Characteristics of the composite platinum-carbon electrode containing carbon nanofibres

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Abstract. This article describes the study of the electrochemical characteristics of the electrode material of the oxygen-hydrogen fuel cell, containing carbon nanofibers (CNF) as a functional additive in the oxygen reduction reaction. The data on the attestation of the researched materials (using the methods of the scanning and transmission electron microscopy, EDX, cyclic and direct voltammetry on a disk stationary and rotating electrode) have been given. It has been shown that in the presence of the oxygen-modified CNF the material has a higher electrode activity, a higher half-wave potential for electroreduction of oxygen (610 and 500 mV in the presence and absence of CNF respectively), demonstrates a 2-time-higher density of the kinetic current of oxygen reduction and has a 2.5-time-higher density of the exchange current in the oxygen reaction. This can be explained by the effect of the oxygen-modified CNF on the surface oxide (PtO) ratio of platinum particles: in the presence of CNF the PtO share is smaller.

1. Introduction

It is well known that an increase of the fuel cell efficiency can be achieved by increasing the electrode activeness of the electrode material and by improving the transport properties of the electrodes [1]. In addition, the stability of the characteristics and the duration of the electrode operation are important. At the same time due to the kinetic features the electrode processes in the oxygen-hydrogen proton-exchange membrane (PEM) fuel cells (FC) it is usually the cathode limits its work [2].

Recently, a lot of work directed on creating materials with given properties [3, 4, 5]. One of the areas of the research aimed at the increasing of the effectiveness of PEM FC is the use of various forms of nanostructured carbon, such as carbon nanotubes [6, 7, 8], carbon nanofibres (CNFs) [9], graphene-like materials [10] etc. Authors of various scientific publications dealing with the use of these carbon materials in electrodes [11] note a number of properties, such as high electron mobility and low electrical resistance, relatively high chemical and electrochemical stability, high specific surface area.

The goal of our study is to determine the kinetic characteristics of the oxygen electroreduction on a composite platinum-carbon electrode containing carbon nanofibers modified with oxygen-containing groups of atoms.
2. Experimental

2.1. Materials and methods
We used commercial platinized carbon black of Vulcan-XC-72 (Pt/C) type (commercial brand E-TEK) with platinum content of 40%, multiple-wall CNFs of Taunite-MD type [12], aqueous-alcoholic solution of the proton-conducting polymer Nafion with a concentration of 20 % (Ion Power Inc.).

Before use CNF were subjected to an oxidizing functionalization, for this diluted (1 : 1) nitric acid was added to CNF, and the mixture was thermostated at a temperature of 80–100°C for 15 min under agitation. Further, the suspension was cooled, filtered, and washed with deionized water to zero acid reaction of washing water (~5 times). The washed CNFs were dried at 80–85°C at air.

The electrode materials were prepared by the two-step technique: mechanical and ultrasonic dispersion of the precise weighed components mix in the isopropanol-water mix. The volume ratio of the liquid components of i-propanol: water was used in the range 1:1 – 1:5. At the same time the solid-to-liquid phase ratio in the final dispersion (catalytic ink) was in the range from 1 : 40 to 1 : 80. The mechanical dispersion was carried out on a Milaform MM-5M magnetic rabble with a core insulated in a plastic case and rotation speed of ~400 rpm for ~0.5 h until a visually homogeneous (without visible lumps) paste was formed. The ultrasonic treatment in the ultrasonic bath (Bransonic 3510 type) was performed during 40–100 h until a visually homogeneous dispersion non-delaminating during 1 minute was obtained.

Component composition of the electrode material samples was:
1. NANG-70: 48 % wt Vulcan XC-72, 32 % wt Pt, 0 % wt CNF, 20 % wt Nafion
2. NANG-73: 22 % wt Vulcan XC-72, 15 % wt Pt, 38 % wt CNF, 25 % wt Nafion

For investigations, a layer of electrode material was formed on the surface of the disk electrode. For this purpose, the required number of drops was successively deposited with a pipette on the glassy carbon electrode surface with an area of 0.07 cm$^2$. After applying of each dispersion portion, it was air dried (~10 minutes). After the layer formation, excess material was gently wiped off the surface outside the glassy carbon electrode.

2.2. Electrochemical research
The samples were investigated by direct and cyclic voltammetry methods on a disk stationary and rotating electrode (RDE) in a standard three-electrode cell in a VED-06 setup and an IPC Pro potentiostat. The working electrode potential was measured relative to a silver chloride reference electrode. Measurements were made in 0.5 M sulfuric acid, with the solution being in equilibrium with air at a temperature of 25 C. The area of the electrochemically active surface of platinum was determined by the electrochemical hydrogen desorption [13, 14].

Density of kinetic oxygen reduction currents were calculated by the Koutecky-Levich method using polarograms registered at different disk rotation speeds of the electrode [15, 16]. The density of the exchange currents for each sample was calculated from the initial section of the resulting polarogram using the Tafel equation.

3. Results and discussions
Figure 1 shows microphotograph of a composite material containing CNF and EDX analysis results. It follows from figure 1(a) that, platinum nanoparticles are located on the carbon black agglomerates with a characteristic size of ~ 40 nm. Separately placed CNFs are practically free of platinum and are connected electrically with it by mechanical contact with platinized carbon black. The elemental composition (figure 1, (b)) shows that the material contains some "excess" amount of oxygen. Based on the elemental composition, about 1 % at. oxygen is connected with sulfur and aluminum oxides, the remaining 2 % at. are for carbon materials accordingly.

The cyclic voltammograms (CVA) of a composite material containing CNF differ from the CVA of a material without CNF by the presence of a pronounced peak both in the cathode (250 - 450 mV) and in the anode (350 - 550 mV). Such effects on the CVA are generally attributed to the appearance of
oxygen-containing groups of atoms on the surface of the carbon material, so it is noted in [17] that in general, the faradaic peak current in cyclic voltammogram of a carbon electrode is known for the redox reaction of quinones which are one of CO bond functional groups [18]. This evidence strongly supports the formation of an oxide layer on the carbon during oxidation in acidic media.

Figure 1.
Microphotographs of electrode material containing CNF: (a) TEM images; (b) elemental composition (EDX)

Figure 2 and Table show data concerning the potential of a half-wave of air oxygen reduction on electrodes of various compositions. From the presented data, it can be seen that $E_{1/2}$ for material containing CNF is significantly higher (by 110 mV) than for material without CNF. These measurements indicate a greater electrode activity of the material containing CNF in the oxygen reduction reaction compared to the material without CNF. Thus, the role of CNF takes place as an activator of the oxygen reduction reaction on the platinum surface. The current density of the exchange of the oxygen reaction of a sample containing CNF is 2.5 times higher than the density of the exchange current of the control sample. This fact conforms to the data given above concerning the potentials of the half-wave and the densities of the kinetic currents of the oxygen electroreduction. The values of the exchange current density of the oxygen reaction for Pt and PtO/Pt given in the literature are $2.8 \cdot 10^{-7}$ and $1.7 \cdot 10^{-10}$ A/cm$^2$, respectively [19]. The values obtained in our study are in this interval. Taking into account the tendency of the platinum electrode to form a surface oxide in the presence of oxygen, it can be assumed that the shift of the exchange current density to higher values in the presence of oxygen-modified CNF is connected with a smaller fraction of the surface oxide due to reduction of its CNF quinone groups [20].
Figure 2. Polarization curves of various samples: 1 - Pt/C; 2 - Pt/C + CNF (1:1); the rotational speed of RDE 1000 min\(^{-1}\), 0.5 M H\(_2\)SO\(_4\) in equilibrium with air, \(T = 25^\circ\)C.

Table 1. Kinetic characteristics of the ORR for various electrode materials: medium - 0.5 M H\(_2\)SO\(_4\) in equilibrium with air, \(v = 1\) mV/s, \(t = 25\) C

| Sample             | Half-wave potential, \(E_{1/2}\) (vs AgCl), V | Density of kinetic current, \(j_k\) at 500 mV (vs AgCl), A/cm\(^2\) (Pt) | Exchange current density, \(j \times 10^{10}\), A/cm\(^2\) (Pt) |
|--------------------|-----------------------------------------------|-----------------------------------------------------------------|--------------------------------------------------------|
| NANG-70 (Pt/C)     | 0.500                                         | 0.061                                                           | 5.70±0.51                                              |
| NANG-73 (Pt/C + CNF) | 0.610                                         | 0.13                                                            | 14.2±0.50                                              |

4. Conclusion
Investigation of the electrode properties of the materials containing oxygen-modified carbon nanofibers showed that they are more active in the oxygen reduction reaction in comparison with similar materials that do not contain CNF. This causes a higher potential of the half-wave of the oxygen reaction, 2-time- higher density of the kinetic current of oxygen reduction, 2.5-time-higher effective density of the oxygen exchange reaction currents. The effective exchange current densities in the oxygen reaction are within the range given in the literature for Pt and PtO / Pt electrodes, which indicates the influence of oxygen-modified carbon nanofibers on the proportion of surface platinum oxide in the electrode.

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