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Mechanical properties and influence of straining on ion conductivity of perfluorosulfonic acid Nafion®-type membranes depending on water uptake

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ABSTRACT

The results of an investigation of the mechanical properties of a perfluorosulfonic acid MF-4SC membrane (Russian analogue of Nafion®) in the H^+ and Na^+ ion forms at different relative humidity (RH) values ranging from 0% to 95% are presented in this article. The dependences of Young's modulus and the proportional limit stress on RH reach a maximum at RH = 32–58%. The influence of the strain on the ionic conductivity measured in parallel and perpendicular directions to the strain is studied. The conductivity of membranes strained within the region of irreversible deformation is lower than the conductivity of the initial membrane but relaxes and increases up to the values of the initial membrane 2 h after the straining. The conductivity of broken membranes maintained at RH = 9% is higher than the conductivity of the initial membranes under similar conditions. Anisotropy is observed in the ion transport of broken membranes. At $RH > 32\%$, the conductivity measured parallel to the straining is higher than that measured perpendicular to the straining, while at $RH \leq 32\%$, the conductivity is higher in the perpendicular direction. Explanations of the processes occurring during the straining and following relaxation of the membranes are proposed.

1. Introduction

Polymer ion-exchange membranes are widely used in practical applications in different fields, including water treatment, concentration and desalination, electrochemical synthesis; and development of alternative energy sources [1,2]. In particular, perfluorosulfonic acid Nafion®-type membranes are most commonly used as solid electrolytes in low-temperature hydrogen-air fuel cells (FCs) [3–5]. Such materials must meet a number of requirements, including high conductivity, low permeability and high chemical and mechanical durabilities. Different types of degradation (thermal, chemical and mechanical) of perfluorosulfonic acid membranes during FC functioning depending on the operation conditions (temperature and RH) are considered in one review [6]. The short lifetime of FC is often caused by mechanical degradation. Microcracks may arise during membrane fabrication and the operation of the membrane-electrode assembly at the boundary between the membrane and the gas diffusion layer, and near the edges of the membrane-electrode assembly [7]. According to previous studies [8–11], the formation and growth of microcracks are caused by local overheating during the inlet of the reactants and/or by the inhomogeneous distribution of water in the membrane. In addition, the membrane is permanently under constant stress between the bipolar plates within the FC, which leads to gradual irreversible deformations [12]. Most of the membrane mechanical degradation processes cannot be studied in situ as part of the membrane electrode assembly or during FC operation. Therefore, they are usually studied by analysing the stress–strain response and operating dynamical mechanical analysis [13,14,6].

The mechanical properties of the ion exchange Nafion®-type membrane are strongly dependent on not only experiment parameters (deformation rate) but also relative humidity, temperature and nature of the counter-ion of the membrane [15–18].

Several works describe the influence of strain on the ion conductivity of ion exchange membranes. The difference between conductivity of Nafion® under and after a load providing 25 and 50% strain has been studied [19]. However, the authors only investigated the conductivity of the membranes in the direction parallel to the strain at 100% RH and ambient humidity. It was shown that the stress influence increases the conductivity and decreases the activation energy relative to the initial membrane [16]

The variation of water uptake of Nafion®-type membranes is followed by structural rearrangement and, consequently, a change of the ion transport mechanism [20]. It is important to study the

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influence of the membrane strain on the ion conductivity as a function of the relative humidity (water uptake of the membrane). The aim of this paper is to reveal the relationships among water uptake, mechanical properties and ion conductivity of homogeneous perfluorosulfonic acid MF-4SC membrane (Russian analogue of the Nafion® membrane) in H^+ and Na^+ forms. The properties are studied both before the straining and in different directions after the straining (parallel and perpendicular to the straining).

2. Experimental

2.1. Preparation of membrane samples

Extruded perfluorosulfonic acid MF-4SC membranes (provided by Plastpolymer, Ltd., Russia, dry sample average thickness of 100 ± 10 μm) were used in all experiments.

All the membranes were pre-treated at 80 °C for 1.5 h in 5% HCl and rinsed twice in deionized water (resistivity of 18.2 MΩ cm). The Na^+-form membrane was obtained by soaking the H^+-form membrane in 2 M NaCl solution under stirring for 72 h, followed by rinsing in deionized water to remove the excess electrolyte. All the membranes were stored in bidistilled water.

To prepare samples with different water uptakes, the membranes were conditioned under atmospheres with different relative humidities given by saturated solutions of the following salts (RH given in parentheses): $MgCl_2$ (32%), NaBr (58%), NaCl (75%), Na_2HPO_4 (95%) and a 85% solution of H_3PO_4 (9%). RH=0% corresponds to the sample dried 8 h at 80 °C under vacuum.

2.2. Methods

Microstructures of obtained materials were examined using a Carl Zeiss NVision 40 scanning electron microscope (micrographs were obtained at a 1-kV acceleration voltage).

The exchange capacity (EC, mmol/g) of the membranes was determined as follows. A weighed membrane sample (mass *m* of approximately 0.5 g) conditioned at RH=95% was immersed in a 0.5 M solution of NaCl ($V_{\text{NaCl}}=0.050$ l) for 24 h under stirring. The NaCl solution was then decanted and titrated by a NaOH solution with a known concentration. The proton concentration in the NaCl solution after immersion of the membrane was determined (C_{H+}, mol/l). The EC was calculated using:

$$EC = \frac{C_{H+} \cdot V_{\text{NaCl}}}{m} \cdot 10^{-3}. \tag{1}$$

The EC of the investigated MF-4SC membrane was 0.78 mmol/g at RH=95%.

Thermal analysis of the samples was performed on a Netzsch-TG 209 F1 instrument coupled with a Netzsch-QMS 403 quadrupole mass spectrometer under an argon atmosphere in aluminium crucibles in the temperature range 25–200 °C (heating rate 10 °C/min). The water uptake was determined as the difference between the starting weight and the weight after drying at 150 °C (for the membranes in the H^+ form at RH ≥ 32%) and 200 °C (for the membranes in the Na^+ form and those in the H^+ form at low RH) divided to the weight after drying. Water uptake (in wt%) was calculated as follows:

$$\text{Water uptake (\%)} = (\text{starting weight} - \text{dry weight})/\text{dry weight} * 100. \tag{2}$$

Number of water molecules per sulfo-group was calculated as follows:

$$n = W/(18 * EC) * 10^3, \tag{3}$$

where *W* is a part of water and 18 is a water molecular weight (g/mol).

The composition of the evolved gases was determined for some samples using a Netzsch Aeolos QMS 403C mass spectrometer.

Stress–strain experiments were performed using a Tinius Olsen H5KT universal testing machine with a Tinius Olsen 100R extensometer and a force sensor at 25 N under ambient conditions (RH=20 ± 2% and $T=27 \pm 1$ °C). Rectangular specimens of 100 mm in length and 10 mm in width were pre-equilibrated at a given RH (five samples were tested for each RH). The thickness and width of each sample were taken as the average values of five points measured before the experiment by a Mitutoyo micrometre. The gauge length of the samples was adjusted to 50 mm for the machine and 20 mm for the extensometer. For all tests, the strain rate was 5 mm/min. Engineering stress–strain curves were obtained from both the machine and the extensometer.

The ion conductivities of the initial and strained membranes were measured in different directions: parallel (*direction 1*) and perpendicular (*directions 2 and 3*) to the strain (Fig. 1). The experiment was performed in cells with constant pressure on the membrane at the given RH and $T=27 \pm 1$ °C (RH and temperature were controlled by a P750 thermohydrometer, Dostman Electronic GmbH). The cell for the conductivity determination in directions 1 and 2 was designed as described in a previous work [21].

Carbon sheets were used to improve the contact between membrane and electrodes. The conductivity was determined by impedance spectroscopy in a frequency range from 10 Hz to 2 MHz using 2B-1 and Agilent 4285A impedance analysers at various time intervals after the stress–strain tests or after the cell for conductivity measurement

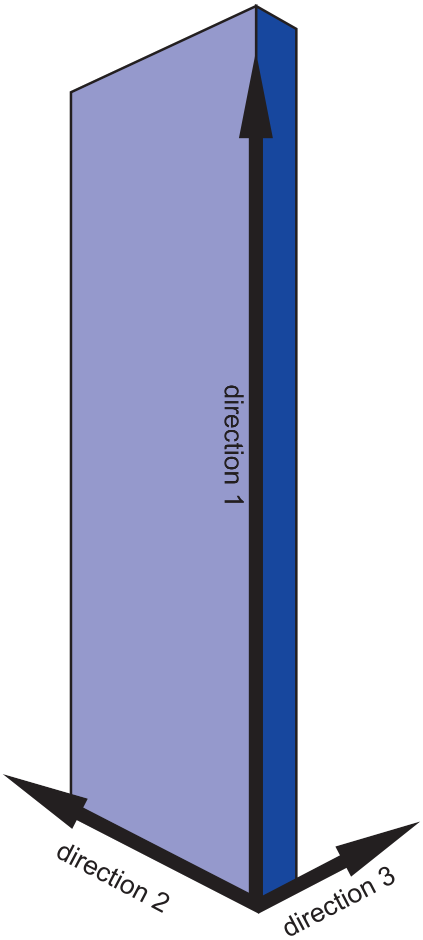

Fig. 1. Directions of conductivity measurements (membrane strain along direction 1).