



# A Study of Capillary Porous Structure and Sorption Properties of Nafion Proton-Exchange Membranes Swollen in Water

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## ABSTRACT

The standard porosimetry method (SPM) was used to study capillary porous and sorption properties of Nafion<sup>®</sup> proton-exchange membranes. Pore volume-size and surface-size distributions were recorded together with water distributions as a function of capillary pressure and desorption isotherms. The measurements were performed at 20 and 80°C; only a small temperature effect was found for the porous volume structure. Using these data, the charge density at the inner pore surfaces was evaluated. The estimate suggested only a small degree of diffuseness of the proton double layer at the inner pore surface.

## Introduction

Capillary porous and sorption properties of ion-exchange membranes (IEM) swollen in water are of significant interest, in particular due to their effect on electrical properties under conditions of variable water content. The porous structure of IEM was studied using various methods: electron microscopy,<sup>1,2</sup> atomic force microscopy,<sup>3</sup> small-angle X-ray scattering,<sup>1,2</sup> mercury porosimetry,<sup>4</sup> hydraulic permeability,<sup>5,6</sup> and other methods.<sup>7,8</sup> Each of these methods has its advantages and restrictions. A significant drawback of these methods is their inability to record such essential information as pore-size distributions of membranes swollen in water. Also, the structure of dry membranes studied by means of electron microscopy and other methods is significantly different from that of membranes swollen in water.

A new thermodynamic method of standard porosimetry (SPM) has been developed at the A. N. Frumkin Institute of Electrochemistry.<sup>9,10</sup> In the SPM procedure the equilibrium amount of the wetting liquid is measured in the sample under study. Simultaneously, the amount of the wetting liquid is measured in a standard specimen of a known porous structure, which is kept in thermodynamic equilibrium with the sample. The comparison of the two characteristics enables one to record (with a minimum number of theoretical assumptions) the volume-size and surface-size distribution curves, specific pore-space surface area, adsorption isotherm, etc., for various wetting liquids.

SPM has the following advantages with respect to other porosimetric methods: the largest range of probed pore radii from 1 to  $3 \times 10^5$  nm, ability to study the structure of

swelling and/or compressed specimens (for example, IEM) under their working conditions (e.g., use of water and other working liquids as measuring liquids and working under compressive strengths, etc.), nondamaging character of the method, etc.<sup>9-12</sup>

SPM was used<sup>9,13-15</sup> to study capillary porous and sorption properties of various ion-exchange membranes and conducting polymers either dry or swollen in water. In particular, SPM enabled the discovery of a significant difference between porous structures of homogeneous and heterogeneous membranes. The observed effects of water swelling, equivalent weight, kind of counterions, fixed groups, production technology, and pretreatment of membranes on their structural and sorption properties agree with the data of other methods. As was shown,<sup>13,14</sup> dry perfluorinated sulfocationite membrane (Russian analog of a Nafion membrane) and other homogeneous membranes (without an inert polymeric filler) have a rather low porosity. Therefore, their hydrophilic pores appear normally as a result of contact with water and some other polar liquids penetrating to ionogenic groups. It was found that these membranes contain a small fraction of hydrophilic and hydrophobic ultramicropores, whose sizes are inaccessible for decane (and octane) molecules but accessible for water molecules, because the latter are smaller than decane (and octane) molecules.

The pore radius distribution in Nafion 117 membranes was discussed in Ref. 16 and 17, where the temperature dependence of the membrane conductivity was measured. Two different activation energies below and above the freezing temperature were obtained, both depending on the water content and, thereby, related to the characteristic size of the pores.

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