Optimal amount of acetylene soot in hydrophobic layer, determined in preliminary experiments, was 0.07 g  $\text{cm}^{-2}$ . Active layer of electrode contained 0.02 g  $\text{cm}^{-2}$  of MWNT modified with manganese dioxide.

Electron images were recorded with use of transmission electron microscope JEM-100 CXII.

### 3. Results and discussion

Electron images of initial MWNT and MWNT, modified with manganese dioxide, are shown in Fig. 1a–c. For the sample of MWNT modified with  $\text{MnO}_2$ , prepared by reduction of potassium permanganate with carbon of MWNT (sample M-50carb), fine nanoparticles of  $\text{MnO}_2$  are observed, which are pasted and uniformly distributed on the surface of nanotubes (Fig. 1b). If potassium permanganate is reduced with formic acid (sample M-50form), the surface of nanotubes is clean, and  $\text{MnO}_2$  is present in form of much larger particles as mechanical mixture with nanotubes (Fig. 1c). It should be noted also that modified MWNT samples prepared by reduction of permanganate by carbon of MWNT at boiling are black at all mass contents of  $\text{MnO}_2$ , while reduction of permanganate with formic acid gives brown hydrated manganese dioxide.

In Fig. 2 there are shown Volt–Ampere characteristics of the oxygen electrodes containing different amounts of manganese dioxide supported by MWNT (Fig. 2, plots 1–4). For comparison, there are shown characteristics of electrodes containing pure  $\text{MnO}_2$  obtained by reduction of potassium permanganate with formic acid (Fig. 2, plot 5), and pure MWNT without  $\text{MnO}_2$  (Fig. 2, plot 6). With increasing of content of manganese dioxide characteristics of the oxygen electrode first became better and reach maximum at 50% of  $\text{MnO}_2$  (plot 3). Further increase of  $\text{MnO}_2$  content results in deterioration of electrochemical characteristics. At the same time electrodes containing 80%  $\text{MnO}_2$  works better than electrodes containing 100%  $\text{MnO}_2$ , up to the current density 175 mA  $\text{cm}^{-2}$  (Fig. 2, plots 4 and 5). Optimum at 50% content of  $\text{MnO}_2$  can be explained by the most uniform distribution and interaction of nanodimensional  $\text{MnO}_2$  with MWNT. This is seen in electron image (Fig. 1b).

Increase of electrochemical characteristics of electrodes with increase of  $\text{MnO}_2$  mass content from 9 to 16.6 and 50% (Fig. 2, plots 1–3) is probably caused by formation of regularly distributed manganese dioxide with optimum structure. Decrease of



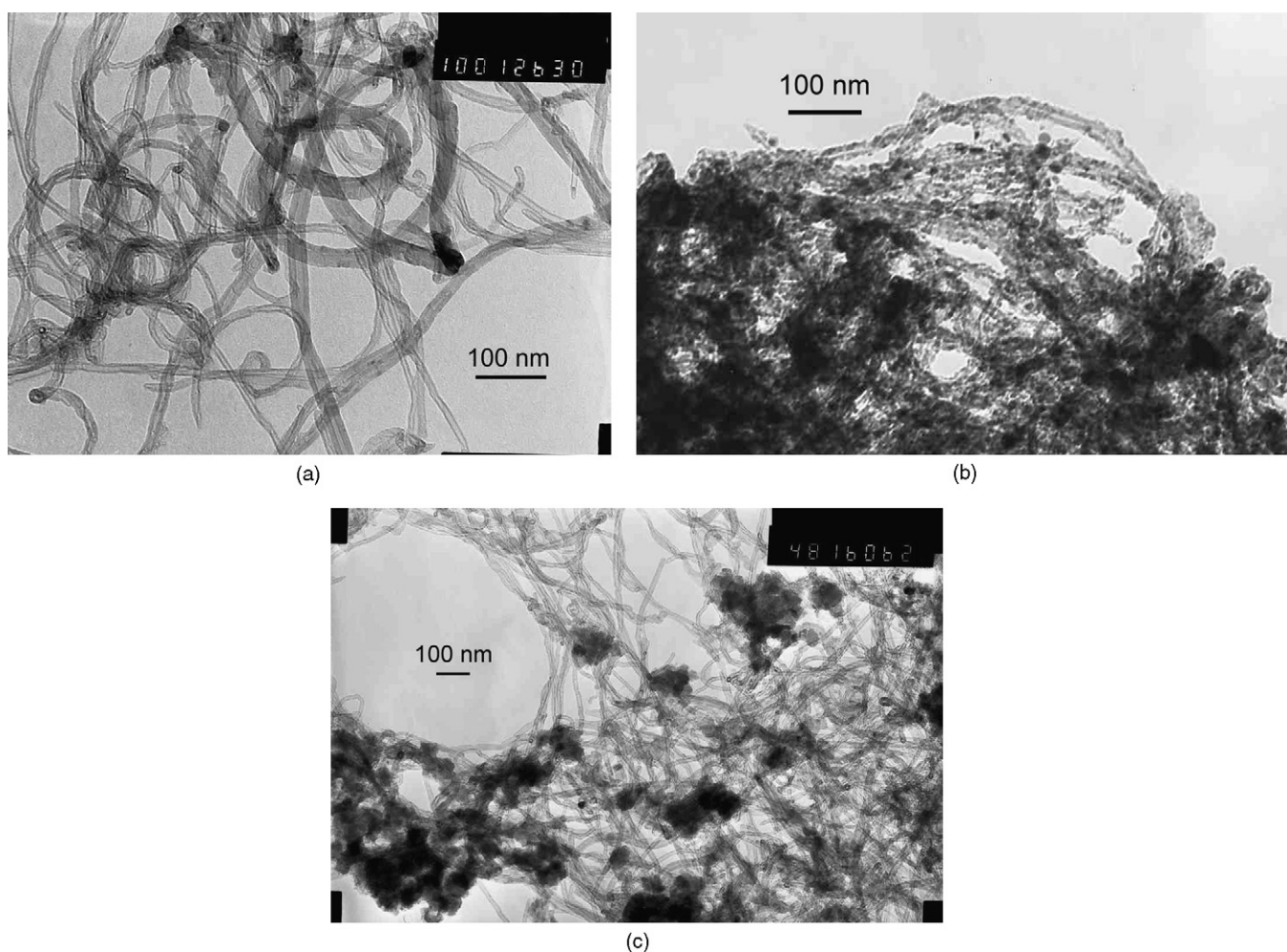


Fig. 1. Electronic images: (a) initial carbon nanotubes; (b) carbon nanotubes modified with manganese dioxide. Sample M-50carb, reduction of permanganate by carbon of nanotubes without addition of formic acid. (c) Carbon nanotubes modified with manganese dioxide. Sample M-50form, reduction of permanganate with formic acid.

electrochemical characteristics with increase of  $\text{MnO}_2$  content to 80% can be explained by formation of superfluous manganese dioxide particles which are not contacting with MWNT.

Thus, electrodes containing manganese dioxide deposited on MWNT have better electrochemical characteristics than electrodes containing pure  $\text{MnO}_2$  obtained by reduction of permanganate with formic acid. This effect of synergism can be explained by interaction of manganese dioxide particles with carbon nanotubes. Namely, one can suppose that  $\text{MnO}_2$  clusters adjacent to graphene layer act as a bifunctional electrocatalyst. That is,  $\text{Mn(IV)}$  activates oxygen molecules while graphene layer provides effective electron transport.

It was also interesting to elucidate how manganese dioxide preparation method influences electrochemical characteristics of oxygen electrodes. In Fig. 3 there are presented Volt–Ampere dependences for electrodes containing modified MWNT, obtained by reduction of permanganate with formic acid in presence MWNT (sample M-50form, Fig. 3, plot 2), and by reduction of permanganate with carbon of MWNT without addition of formic acid (sample M-50carb, Fig. 3, plot 1). In Fig. 4 analogous plots are presented for electrodes contain-

ing modified MWNT at higher content of  $\text{MnO}_2$  (samples M-80carb, Fig. 4, plot 2, and M-80form, plot 1). As it follows from Figs. 3 and 4, electrochemical characteristics for electrodes, obtained by reduction of potassium permanganate only with carbon of MWNT, are better, than for electrodes in which modified MWNT was obtained by reduction of permanganate with formic acid. Probably, the reason of this is that reduction of permanganate with carbon of MWNT gives nanodimensional manganese dioxide which is deposited directly on MWNT surface (Fig. 1b). On contrary, reduction of permanganate with formic acid gives colloidal particles of manganese dioxide, adsorption of which on MWNT surface is limited to about 17–20% in conditions of our experiments. In each case, excess of permanganate results in formation of superfluous manganese dioxide (Fig. 5, plot 2) which have better electrochemical characteristics than electrolytic manganese dioxide used in commercial batteries (Fig. 5, plot 1). Thus, manganese dioxide obtained by reduction of potassium permanganate with carbon of CNTs possesses a still higher electrocatalytic activity than that obtained by reduction with formic acid from potassium permanganate or electrolytic manganese dioxide used in commercial batteries.

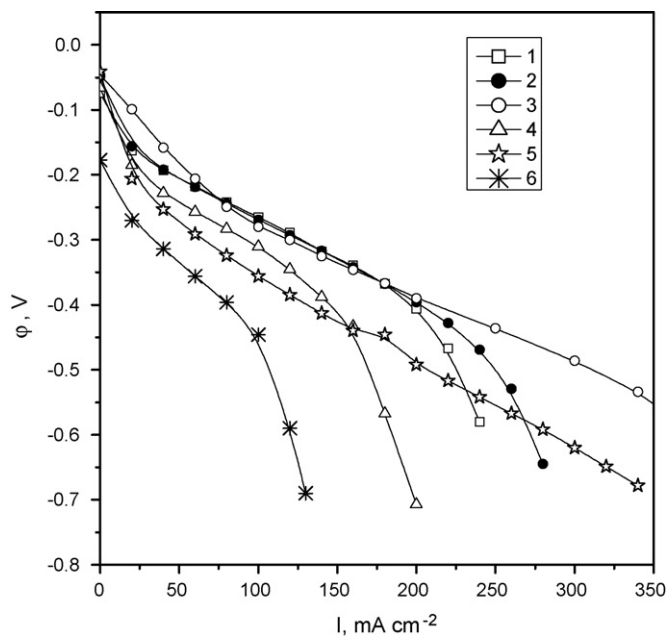


Fig. 2. Volt–Ampere plots for oxygen electrodes containing modified carbon nanotubes with different content of manganese dioxide: (1) 9% (sample M-9carb); (2) 16.7% (sample M-16.7form); (3) 50% (sample M-50carb); (4) 80% (sample M-80carb); (5) pure MnO<sub>2</sub>; (6) pure MWNT.

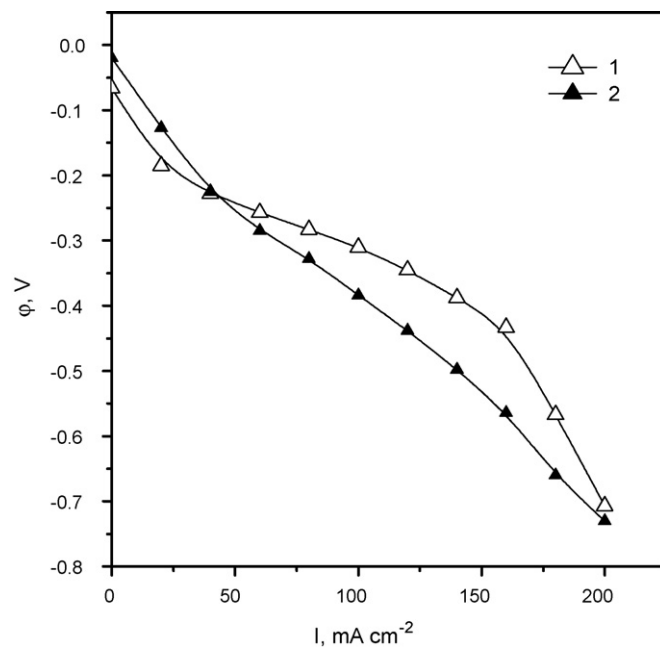


Fig. 4. Volt–Ampere plots for oxygen electrodes containing carbon nanotubes modified with manganese dioxide obtained by different methods: reduction of potassium permanganate by (1) carbon of nanotubes; (2) formic acid. Content of MnO<sub>2</sub> = 80% from MnO<sub>2</sub> + MWNT.

As was mentioned above, maximum power density of 623 mW cm<sup>-2</sup> was obtained for Pt/CNT material at 70 °C and 0.3 MPa [10]. For our MnO<sub>2</sub>/CNT sample (Fig. 3, plot 1) power density is 210 mW cm<sup>-2</sup> at 20 °C and 0.1 MPa. It is probable that at increased pressure and temperature performance of the MnO<sub>2</sub>/CNT sample could be comparable with Pt/CNT described in Ref. [10].

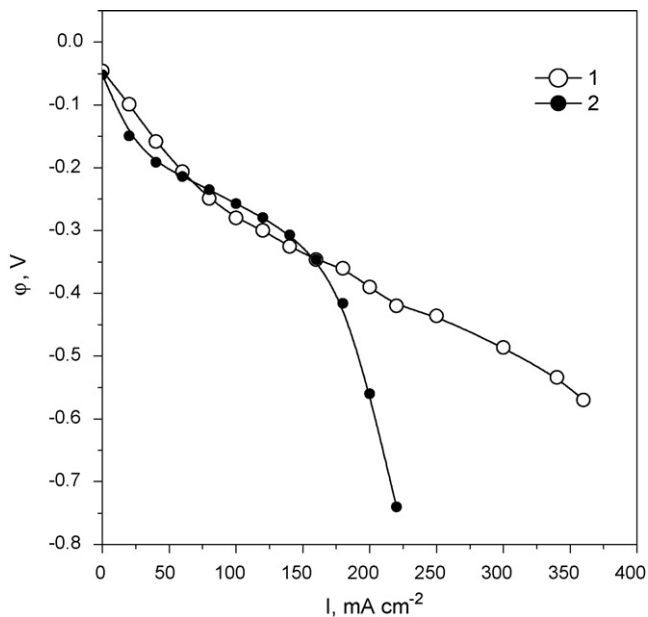


Fig. 3. Volt–Ampere plots for oxygen electrodes containing carbon nanotubes modified with manganese dioxide obtained by different methods: reduction of potassium permanganate by (1) carbon of nanotubes; (2) formic acid. Content of MnO<sub>2</sub> = 50% from MnO<sub>2</sub> + MWNT.

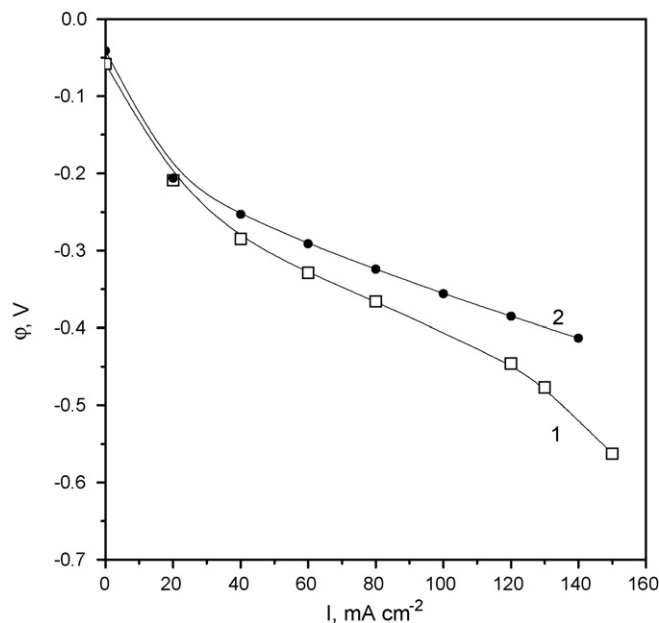


Fig. 5. Influence of manganese dioxide preparation method on electrochemical characteristics of oxygen electrodes: (1) electrolytic manganese dioxide used in commercial sources of current; (2) manganese dioxide, obtained by reduction of potassium permanganate with formic acid.

#### 4. Conclusions

1. Carbon nanotubes, modified with catalyst, can be used as efficient electrode material for fuel cells.
2. Manganese dioxide, deposited on surface of carbon nanotubes, has better electrochemical characteristics as a com-

ponent of air electrodes than manganese dioxide as a separate phase.

3. The best characteristics of air electrodes are observed for MWNT–MnO<sub>2</sub> composite containing 50% of deposited manganese dioxide.

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