

The Polymer Materials as Effective Matrix-Supports in Autonomous Energy Sources

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Abstract

This article is devoted to formation and investigation of composite materials with platinum-palladium nanoparticles on polymer matrix support. By means of electron microscopy and small-angle X-ray scattering methods the behavior 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 device in which the chemical energy of a fuel (reducing agent) and oxidizer, continuously and separately supplied to the electrodes, is directly converted into electrical energy is called a fuel cell (FC) [1-3]. In principle, FC is a kind of galvanic cell and is characterized by an electrochemical system, i.e. a set of oxidizer, reducing agent and ion conductor (electrolyte). In the galvanic cell, the reducing agent and oxidizer (active substances) are part of the electrodes and during the discharge experience various transformations.

fuel electrooxidation-reaction is occurred. On the cathode the electrochemical reduction of the oxidant, usually oxygen – reaction can be observed. The electrodes in fuel cells serve to conduct electrochemical reactions and to supply or electrons removal. Positively and negatively charged particles (ions) move in the electrolyte. The ion conductor also serves to separate the oxidizer and the reducing agent. When the FC works anode and cathode are closed by first kind conductor, on which the electrons move from the anode to the cathode, making work [1,2].

The proton exchange membrane (PEM) [4-18] plays a central role as a medium for proton conduction in PEM fuel cells (FC). Due to the importance of proton transport on fuel cell performance, studies on this effect have been conducted not only for understanding the transport mechanism but also for help in designing alternate PEMs based on a fundamental appreciation. Nafion, the most attractive polymer electrolyte developed so far, shows excellent proton conductivity, but only when soaked in water, which is the medium for proton transport [4-16]. The study of proton transport in water solution has received considerable attention for over a century because of its paramount importance in chemical, biological, and electrochemical systems.

2. SOLID POLYMER ELECTROLYTES IN POWER SOURCES

2.1. Characteristics of transfer phenomena in PEMFC

In general, the following main processes take place inside the fuel cell:

- gas flow through the channels;
- gas diffusion through porous media;
- electrochemical reactions at the anode and cathode;
- proton transfer through solid polymer electrolyte;
- water transport through polymer membrane and catalyst layer.

The design of the cell components must comprise a trade-off of these processes with minimum losses. A typical example is the porosity of the gas-diffusion layer (GDL): while high porosity would help the gas diffusion, this would hinder the electric conductivity and thus the cell performance. In general, the processes depicted above are tightly coupled in the cell.

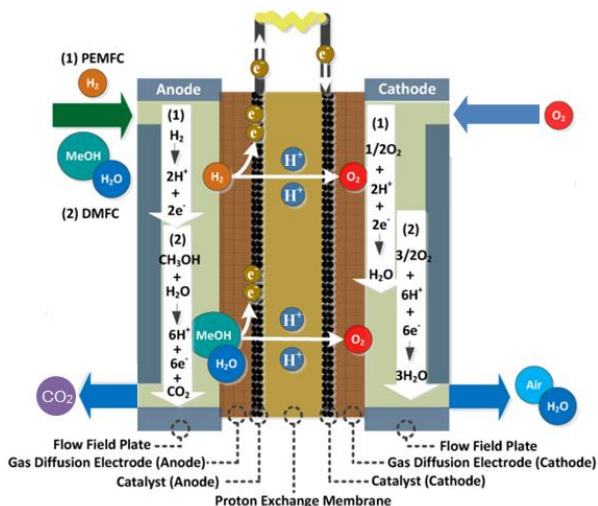


Fig.1. Membrane-electrode assembly based proton exchange membrane. Fuel: 1) hydrogen, 2) methanol.

The simplest FC scheme is shown in Fig. 1. The element consists of two electrodes with electrode chambers and an ion conductor (electrolyte) between them. On anode a reaction of

On the cathode, the reaction is likely to suffer from mass transport limitations at high current densities, when depletion of oxygen in the air stream becomes significant. This limitation can be further extended by flooding of the electrode pores by the product water and blocking of pathways for oxygen transport to the reaction sites. Effective removal of excess water is thus essential, but must be balanced against the need to prevent drying of the adjacent proton conducting media (membrane), which not only causes deterioration in protonic conductivity (and thus higher ohmic losses and lower efficiency), but also impacts durability [1-3].

In this work mechanism and modeling of proton transport through proton-conductive polymer membrane. In order to easily understand how solid polymer membranes allow proton transfer it is better to have a preview on the mechanism of proton transport in water.

2.2. Properties of solid polymer electrolytes in FC

The performance and durability of low-temperature fuel cells strongly depend on the choice of the catalyst matrix support. It provides electronic conductivity, uniform distribution of catalyst particles on the substrate surface and facilitates the transfer of gas into the formed porous catalyst layer. 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 [8,9], such as soot, was one of the main reasons for the decrease in the performance of fuel cells. Subsequently, many attempts were made either to stabilize carbonaceous materials or to find new materials that could meet the following requirements [4-18]:

- 1) the optimal electronic conductivity of the substrate material (> 0.1 S/cm), which would not cause ohmic losses in the catalytic layer at the selected temperature mode of device operation ($-20-80$ °C);
- 2) the ability of the substrate material to form porous structures with pore sizes greater than 25 nm in the catalytic layer. Soot, for example, has a porosity of 80% with average pore sizes in the range of 20-100 nm;
- 3) the substrate material shall not dissolve in the process when the fuel cell is operated under appropriate conditions;
- 4) substrate materials must provide a surface area of more than 50 m²/g.
- 5) low cost of substrate materials – the price should not exceed the cost of carbon with a highly developed surface.

Currently, among the solid polymer membranes used by researchers as electrolytes in chemical current sources, it is necessary to distinguish the perfluorinated polymer membrane developed by DuPont – Nafion, which has a high chemical resistance and proton conductivity.

The structure of the Nafion membrane (chemical formula is $C_7HF_{13}O_5SC_2F_4$) is shown on Fig. 2. Nafion is a

polyelectrolyte consisting of a tetrafluoroethylene (TFE) segment (CF_2-CF_2), which is the base of the polymer, and a perfluorosulfoviny ether (PFSE) ($CF_2-CF(OCF_2-CF(CF_3)-CF_2-CF_2-SO_3H)$) as a side chain (Fig. 2) [4-18]. The polymer base is non-polar (hydrophobic), which provides mechanical strength and heat-resistant properties of the Nafion membrane. The lateral sulfogroup (SO_3H) of the membrane is polar (hydrophilic) and can carry protons. The x value for the Nafion membrane is 6.5.

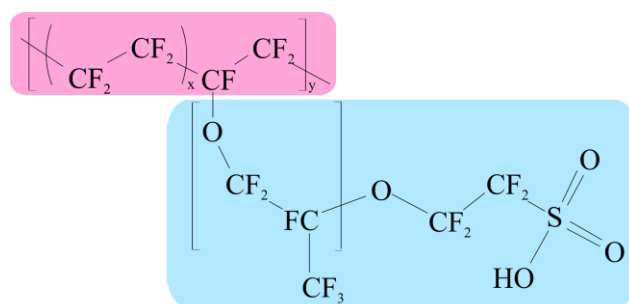


Fig. 2. Membrane Nafion chemical structure.

In power sources, the water that is released at the cathode as a result of an electrochemical reaction using humidified air is partially absorbed by the membrane. This leads to its swelling, and therefore to change in its geometric dimensions. However, excessive swelling of the membrane with its subsequent drying during repeated cycling is extremely undesirable, since this can lead to the destruction and exfoliation of the thin active layer and, as a consequence, to the deterioration of the parameters of the energy source. Therefore, it is imperative to control the degree of swelling of the membrane, reducing this value to a minimum.

As a result, polymer membranes of the Nafion type cannot be used as an electrolyte in energy sources operating at high temperature and relatively low humidity due to the phenomenon of membrane swelling [4-18]. This paper also focuses on the mechanisms and modeling of proton transport processes in a polymer membrane.

2.3. Mechanism of proton conductivity in Nafion membrane

Due to the high rate of proton exchange in the hydrogen-bonded system, the excess proton is accommodated equally among the other water protons. There is therefore no free excess proton in water. Three main ways had been discussed in the literature [17,18].

- a) the proton excess can be a part of an hydronium (H_3O^+) ion, in which all three protons are equivalent (the "Simplistic" picture);
- b) it can reside in a Zundel [17,18] $H_5O_2^+$ cation complex with a proton between two water molecules, binding them in a cluster;

- c) it can be present as an Eigen [17,18] $H_9O_4^+$ cluster, which consists of H_3O^+ and three strongly bound H_2O molecules, each attached to one of the H_3O^+ protons.

The structures of complex Eigen and Zundel ions are shown in Fig. 3. In any case, all the clusters are short-lived in water, and their life and disappearance are crucial parts of the proton transport dynamics.

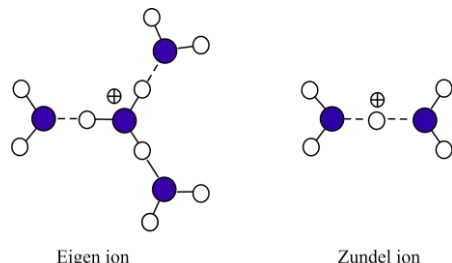


Fig. 3. The structures of complex Eigen and Zundel ions.

The proton conductivity in Nafion is strongly dependent upon its nanostructure and water content. At low water contents, not all acid sites are dissociated and the interaction among water molecules via hydrogen bonding is low, resulting in a low dielectric constant and low rate of proton transfer, which is limited primarily to the surface region, providing very low conductivity. At high water contents, however, the properties of water in Nafion approach those of bulk water (Fig. 4). Thus, two different water environments in Nafion have usually been distinguished. For instance, the water in the middle region of the pore is referred to water pool through which the mobility of protons is fast. However, water near the pore surface along the array of SO_3^- groups is referred to as ‘‘surface water’’ and the proton mobility through the surface is considerably smaller than that in the bulk, due to the strong electrostatic attraction of SO_3^- groups.

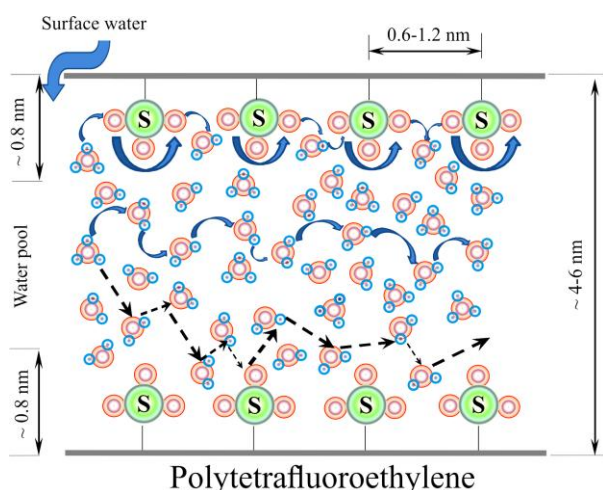


Fig. 4. A simplified picture of structure and proton transfer in Nafion in hydrated state.

It is assumed that three types of diffusion can be carried out in Nafion membrane:

- a surface diffusion mechanism occurring near the pore wall;
- a bulk diffusion via the Grotthuss mechanism in the central region of the pore;
- the so-called *en masse* diffusion.

The proton conductivity in a pore σ_p can be written as:

$$\sigma_p = \sigma_{H^+}^{\Sigma} + \sigma_{H^+}^G + \sigma_{H^+}^E \quad (1)$$

where $\sigma_{H^+}^{\Sigma}$, $\sigma_{H^+}^G$ and $\sigma_{H^+}^E$ represent the surface diffusion, Grotthuss diffusion, and *en masse* mechanisms [12].

The proton conductivity can be written in terms of diffusion coefficient using the Nernst-Einstein relation:

$$\sigma_{H^+}^{\alpha} = \frac{F^2}{RT} D_{H^+}^{\alpha} C_{H^+}^{\alpha} \quad (2)$$

For *en masse* diffusion, the diffusion coefficient can be written as [4,5,12-16]:

$$\frac{1}{D_{H^+}^E} = \frac{x_w}{D_{H^+}^w} \left(1 + \frac{1-x_w}{x_w} \frac{D_{H^+}^w}{D_{H^+}^M} \right) \quad (3)$$

where x_w is the mole fraction of water in the membrane phase, the $D_{H^+}^w$ and $D_{H^+}^M$ are the Stefan-Maxwell diffusion coefficient of hydronium ion and bulk water in the pore, and hydronium ion and the polymer matrix M , respectively.

Because the water mole fraction in PEMs is high even at low activity, e.g., $x_w = 0.67$ at activity $a_i = 0.1$, and quickly approaches 1, Eq. 3 may be simplified to:

$$\frac{1}{D_{H^+}^E} \approx \frac{1+\delta_c}{D_{H^+}^w} \quad (4)$$

where $\delta_c \equiv \left(\frac{D_{H^+}^w}{D_{H^+}^M} \right) \left[\frac{1-x_w}{x_w} \right]$.

Thus, the total proton conductivity in a pore within Nafion can be written in terms of diffusion coefficients, concentrations, and the ratio δ_c :

$$\sigma_p = \frac{F^2}{RT} \left(D_{H^+}^{\Sigma} C_{H^+}^{\Sigma} + D_{H^+}^G C_{H^+}^G + \frac{D_{H^+}^w}{1+\delta_c} C_{H^+}^w \right) \quad (5)$$

When modifying polymer membranes with nanoparticles of different metals [4,5,12-16], an important practical task is to study the structure of the ionomer inside the membrane pore. Modification of membranes allows to obtain effective electrode materials for the construction of membrane-electrode blocks of energy sources with increased specific characteristics. The aim of this work was to form and study bimetallic polymer nanocomposite materials based on perfluorinated Nafion membrane modified with Pt-Pd nanoparticles.

3. MATERIALS AND METHODS

3.1. Nanocomposites formation

Bimetallic platinum-palladium nanoparticles were synthesized by chemical reduction with sodium borohydride NaBH_4 (98%, Merck, Germany) in reverse microemulsion solutions [8,9,11] using Triton X-100 as nonionic surfactant. The method of solution preparation was as follows: a water-organic solution of 0.01 M H_2PtCl_6 and $[\text{Pd}(\text{NH}_3)_2]\text{Cl}_2$ (Sigma Aldrich, USA) mixture was prepared. For reverse microemulsions formation the nonionic surfactant Triton X-100 (Sigma Aldrich, USA) have been used. Then, a microemulsion of a similar composition containing 0.1 M water solution of the reducing agent – NaBH_4 was added to 0.15 M surfactant solution with metal salts under ultrasonic stirring for 2-3 min. During mixing process of two microemulsions the simultaneous reduction of platinum and palladium ions in micelle water pools – microreactors was observed. The molar water/surfactant ratio (ω) 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. The molar ratio of platinum metals in bimetallic Pt-Pd nanoparticles was 3:1.

Metal-polymer films of Nafion (Nf) membranes with bimetallic Pt-Pd nanoparticles were synthesized as described in [8,9,11]. The perfluorinated membrane of the Nafion 115 type (Sigma Aldrich, USA) with a thickness of 0.127 mm was used for the formation of the metal-polymer films. The solubilization of solutions was performed on an. For obtaining the metal-polymer films, the samples of the Nafion membranes were placed in cells with a reverse microemulsion solution with Pt-Pd nanoparticles and solution was sonicated on Ultrasonis Cleaner UD150SH-6L ultrasonic disperser (Eumax, Germany). After that, the modified metal-polymer membrane was washed by distilled water and ethanol to remove the surfactant excess and the organic solvent.

3.2. Investigation methods

The small-angle X-ray scattering (SAXS) experiments were performed at a specialized SAXSess diffractometer (Anton Paar, Austria) in a vacuum chamber at room temperature using monochromatic $\text{Cu K}\alpha$ radiation. Small-angle X-ray scattering was measured in the transmission geometry, the sample was placed in a non-scattering adhesive tape.

The surface morphology of platinum-palladium nanocomposites on polymer membrane was studied through scanning electron microscopy (SEM) at JSM-7401F (Jeol, Japan) instrument with the INCA analyzer (Oxford Instruments, England).

4. RESULTS AND DISCUSSION

Platinum-palladium nanocomposites were formed in microemulsion solutions with nonionic surfactant (Triton X-100) in contact with Nafion. Figure 5 shows a SEM image of Pt-Pd(3:1)/Nf nanocomposites formed at $\omega = 1.5$.

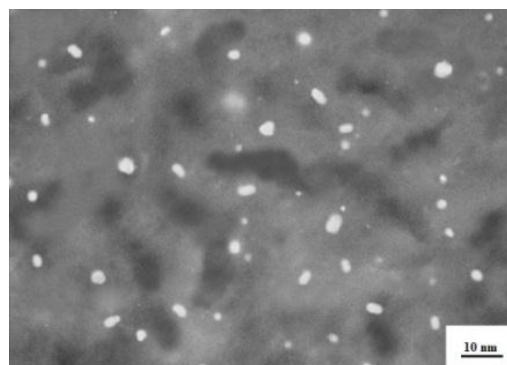


Fig. 5. SEM image of Pt-Pd(3:1)/Nf composite ($\omega = 1.5$).

Uniform distribution of nanoparticles on the surface of the polymer film can be achieved by ultrasonic treatment at the of metal polymer formation stage. The absence of large aggregates of nanoparticles on the membrane surface can be noted. As can be seen from the microphotograph, the main contribution to the Pt-Pd nanocomposites formation is made by ellipsoidal nanoparticles with lateral sizes from 3 to 5 nm. With an increase of the solubilization coefficient (ω) from 1.5 to 8, the size of the nanoparticles increased to 10-12 nm.

The microstructures of the Pt-Pd/Nafion composites had been comprehensively investigated by SAXS, as shown on Figure 6. The scattering maximum of SAXS, the ionomer peak, is typically observed at 1-2 nm^{-1} of the scattering vector (q), following this equation [14]:

$$q = 4\pi / \lambda \sin \theta \quad (6)$$

where 2θ is the scattering angle and λ is wavelength. The Bragg spacing of d , which corresponds to the size of the ionic cluster, is inversely proportional to q as $d = 2\pi/q$. The pristine Nafion membrane showed a broad peak with a q value of 1.27 nm^{-1} , which is in good agreement with literature data [14]. When Pt-Pd NPs were incorporated into Nafion membranes, the q values changed indicating the re-structuring of the ionomer. Thus, this method confirms the modification of platinum metal nanoparticles not only the surface of the polymer membrane (according to REM), but also the volume of the Nafion film.

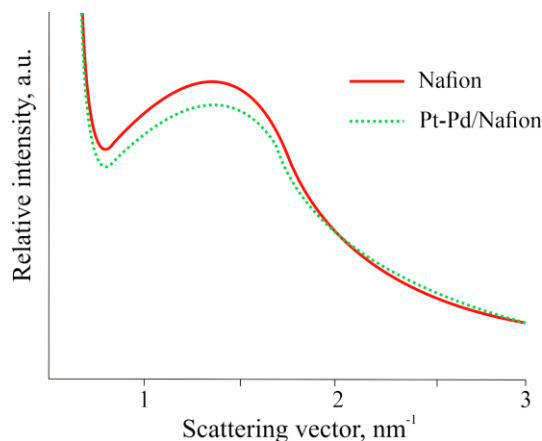


Fig. 6. SAXS curves of Nafion and Nafion membrane with Pt-Pd(3:1) NPs at $\omega = 1.5$.

Thus, the study of metal-polymer composites with bimetallic nanoparticles Pt-Pd. The sizes of nanoparticles on the polymer membrane surface were studied by electron microscopy. The introduction of nanoparticles into the polymer matrix according to SAXS data had been proved.

5. CONCLUSIONS

In this paper, the study of proton transport mechanisms on the basis of well-known diffusion models, as well as the formation of bimetallic polymer materials had been carried out. According to SEM data and by means of SAXS method the incorporation of Pt-Pd nanoparticles into intercrystalline amorphous Nafion layers had been confirmed. Formed composites are effective electrode materials for the construction of autonomous energy sources with increased specific characteristics.

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