The features of bimetallic Pt-Ru nanoparticles formation on the Nafion membrane for electrodes of chemical power sources

M V Lebedeva¹, A V Ragutkin², A P Antropov¹, N A Yashtulov³

1 Associate professor, MIREA – Russian Technological University, Moscow, Russia
2 Vice-rector for innovation development, MIREA – Russian Technological University, Moscow, Russia
3 Professor, MIREA – Russian Technological University, Moscow, Russia
E-mail: lebedevamv@mitht.ru

Abstract. In this work the electrode materials on Nafion 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 at different temperatures had been investigated.

1. Introduction

The performance and durability of low-temperature fuel cells (FC) heavily depend on the choice of the catalyst substrate matrix [1-13]. It provides electronic conductivity, uniform distribution of Pt-containing catalyst particles on the substrate surface and facilitates the transfer of gas to the formed porous catalyst bed. Catalysts deposited on carbon materials with a highly developed surface are widely used in low-temperature fuel cells. However, corrosion of catalysts based on carbonaceous materials, such as soot, was one of the main reasons for the reduction of fuel cell performance [1-5].

Over the last ten years, the research group started to look for corrosion-resistant (“non-carbon”) of the matrix substrate for Pt electrocatalysts for FC. Various conductive and semiconductor materials were studied as functional matrix substrates for electrocatalysts in acidic media, as well as carbides, nitrides, etc [2-5].

Currently, among the solid polymer membranes used by researchers as electrolytes in chemical power sources, it is necessary to distinguish a perfluorinated polymer membrane developed by DuPont – Nafion (Nafion), which has high chemical resistance and proton conductivity [1-6].

Figure 1. Nafion cluster model [6].
The cluster structure of Nafion membrane is shown in Figure 1 [6]. The polymer has a non-polar (hydrophobic) base, which provides mechanical strength and heat-resistant properties of the Nafion membrane. Side sulfo group (SO$_3$H) of the membrane is polar (hydrophilic) and can transfer protons.

The possibility of changing the physical and chemical properties of electrode materials by modifying the polymer matrix by nanoparticles [7, 9, 11, 13] of various metals stimulate the development of proton-conductive composite membranes suitable for use in FC, which can operate at temperatures above 100 °C and relatively low humidity. Thus, studies are aimed at improving the performance of the membrane, suitable as an electrolyte for FC with high temperature and low humidity [6, 10].

The aim of this work is physico-chemical investigations of platinum-ruthenium/Nafion composites as effective electrode materials for chemical power sources.

2. Experimental

2.1. Platinum-ruthenium nanoparticles synthesis

Platinum-ruthenium nanoparticles were synthesized by chemical reduction in reverse microemulsions with sodium tetrahydroborate NaBH$_4$ (98%, Merck, Germany), using anionic surfactant – AOT in isooctane. The method of solution preparation was as follows: a water-organic solution of K$_2$PtCl$_4$ and RuCl$_3$ 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 – NaBH$_4$, 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 ration was 3:1.

2.2. Nafion 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.

2.3. Instrumentation

The morphology of the nanocomposite was studied by scanning electron microscopy (SEM) on a JSM-7401F microscope (Jeol, Japan). The X-ray photoelectron spectrometer PHI 5500 ESCA (USA) was used to estimate the electrodes composition. 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. Estimation of the electrodes composition

Figure 2 shows SEM-micrographs of bimetallic Pt-Ru with nanoparticles at the metals ratio of 3:1 and the solubilization coefficient ω = 1.5 on the surface of the Nafion membrane. The uniform nanoparticles distribution on the polymer film surface can be achieved by ultrasonic treatment at the formation stage of the metal polymer. As can be seen from the image, the main contribution to the formation of Pt-Ru nanocomposites is made by spherical nanoparticles with sizes from 7 to 9 nm. It can be noted that the large nanoparticle aggregates on the membrane surface are absence.
To confirm the possible formation of oxide forms of palladium and ruthenium in the nanocomposites, the method of X-ray photoelectron spectroscopy (XPS) was used. Figure 3 shows fragments of high-resolution spectra for Pt(4f) in the XPS spectrum of bimetallic Pt-Ru/Nf nanoparticles (metal ratio 3:1) at $\omega = 1.5$. The spectrum consists of two pairs of overlapping Lorentz curves. Pt4f$_{7/2}$ and Pt4f$_{5/2}$ lines with a binding energy of 71.30 eV (peak 1) and 74.57 eV (peak 3) can be attributed to metal platinum Pt$^0$. The second pair of curves was evident at 72.49 eV (peak 2) and 75.88 eV (peak 4), which can be attributed to Pt$^{II}$ in the platinum oxide PtO and the platinum(II) hydroxide Pt(OH)$_2$. Comparison of peak heights indicates that metallic Pt$^0$ prevails in the Pt-Ru/Nf nanocomposite.

The Ru(3p) XPS spectra in bimetallic Pt-Ru/Nf nanocomposite was also analyzed (figure 4). Ru3p$_{3/2}$ has three components with energies 461.32 eV (peak 1), 463.41 (peak 2) and 465.72 eV (peak 3), which can be attributed to metallic ruthenium Ru$^0$, Ru$^{IV}$ (e.g., RuO$_2$) and ruthenium in a higher oxidation – Ru$^{VI}$ in RuO$_3$. XPS results indicate the presence of oxides and metallic Ru in the nanocomposite. It is likely that the surface of the nanocatalyst consists mainly of Ru oxides and metallic Pt$^0$. Therefore, it seems that Ru in the composition of Pt-Ru/Nf nanocomposites undergoes noticeable oxidation under the influence of air oxygen, forming ruthenium oxide. However, the presence of ruthenium oxides in the nanocomposite can improve the catalytic properties in the CO oxidation reaction for methanol-air fuel cells.
3.2. CH$_3$OH oxidation investigation at different temperature

The electrocatalytic activity of Pt-Ru electrodes in methanol oxidation reaction was investigated. Fig. 5 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 nanocomposite. The peak of the reverse sweep at 0.44 V derives from the intermediates oxidation. To assess the effect of temperature on the current density parameters, a study was conducted at different temperatures: 25 °C, 60 °C and 80 °C.

4. Conclusion

In this paper anode materials with bimetallic Pt-Ru nanoparticles on the polymer membrane Nafion had been proposed. A study of the sizes of the nanoparticles in the polymer matrix by electron microscopy was carried out. The composites structure investigation made by X-ray photoelectron spectroscopy indicated a small number of ruthenium and platinum oxide forms in the nanocomposite. As a result of the study of catalytic activity, it was found that the optimal temperature for such electrode materials in the methanol oxidation reaction is 60 °C. As the temperature rises, the current density decreases.
Acknowledgments
The research was carried out with financial support of the grant "University" of centralized Fund № NICH-45.

References
[1] Linse N, Gubler L, Scherer G G, Wokaun A 2011 Electrochimica Acta 56 7541-7549.
[2] Noto V D, Negro E, Giubizzi R, Gross S et al. 2007 Journal of Electrochemical Society 154 B745-B756.
[3] Cui G, Shen P K, Meng H, Zhao J et al. 2011 Journal of Power Sources 196 6125-6130.
[4] Wickman B, Wesselmark M, Lagergren C, Lindbergh G 2011 Electrochimica Acta 56 9496-9503.
[5] Liu Y, Ishihara A, Mitsushima S, Ota K 2010 Electrochimica Acta 55 1239-1244.
[6] Spry D B, Goun A, Glusac K, Moilanen D E 2007 Journal of American Chemical Society 129 8122-8130.
[7] Battirola L C, Schneider J F, Torriani I C L, Tremiliosi-Filho G 2013 International Journal of Hydrogen Energy 38 12060-12068.
[8] Yashtulov N A, Lebedeva M V 2017 Russian technological journal 5 58-73.
[9] Lebedeva M V, Antropov A P, Ragutkin A V, Yashtulov N A 2018 International Journal of Applied Engineering Research 13 16770-16773.
[10] Goodarzi G A, Hayes J G 2018 Electric powertrain : energy systems, power electronics & drives for hybrid, electric & fuel cell vehicles John Wiley & Sons 557 p.
[11] Lebedeva M V, Yashtulov N A, Flid V R 2019 Kinetics and Catalysis 60 118-122.
[12] Li X, Zhou Y, Du Y, Xu J et al. 2019 International Journal of Hydrogen Energy 44 18050-18057.
[13] Kim T H, Yoo J H, Maiyalagan T, Yi S C 2019 Applied Surface Science 481 777-784.