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Effect of ultrasonic treatment of Nafion® solution on the performance of fuel cells

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Preparation of membranes

Membranes were obtained by casting from Nafion® solutions (5 wt% in a mixture of lower aliphatic alcohols, Sigma Aldrich, equivalent weight - 1100) without ultrasonic treatment (***Nafion*** sample) and after 60 minutes of ultrasonic treatment (***Nafion US60*** sample). Ultrasonic treatment was carried out using a Sonics Vibra cell VSX130 disperser (frequency 20 kHz) with an immersion probe 6 mm in diameter (amplitude 35%; the ultrasonic power estimated by the calorimetric method was $P = 5.2 \pm 0.2$ W). A polymer solution (20 ml) was placed in a glass container 1.5 cm in diameter and the probe was immersed in such a way that it was at a distance of 2-3 mm from the container bottom and equidistant from the walls. The container was placed in an ice bath to prevent the polymer solution from heating during treatment and to increase the intensity of the ultrasonic exposure.

Polymer solutions were poured onto the surface of plastic Petri dishes and the solvent was removed by drying in the following mode: for 12 h 40°C; for 1 h at each 60, 70, 80, 85°C; and then for 4 h at 60°C. After that, the films were carefully removed from the surface of Petri dishes and hot pressed under a pressure of 5 MPa for 3 min at 110°C to ensure better strength. All the membrane samples prepared were conditioned to standardize and convert to protonic form. To do so, they were sequentially treated at room temperature, first twice with 5% HCl solution for 1.5 hours, then washed with deionized water until the reaction for Cl^- ions ceased.

Study of membranes

To determine the ion exchange capacity (IEC, meq g^{-1}), a dry sample of a membrane weighing ~ 0.3 g was kept in 50 ml of 0.1 M NaCl solution for 12 hours with continuous stirring. After that, the salt solution with the membrane was titrated with 0.05 M NaOH solution. The IEC (meq g^{-1}) was calculated with respect to the weight of the dry membrane.

Thermal analysis of the samples was carried out using a Netzsch-TG 209 F1 thermobalance in platinum crucibles in an argon atmosphere, in the temperature range from 25 to 150°C. The heating rate was 10 K min^{-1}. The water uptake of the membranes was determined from the weight difference before the heat treatment and after keeping at 150°C. The water uptake was determined for the samples pre-equilibrated at RH = 95%, t = 25°C. The required relative humidity and temperature were maintained using a Binder MKF115 environmental chamber (humidity control accuracy was ±2.5%).

The proton conductivity of the membranes was determined in the temperature range of 20-85°C at RH 95%. The required relative humidity and temperature were maintained using a Binder MKF115 environmental chamber. The measurements were performed on an Elins E-1500 AC bridge (in the frequency range of 10 Hz - 3 MHz) on symmetric carbon/membrane/carbon cells with an active surface area of 1 cm^2. The compression ratio was controlled with a torque screwdriver. The conductivity value (S cm^{-1}) was calculated from the resistance found from the impedance hodograph, based on the cutoff on the active resistance axis.

The hydrogen permeability through the membranes was determined by gas chromatography using a GC-4000M Krystallux chromatograph with a thermal conductivity detector (current = 30 mA) and a packed column (MoleSeive 5 A sorbent, 2 m, 30°C, 20 cm^3 min^{-1}, Ar). Hydrogen was obtained from a hydrogen generator manufactured by LTD NPP Khimelektronika. The experiment was carried out in a temperature controlled cell, one part of which was fed with pure hydrogen and the other with argon at a rate of 20 ml min^{-1}. To create the required humidity level in the hydrogen and argon streams, each gas was passed through two bubblers with water (100 % humidity) that were kept in a thermostat at the same temperature as the cell. The hydrogen permeability coefficient P (cm^2 s^{-1}) was calculated by the formula:

$$P = \frac{d}{C_H - C_{Ar}}, \tag{1}$$

where *d* is the membrane thickness, C_H is the mean volume concentration of hydrogen in the chamber into which hydrogen was fed, and C_{Ar} is the mean volume concentration of hydrogen in the chamber into which argon was fed. The gas flow *j* through the membrane was calculated from the ratio:

$$j = \frac{C_{Ar} V_t}{S}, \tag{2}$$

where C_{Ar} is the mean volume concentration of hydrogen in the chamber into which argon was fed brought to normal conditions, V_t is the volume flow rate of the carrier gas, and S is the active area of the membrane.

Preparation and testing of MEA FCs

Membrane-electrode assemblies (MEAs) for testing hydrogen-oxygen fuel cells (FCs) with an area of 4 cm^2 were formed by spraying a Sigracet 10 BC water-alcohol suspension of the catalyst and Nafion® binder in low-molecular aliphatic alcohols (Aldrich) onto a gas-diffusion layer (GDL) with an airbrush by the technique reported elsewhere[S1]. The HiSPEC 9100 (60% Pt) (manufactured by Johnson Matthey) catalyst was used. It was applied in amounts of 0.6 mg_{Pt} cm^{-2} to the cathode and 0.3 mg_{Pt} cm^{-2} to the anode. The ratio of the mass of Nafion (with respect to the dry compound) to the mass of the catalyst support (carbon black) was 0.9. The GDL with applied active layers was compressed with the membrane to be studied at a temperature of 140°C for 3 min at a pressure of 2 MPa. Before testing, the MEA was sealed in an ElectroChem cell using Teflon gaskets at a compression ratio of ~ 20%.

The MEAs were tested using an ElectroChem test bench. The voltametric characteristics were determined under nearly-stationary conditions by feeding hydrogen and oxygen into the cell without excessive pressure with humidification corresponding to a relative humidity of RH ~100% at a cell temperature of $t = 65°C$. The area of electrochemically active platinum surface (S_{Pt}**)** within the cathode was estimated from cyclic voltammograms recorded during nitrogen passage through the cathodic part of the ElectroChem cell[S2,S3]. S_{Pt} increased from 42 to 49.8 m^2 g_{Pt}^{-1} on transition from Nafion to Nafion US60. All the electrochemical measurements were performed using Elins P-45x potentiostat-galvanostats with FRA and Elins P-150x units.

References

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