INTRODUCTION

Proton-exchange membrane fuel cells (PEMFC) are one of the most promising types of fuel cells [1, 2]. The basic PEMFC is a membrane–electrode assembly. It consists of a proton-exchange membrane (Nafion type, for example), which is in contact with the two sides of the anode and cathode catalyst layers (CL), as well as with two gas-diffusion layers. The CL itself, in turn, is a composite of complex structure. It generally contains particles of a catalyst that is based on platinum-group metals and applied to particles of a highly dispersed carbon substrate (CS); particles of a proton-exchange resin (ionomer); and particles of a hydrophobic polymer, most often polytetrafluoroethylene (PTFE) [1, 2]. A schematic representation of the CL is shown in Fig. 1. Resin particles of hydrated polyperfluorosulfonic acid (PFSA) are usually used as the proton-exchange resin or ionomer and are introduced into the CL from a Nafion solution. Membranes and the Nafion resin are prepared from a perfluorosulfonate cation-exchange polymer. Ionomer particles are introduced into the CL for proton conductivity. The volume fractions of CS, as well as of PFSA particles, must be sufficient for electron and proton conductivity, respectively [3]. In addition, the character of the PFSA distribution in the CL and in the mixture with CS particles is very important. This is important for selecting the optimal CS, so that resin particles, on the one hand, block the catalyst surface as little as possible, but, on the other hand, provide sufficiently large proton and electron conductivity in the CS. Detailed investigations of the porous structure of CL are necessary to establish the patterns of ionomer distribution in CS pores and its influence on the CL porous structure. It is clearly insufficient just to carry out such investigations. Since the range of pore sizes in the CL extends over many orders of magnitude, a suitable porometric method should be used to solve this problem. Until recently, the most common porometric methods were mercury intrusion porosimetry (MIP) [4] and adsorption porosimetry [5]. However, the latter is used only for the smallest pores with dimensions on the order of 1–70 nm. MIP is seldom applied in studies like this since it requires the use of very large mercury intrusion pressures, amounting to several hundred MPa, on the samples under investigation. This causes the destruction of most materials, including soft ones like the CL in PEMFC. Other drawbacks of MIP are the amalgamation of most metals, including platinum-group metals, on which PEMFC catalysts are based; the dependence of the wetting angle of mercury on the type of material; mercury toxicity; etc.

Porous Structure of the Catalyst Layers of Electrodes in a Proton-Exchange Membrane Fuel Cell: A Stage-by-Stage Study

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Abstract—Porous structure is studied by standard contact porosimetry after each stage in the preparation of a catalyst layer, which contains a carbon substrate (CS), an ionomer in the form of Nafion resin, and a platinum catalyst. The influence of the ionomer on the porous structure of ten different CS is investigated. The structure of these samples is studied over the maximum range of their pore radii $r \sim 0.3–10^5$ nm. Pores of main volume within particles of the CS under investigation are mainly distributed over the maximum range of their radii from $r \leq 1$ to $\sim 50$ nm. Ionomer introduction into all the CS under investigation leads to an increase in the integral porosity due to the porosity of the intergranular structure. The change in porosity of the intragranular structure is caused by ionomer blocking small pores in the CS. In most CS, ionomer blocks pores of different sizes, from micropores with radii $r \leq 1$ nm and up to $r \sim 1000$ nm. It is concluded that the extent of blockage of CS pores is largely determined by the surface properties of the CS and Nafion resin and, more precisely, by the difference in resin adhesion to the CS surface because of the presence of different surface groups on the CS surface. When platinum is applied to CS, this leads to an increase in the specific volume of the micropores. The smallest dimensions of platinum particles are estimated to be on the order of 1 nm.

Key words: proton-exchange membrane fuel cell, carbon substrates of the catalyst, standard contact porosimetry, ionomer, platinum, pore blockage

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For studies of Nafion type membranes [6–8], CL in PEMFC, and gas-diffusion layers in PEMFC, the method of standard contact porosimetry (MSP) [9–14] has been used, and this method makes it possible to investigate porous structure over the maximum range of pore radii from \( r \approx 1 \) to \( \sim 3 \times 10^5 \) nm. MSP makes it possible to obtain a great deal of diverse information about porous structure, as well as about sorption and hydrophilic–hydrophobic properties, of all porous and disperse bodies.

As is well known, particles of a hydrophobic polymer—polytetrafluoroethylene, for example—are introduced into the CL for the creation of gaseous pores. These are transport channels for delivering gaseous reagents (oxygen and hydrogen) to the catalyst surface, as well as removing water vapor, which is the product of the electrochemical reaction at the cathode, from this surface. It is clear from this that the hydrophilic–hydrophobic properties of CL significantly affect the electrochemical characteristics of these layers and the entire PEMFC. Although this fact has been known for a long time, until recently, however, the hydrophilic–hydrophobic properties of CL have seldom been studied because of the fact that there was no suitable experimental method. In the first work in which such a study used MSP, only one type of CL was examined, and it consisted of 40% Pt and 60% Vulcan XC-72 carbon black (manufactured by the well-known firm E-TEK) and 5% (by weight of the catalyst) Nafion resin [7]. This was not a systematic study since it involved only one ready-made CL. Therefore, it was not established how each of the components of this layer affects its porous structure and hydrophilic–hydrophobic properties.

The goal of this work is a systematic stage-by-stage study of the porous structure and hydrophilic–hydrophobic properties of CL based on a large number of different types of CS, which have significantly different values of specific surface area and different types of porous structure. Such an approach, in our opinion, offers the possibility of investigating patterns of the influence of the type of CS and of its porous structure on ionomer distribution in it and thus on the electrochemical characteristics of the CL and the entire PEMFC.

**EXPERIMENTAL**

The method of standard contact porosimetry mentioned above was used as our experimental method. It is based on the fact that in a state of capillary equilibrium throughout the entire volume of a system of porous bodies in contact with each other, equilibrium in the capillary pressures \( p^c \) exists for all these bodies. According to the Laplace equation,

\[
p^c = 2 \sigma \cos \theta / r,
\]

where \( \sigma \) is surface tension, \( \theta \) is wetting angle, and \( r \) is pore radius. MSP involves weighing with an analytical balance the equilibrium amount of a measuring liquid in the pores of the sample under investigation relative to its amount in the pores of the standard porous sample in contact with it. With a function of the liquid volume distribution with respect to values of \( p^c \) (an isotherm of capillary pressure) or the pore distribution curve with respect to radii as the standard from independent measurements, the appropriate isotherm of capillary pressure or pore distribution curve with respect to radii is obtained for the sample under investigation. Octane can be used as the measuring liquid for investigating porous structure since it nearly ideally wets all materials. MSP is used for all materials, including those that are readily compressed and amalgamated, and it offers the possibility of investigating these materials over the maximum range of \( r \) approximately from 1 to \( 3 \times 10^5 \) nm. Based on the molecular dimensions of octane, which is generally used as the measuring liquid, MSP makes it possible to estimate porosity in a very broad interval of values of \( r \), beginning with \( r \approx 0.3 \) nm. An automated porosimeter has been developed on the basis of MSP [13, 14]. Measurements were carried out in the process of octane evaporation. Developed by a special technique, cermet disks with a diameter of 20 mm and a thickness of \( \sim 1.5 \) mm were used as standards. This technique guarantees that they contain a sufficient volume of pores over the entire range of radii approximately from 0.3 to \( 3 \times 10^5 \) nm. For good contact between the standard samples and the samples under investigation, as well as for reproducibility of measurements, the systems of