

# Platinum-Based Nanocomposite Materials For Autonomous Power Sources

Marina V. Lebedeva\*, Nicolay A. Yashtulov

MIREA – Russian Technological University, Vernadskogo Avenue, 78, 119454, Moscow, Russian Federation.

## Abstract

This article is devoted to formation and of composite materials with platinum nanoparticles on combine polymer-carbon matrix support. By means of electron microscopy and cyclic voltammetry methods the physico-chemical investigations characteristics of nanoparticles on the surface and in the volume of the polymer membrane had been studied.

**Keywords:** Nafion polymer membrane, mechanism of proton transfer, electron microscopy.

## 1. INTRODUCTION

A fuel cell is an electrochemical device that continuously and directly converts the chemical energy of externally supplied fuel and oxidant to electrical energy [1-5]. Fuel cells are customarily classified according to the electrolyte employed. The five most common technologies are polymer electrolyte membrane fuel cells (PEM fuel cells or PEMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs). However, the popularity of PEMFCs, a relatively new type of fuel cell, is rapidly outpacing that of the others.

Unlike most other types of fuel cells, PEMFCs use a quasi-solid electrolyte, which is based on a polymer backbone with side-chains possessing acid-based groups. The numerous advantages of this family of electrolytes make the PEM fuel cell particularly attractive for smaller-scale terrestrial applications such as transportation, home-based distributed power, and portable power applications. The distinguishing features of PEMFCs include relatively low-temperature (under 90 °C) operation, high power density, a compact system, and ease in handling liquid fuel.

The main function of the membrane in PEM fuel cells is to transport protons from the anode to the cathode; membrane polymers have sulfonic groups, which facilitate the transport of protons. The other functions include keeping the fuel and oxidant separated, which prevents mixing of the two gases and withstanding harsh conditions, including active catalysts, high temperatures or temperature fluctuations, strong oxidants, and reactive radicals. Thus, the ideal polymer must have excellent proton conductivity, chemical and thermal stability, strength, flexibility, low gas permeability, low water drag, low cost, and good availability.

Different types of membranes have been tested for use in PEM fuel cells. The membranes are usually polymers modified to

include ions, such as sulfonic groups. These hydrophilic ionic moieties are the key for allowing proton transport across the membrane. The favored polymer structure has changed to improve membrane lifetime and slow down membrane degradation.

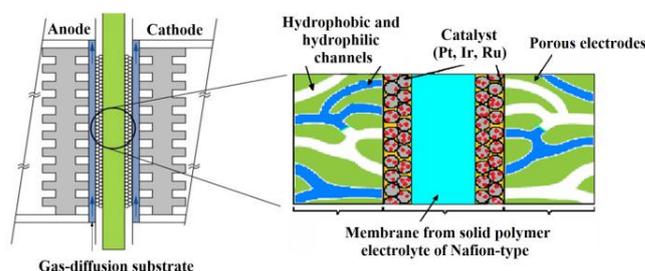


Fig. 1. Design of a cell for a fuel element with solid polymer electrolyte.

Development of catalytically active electrode nanocomposite materials for high-efficiency conversion of hydrogen-containing fuels is a fundamental scientific problem of modern physical chemistry and nanotechnology. The size and shape of nanoparticles (NPs) embedded in the functional matrix – for example, polymer membrane or carbon nanotubes (CNT) – play a key role in selectivity and stability of power sources [1-16]. In the nanoscale state, catalysts are able to exhibit unique properties, so the improvement of physical and chemical methods for the formation and stabilization of nanoparticles on polymer matrices allows to obtain materials with enhanced functional characteristics. This is most important for modern energy sources engineering, which require a significant increase in specific parameters (current density, specific power, weight and size, service life) compared to traditional current sources. It is reasonable to expect that polymetallic membrane nanocomposites formation will solve a number of the above problems and stimulate the creation of structural materials for new generation energy sources with high specific parameters [1-16].

The objective of presented work is the controlled synthesis of Pt nanocatalysts on Nafion polymer membranes with carbon nanotubes and determination of nanocomposites specific characteristics in hydrogen-oxygen fuel cells.

## 2. MATERIALS AND METHODS

### 2.1. Nanoparticles synthesis

Platinum nanoparticles were synthesized by chemical reduction with sodium borohydride  $\text{NaBH}_4$  (98%, Merck, Germany) in reverse microemulsion solutions [10-12,16] using Triton X-100 (Sigma Aldrich, USA) as nonionic and AOT (Sigma Aldrich, USA) as anionic surfactants. The method of solution preparation was as follows: a water-organic solution of 0.01 M  $\text{K}_2\text{PtCl}_6$  (Sigma Aldrich, USA) was prepared. Then, a microemulsion of a similar composition containing 0.1 M water solution of the reducing agent –  $\text{NaBH}_4$  was added to solution with Pt salt under ultrasonic stirring for 2-3 min. During mixing process of two microemulsions the simultaneous reduction of platinum ions in micelle water pools – microreactors was observed. The molar water/surfactant ratio ( $\omega$ ) in the experiments was varied from 1.5 to 8 and was the same for the emulsion mixture with metal salts and reducing agent. In order to prevent the destruction of nanoparticles under the light influence, microemulsion solutions were stored at room temperature in a dark room.

### 2.2. Nanocomposites formation

Metal-polymer films of Nafion (Nf) membranes with Pt nanoparticles were synthesized as described in [8,9,11]. 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 nanoparticles and sonicated during 3-5 minutes. After that, the modified metal-polymer membrane was washed by distilled water and ethanol to remove the excess surfactant and the organic solvent.

To obtain combined metal-polymer films with CNT, the Nafion membrane modified with Pt nanoparticles was immersed in a water solution of propanol-2 and glycerol (Merck, Germany) with CNT. In work the single-wall (SWs) and multi-walled (MWs) 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 palladium, the polymer, and CNT was dried on a glass substrate at 70°C in an argon atmosphere. The obtained Pt/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 nanoparticles were washed in isooctane, ethanol and distilled water.

### 2.3. Investigation methods

The size of Pt nanoparticles was estimated by means of atomic force microscopy (AFM) with N-Tegra Prima microscope (NT MDT, Russia).

The surface morphology of platinum nanocomposites on polymer-carbon membrane was studied through scanning electron microscopy (SEM) at JSM-7401F (Jeol, Japan)

instrument with the INCA analyzer (Oxford Instruments, England).

The catalytic activity and stability of electrodes were estimated using cyclic voltammetry at IPC PRO M (Tekhnopribor, Russia). The main measure of activity of nanocomposite electrodes in cyclic voltammetry is the current density ( $j = I/S$ ,  $\text{A}/\text{m}^2$ ), which is proportional to the rate of electrode reaction [8,9,11]. The scanning rate was varied from 5 to 20 mV/s. The data of cyclic voltammetry were measured in standard  $\text{HClO}_4$  solutions after the parameters of voltammograms were stabilized. The error of current density measurement did not exceed 2-3%.

## 3. RESULTS AND DISCUSSION

Figure 2 shows an example of AFM image for Pt nanoparticles with solubilization coefficient  $\omega = 1.5$ . Pt nanoparticles are characterized by the spherical form.

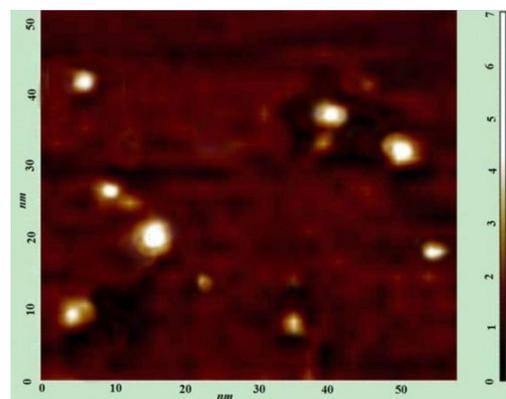


Fig. 2. AFM image of Pt nanoparticles at  $\omega = 1.5$ .

For water organic Pt solutions with minimum solubilization coefficient  $\omega$ , the average particle size was 4-5 nm. It was found that with solubilization degree increasing from 1.5 to 8, the average size of platinum nanoparticles increases to 7-9 nm (Fig. 3).

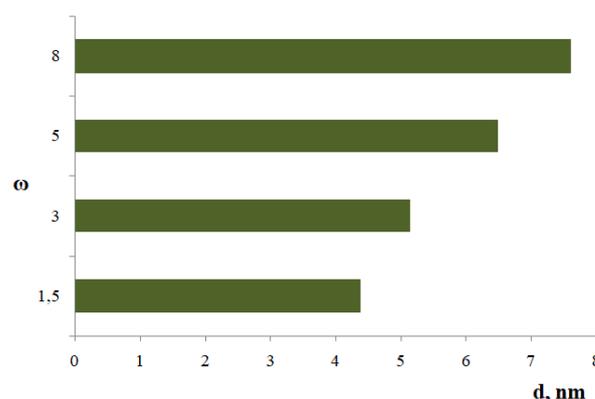


Fig. 3. Effect of the solubilization coefficient  $\omega$  on the average platinum nanoparticles diameter according to AFM data.

The formation of platinum nanoparticles on the combined Nafion-carbon nanotubes matrix was carried out as described above. Hot-pressing treatment improved the interfacial

bonding between Nafion and CNT. Without proper hot-pressing treatment, CNT disintegrated from the Nafion membrane when the composite was immersed in water.

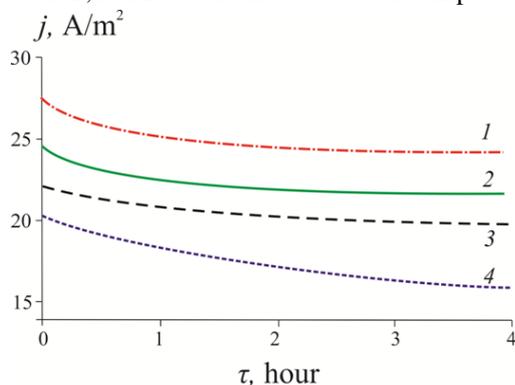
Table 1 presents a comparison of the Pt nanoparticle sizes obtained by chemical reduction with nonionic (Triton X-100) and anionic surfactant (AOT) surfactants in the Pt/Nf composites. The size of nanoparticles in water-organic solutions obtained by chemical reduction with Triton X-100 at all values of the degree of solubilization  $\omega$  is smaller than that of nanoparticles formed by chemical method with anionic surfactant.

**Table 1.** Size distribution of Pt nanoparticles obtained by chemical reduction methods with anionic (AOT) and nonionic surfactant (Triton X-100) on Nafion-MWCNT support.

| Surfactant          | d, nm          |                |                |                |
|---------------------|----------------|----------------|----------------|----------------|
|                     | $\omega = 1.5$ | $\omega = 3$   | $\omega = 5$   | $\omega = 8$   |
| AOT                 | 2.6-3.4        | 3.6-4.2        | 4.5-6.8        | 5.9-8.1        |
| <b>Triton X-100</b> | <b>2.1-2.6</b> | <b>2.5-3.1</b> | <b>3.0-3.9</b> | <b>3.2-4.6</b> |

For platinum nanocomposites formed both on combined matrices with single-walled nanotubes and on mono-component matrices (Nafion, MWCNT, SWCNT), the sizes of platinum nanoparticles at all values of  $\omega$  exceeded the sizes obtained in Table. 1. This is due to: first, the worst stabilization of nanoparticles on mono-substrates-Nafion and CNT, and secondly, due to the  $\pi$ -interaction between Pt and MWCNT which are stronger most in Pt/Nf-MWCNT composites.

An important indicator of nanocatalysts efficiency in fuel elements is their stabilization on the substrate matrix preventing agglomeration upon operation as a part of membrane-electrode units. The stability resource of catalytic activity was tested for the synthesized Pt/Nf-CNT samples in the course of an amperometric analysis of time evolution of the current density at a fixed oxidation potential (Fig. 4) [11]. It was discovered that Pt/Nf-MWCNT nanocatalysts manifest noticeably higher stability than the Pt/Nf-SWCNT, Pt/MWCNT and Pt/SWCNT samples.



**Fig. 4.** Dependence of the current density from the cycling time in hydrogen-air fuel cells for nanocomposites ( $\omega = 1.5$ ): 1 – Pt/Nf-MWCNT, 2 – Pt/Nf-SWCNT, 3 – Pt/MWCNT, 4 – Pt/SWCNT.

These results prove the possibility of forming high-efficiency stable platinum nanocomposites on combined polymer-carbon substrates obtained by metal ion reduction in reverse microemulsion solutions with nonionic surfactant for the hydrogen oxidation and oxygen reduction reactions in autonomous energy sources.

#### 4. CONCLUSIONS

In present work new effective polymer-containing composite electrodes, obtained by chemical reduction (using anionic and nonionic surfactants) of platinum ions on carbon nanotubes-Nafion support have been formed. The sizes of platinum nanoparticles in the composition of combined carrier matrices were determined by electron microscopy. Chronoamperometric dependences of electrode materials in the reaction of hydrogen oxidation and oxygen reduction are investigated. It had been demonstrated that the greatest stability is shown by nanocomposites with platinum nanoparticles formed with nonionic surfactant (Triton X-100) at  $\omega = 1.5$ .

Thus, in this work the possibility of formation of effective multifunctional electrode materials based on combined matrix-supports modified with platinum nanoparticles for the chemical power sources construction with high specific characteristics is confirmed.

#### ACKNOWLEDGEMENT

This work was supported by Russian Science Foundation (№ 18-79-00017).

#### REFERENCES

- [1] Samir, J., 2018, “Hybridization, diagnostic and prognostic of proton exchange membrane fuel cells: durability and reliability”, ISTE; Hoboken, 216 p.
- [2] Lipman, T.E., Weber, A.Z., 2019, Fuel Cells and Hydrogen Production, Springer New York, 1182 p.
- [3] Mudryk, K., Werle, S., 2018, “Renewable energy sources: engineering, technology, innovation”, Springer International Publishing, 834 p.
- [4] Dicks, A., Rand, D.A.J., 2018, “Fuel cell systems explained”, Wiley, 460 p.
- [5] Kus, P., 2019, “Thin-Film Catalysts for Proton Exchange Membrane Water Electrolyzers and Unitized Regenerative Fuel Cells”, Springer International Publishing, 101 p.
- [6] Serov, A., Shum, A.D., Xiao, X., De Andrade, V., Artyushkova, K., Zenyuk, I.V., Atanassov, P., 2018, “Nano-structured platinum group metal-free catalysts and their integration in fuel cell electrode architectures”, Applied Catalysis B: Environmental, 237, pp. 1139-1147.

- [7] Yao, A., Xu, G., Zhao, Z., Guo, J., Li, S., Cai, W., Zhang, S., 2019, "An enhanced proton conductivity and reduced methanol permeability composite membrane prepared by sulfonated covalent organic nanosheets/Nafion", *International Journal of Hydrogen Energy*, 44, pp. 24985-24996.
- [8] Lebedeva, M.V., Yashtulov, N.A., Flid, V.R., 2019, "Nanocatalysts of Palladium on Combined Matrices-Supports for Portable Sources of Electric Current", *Kinetics and Catalysis*, 60, pp. 118-122.
- [9] Yashtulov, N.A., Lebedeva, M.V., Pestov, S.M., 2016, "Catalysts for anode oxidation of formic acid on carbon nanotubes Taunit", *Fine chemical technologies*, 11, pp. 59-64.
- [10] Xiong, X., Chen, W., Wang, W., Li, J., Chen, S., 2017, "Pt-Pd nanodendrites as oxygen reduction catalyst in polymer-electrolyte-membrane fuel cell", *International Journal of Hydrogen Energy*, 42, pp. 25234-25243.
- [11] Lebedeva, M.V., Antpopov, A.P., Ragutkin, A.V., Yashtulov, 2018, "The Electrode Materials Based on Carbon Nanotubes and Polymer Matrix Modified With Platinum Catalysts for Chemical Power Sources", *International Journal of Applied Engineering Research*, 13, pp. 16774-16777.
- [12] Choi, P., Jalani, N.H., Datta R., 2005, "Thermodynamics and Proton Transport in Nafion II. Proton Diffusion Mechanisms and Conductivity", *Journal of The Electrochemical Society*, 152, pp. E123-E130.
- [13] Parnian, M.J., Rowshanzamir, S., Moghaddam, J.A., 2018, "Investigation of physicochemical and electrochemical properties of recast Nafion nanocomposite membranes using different loading of zirconia nanoparticles for proton exchange membrane fuel cell applications, *Materials Science for Energy Technologies*, 1, pp. 146-154.
- [14] Sui, S., Wei, Z., Su, K., He, A., Wang, X., Su, Y., Hou, X., Raffet, S., Du, S., 2018, "Pt nanowire growth induced by Pt nanoparticles in application of the cathodes for polymer electrolyte membrane fuel cells (PEMFCs)", *International Journal of Hydrogen Energy*, 43, pp. 20041-20049.
- [15] Battirola, L.C., Schneider, J.F., Torriani, I.C.L., Tremiliosi-Filho, G., 2013, "Improvement on direct ethanol fuel cell performance by using doped-Nafion 117 membranes with Pt and Pt-Ru nanoparticles *International Journal of Hydrogen Energy*, 38, pp. 12060-12068.
- [16] Teixeira, F.C., de Sá, A.I., Teixeira, A.P.S., Rangel, C.M., 2019, "Nafion phosphonic acid composite membranes for proton exchange membranes fuel cells", *Applied Surface Science*, 487, pp. 889-897.