Nafion-carbon containing nanocomposite materials with high catalytic activity for portable energy sources

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Abstract. In this work the electrode materials on combined polymer-carbon matrix-supports modified by bimetal platinum-ruthenium nanoparticles have been formed. The functional characteristics of the electrodes have been studied by atomic force microscopy, scanning electron microscopy and voltammetry methods. The catalytic activity of the synthesized composites in the methanol oxidation reaction had been studied.

1. Introduction

The direct methanol fuel cells (DMFC) are advantageous devices due to easy transportation and storage of the fuel, reduced system weight, and high energy efficiency potential energy sources for portable devices, electronic and transportation purposes [1-7]. Methanol is a suitable fuel for fuel cells from the perspective of its high energy density, relatively easy and safe handling. Low-temperature DMFCs with proton exchange membrane (PEM), for example, Nafion-type membrane [7-10, 13] are usually operated at 50-80 °C with the liquid methanol fuel.

Pt is well known catalyst for methanol electro-oxidation reaction. However, Pt is poisoned by carbon monoxide CO and other reaction intermediates under the low-temperature reaction conditions of DMFCs. To solve the catalyst poisoning problem on methanol electro-oxidation reaction, the use of bimetallic anode catalysts is an effective way for construction of fuel cells with increased activity and stability. Therefore, the addition of Ru improves the methanol electro-oxidation activity of Pt catalyst due to bi-functional mechanism. Catalysts based platinum and ruthenium nanoparticles are of great interest as anode materials with superior performance in methanol oxidation reaction [1-7, 11-14].

For the formation of electrode materials for fuel cells it is necessary to select the optimal matrix-support [4, 7-10, 13]. One of such matrix-carriers are solid polymer membranes, to which the following requirements are presented:
- high proton conductivity – (impedance);
- low electronic component – (voltammetry);
- low membranes permeability on fuel and O₂;
- resistance to oxidizing media;
- good mechanical properties (flexibility, etc.).

Polymer membrane like Nafion, in general, meets these requirements. However, in order to achieve the best catalytic characteristics, many authors modify the polymer membrane with various inorganic additives, including nanoparticles of various metals [4, 7-10, 13].
It should be mentioned that carbon carriers (carbon black, graphene, carbon nanotubes) are also effective matrix carriers with a high surface area. The combined electrode materials which are composed of a polymer and a carbon component are of great interest because they allow to achieve high parameters in the studied fuel cells.

The aim of this work is formation of composite electrodes based on Nafion-carbon nanotubes support with platinum-ruthenium nanoparticles and evaluation of nanocomposite catalytic in methanol oxidation reaction.

2. Experimental

2.1. Platinum-ruthenium nanoparticles synthesis

Platinum-ruthenium nanoparticles were synthesized by chemical reduction in reverse microemulsions with sodium tetrahydroborate NaBH₄ (98%, Merck, Germany), using anionic surfactant – AOT in isooctane. The method of solution preparation was as follows: a water-organic solution of K₂PtCl₄ and RuCl₃ salts (Sigma Aldrich, USA) had been prepared. To form a microemulsion medium a 0.2 M solution of AOT (Sigma Aldrich, USA) and isooctane was used. Then, a microemulsion of the similar composition, contained 0.1 M water solution of the reducing agent – NaBH₄ was added to this solution under ultrasonic action for 2-3 min. The molar water/surfactant ratio (ω) while making the experiments was changed from 1.5 to 8. In order to prevent the sunlight destruction of nanoparticles, the solutions of microemulsions were stored in darkness at room temperature. Pt:Ru molar rations were 1:1, 1:3 and 3:1.

2.2. Nafion-carbon nanotube composites formation

Metal-polymer films of Nafion (Nf) membranes with Pt-Ru nanoparticles were synthesized as described in [9, 10]. The solubilization of solutions was performed on an Ultrasonis Cleaner UD150SH-6L ultrasonic disperser (Eumax, Germany). For obtaining the metal-polymer films, the samples of the Nafion membranes were placed in cells with a reverse microemulsion solution with Pt-Ru nanoparticles and solution was sonicated during 3-5 minutes. After that, the modified metal-polymer membrane was washed to remove the excess surfactant and the organic solvent.

To obtain combined metal-polymer films with CNT, the Nafion membrane modified with Pt-Ru nanoparticles was immersed in a water solution of propanol-2 and glycerol (Merck, Germany) with CNT. In work the single-wall (SW) and multi-walled (MW) carbon nanotubes (Sigma Aldrich, USA) were applied as main components of the mixed Nafion-CNT membrane. The diameter of single-walled nanotubes was 1.3-2.3 nm, multi-walled – 110-170 nm. The resulting suspension was sonicated for 10-15 min. The homogeneous suspension containing a required amount of platinum-ruthenium catalyst, the polymer, and CNT was dried on a glass substrate at 70°C in an argon atmosphere. The obtained Pt-Ru/Nf-CNT composites were then hot pressed at 120°C to assure good adhesion between CNT and the Nafion membrane. In order to clean the electrodes from traces of surfactant and solvent, Nafion-CNT samples with Pt-Ru nanoparticles were washed in isooctane, ethanol and distilled water.

2.3. Instrumentation

The sizes, shape, and distribution of platinum-ruthenium nanoparticles were studied by atomic force microscopy (AFM) on NTegra Prima scanning microscope (NT MDT, Russia). The morphology of the nanocomposite was studied by scanning electron microscopy (SEM) on a JSM-7401F microscope (Jeol, Japan). The catalytic activity of the electrodes was estimated by cyclic voltammetry (CVA) method on IPC PRO M device (Tekhnopribor, Russia). The scanning rate was varied from 10 to 100 mV/s. The CVA data were fixed after the stabilization of the parameters of voltamperograms.
3. Results and discussions

3.1. Studies of nanoparticles size and shape

On figure 1 the AFM image of Pt-Ru nanoparticles, obtained by the method of chemical reduction using anionic surfactant with solubilization coefficient $\omega = 1.5$ and when the metals ratio of 3:1 is presented. As it can be seen from the microphotograph, Pt-Ru nanoparticles are primarily characterized by the spherical shape. For water organic solutions of Pt-Ru with a minimum value of the solubilization coefficient, the average particle size was 3-4 nm. The increase of the solubilization degree to 5 was contributed to the increase in size of nanoparticles at all the metals ratio.

![AFM image of Pt-Ru nanoparticles](image)

*Figure 1. AFM image of Pt-Ru nanoparticles (metal ratio of 3:1) at $\omega = 1.5$.*

Feature of solid polymer membranes of the type Nafion is nanometer pore size with the membrane thickness less than 0.2 mm. Transport of hydrated protons is carried out through the membrane channels with a width of 1-2 nm, which are linked sulfacetamide hollow nanoscale clusters with an average diameter of 6 nm. The arrangement in the polymer matrix protects the nanoparticles from both desorption and agglomeration. On the surface of the membrane fragments of the internal cavities of the clusters of the polymer chain stimulate the adsorption of the low-dimensional nanoparticles, limiting their agglomeration, facilitate uniform distribution of nanoparticles in the film (Table 1). The size of nanoparticles in the membrane volume should probably not exceed 6 nm. Nanoparticles larger than 6 nm are fixed to the surface of the membrane. In addition, the presence of carbon nanotubes in the matrix-carrier contributes to additional stabilization and reduction of the size of nanoparticles in the composite membrane. The smallest particle size in the matrix is observed in nanocomposites formed at metals ratio of 3:1 and a minimum solubilization degree equal to 1.5.

| Pt:Ru | $d$, nm | $\omega = 1.5$ | $\omega = 3$ | $\omega = 5$ |
|-------|---------|---------------|---------------|---------------|
| 3:1   | 2.3-3.2 | 2.8-3.6       | 3.4-4.1       |
| 1:1   | 2.9-3.7 | 3.3-4.5       | 3.8-4.9       |
| 1:3   | 3.1-4.0 | 3.7-5.0       | 4.4-5.7       |

3.2. Catalytic activity investigation

The CH$_3$OH oxidation reaction within a bi-functional mechanism with Pt-Ru catalyst can be described by the following reactions [11]:

$$\text{Pt} + \text{CH}_3\text{OH} = \text{Pt(CHOH)}_{\text{ads}}$$ (1)
Pt(CH$_3$OH)$_{ads}$ – 4ē = Pt(CO)$_{ads}$ + 4H$^+$  
(2)
Ru + H$_2$O – ė → Ru–OH + H$^+$  
(3)
Pt(CO)$_{ads}$ + Ru–OH – ė → Pt + Ru + CO$_2$ + H$^+$  
(4)

As a result of the adsorption/dehydrogenation reaction of CH$_3$OH that takes place on Pt sites, an intermediate «CO»-type species is formed. This species is believed to be oxidized to CO$_2$ with the assistance of –OH species, which are formed by the partial oxidation of H$_2$O on Ru surface sites. Based on this reaction scheme, it is clear that the ratio and distribution of Pt and Ru catalyst surface sites influences the CH$_3$OH oxidation kinetics.

Figure 2. Cyclic voltammograms of Pt-Ru (3:1)/Nf-MWCNT (1), Pt-Ru (1:1)/Nf-MWCNT (2) and Pt/Nf-MWCNT (3) composites in 0.5 M H$_2$SO$_4$ + 1 M CH$_3$OH solution (the scan rate of 20 mV/s, Pt loading was 0.2 mg/cm$^2$)

The electrocatalytic activity of Pt-Ru electrodes in methanol oxidation reaction was investigated. Fig. 2 shows cyclic voltammograms (CVs) in 0.5 M H$_2$SO$_4$ + 1.0 M CH$_3$OH solution. The figure shows that the highest value of the peak of direct oxidation of methanol at 0.7 V exhibits Pt-Ru (3:1)/NF-MWCNT nanocomposite. The peak of the reverse sweep at 0.44 V derives from the intermediates oxidation. According to Table 2, composites on multi-walled carbon nanotubes exhibit the highest current density than that on single-walled nanotubes, which is explained by the larger surface area of the MWCNT, as well as a larger number of π-electrons compared to the SWCNT.

Table 2. Catalytic characteristics of Pt-Ru(3:1) nanocomposites on various carriers type, according to CVA data (current density, $j$, is represented by direct oxidation peak at 0.7 V)

| Support type   | $\omega$ | $j$, A/m$^2$ |
|----------------|----------|--------------|
| Nf-MWCNT       | 1.5      | 19,8         |
|                | 5        | 17,4         |
| Nf-SWCNT       | 1.5      | 16,6         |
|                | 5        | 12,7         |

4. Conclusion

Composite materials on combined polymer-carbon matrix carriers with bimetallic platinum-ruthenium nanoparticles had been obtained. The size and shape of nanoparticles had been investigated by electron microscopy methods. By cyclic voltammetry it was discovered that the higher catalytic activity in methanol oxidation reaction demonstrate the composites formed at a solubilization degree of 1.5 and Pt:Ru ratio of 3:1.
Acknowledgments
The research was carried out with financial support of the Russian Science Foundation (№ 18-79-00017).

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