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Studies of bibenzimidazole and imidazole influence on electrochemical properties of polymer fuel cells

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ABSTRACT

Binary and ternary membranes were prepared by immersion of Nafion-115 in 2,2′-bis(4-aminophenyl)-5,5′-bibenzimidazole (BAPBI) or/and in imidazole (Im) and were used in proton exchange membrane fuel cells (PEMFCs) with Pt/C gas diffusion electrodes and graphite single-serpentine monopolar plates. Membranes were activated in 0.2 M H_2SO_4. BAPBI was synthesized in poly(phosphoric) acid and the chemical structure was confirmed by ^1H, ^{13}C NMR and ATR-FTIR spectroscopy. Membranes were characterized by FTIR spectroscopy, TGA, AFM techniques. Also the water uptake was determined. PEMFCs were investigated by electrochemical impedance spectroscopy, polarization curves, cyclic voltammetry and linear sweep voltammetry taking into consideration the kind of imidazole applied and the temperature used (25 or 60 °C). The maximum power density of 146 mW/cm^2 at the current density of 345 mA/cm^2 was detected for Nafion-115-BAPBI membrane. For all constructed PEMFCs the efficiency at 0.6 V was found about 41%. The immersion of Nafion-115 in Im, BAPBI or BAPBI-Im increased the thermal stability and mechanical properties of membranes. The Nafion-115-BAPBI membrane showed good prospective for application in PEMFCs while in opposite to Nafion-115-Im, the poisoning effect on Pt catalyst was not observed.

1. Introduction

Tetrafluoroethylene-perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid copolymer commercially known as Nafion is one of the most popular polymer applied in the proton exchange membrane fuel cells (PEMFCs) [e.g. 1–6]. Nafion exhibited such advantages as high proton conductivity, and chemical and physical stability at 80 °C [1,2][e.g. 1,2]. The proton conductivity of Nafion strongly depends on the presence of water and under fully hydrous conditions can reach even 0.1 S/cm [1,2][e.g. 1,2]. This fact makes the PEMFCs with Nafion membrane complex and expensive and caused that at temperature above 100 °C the membrane dehydrates and the proton conductivity is sharply decreased.

There are two types of polymer fuel cells: low (LT) and high (HT) temperature PEMFCs distinguished due to maximum temperature of operation up to ca. 80 °C and 200 °C, respectively [e.g. 1–8].

To improve properties of LT PEMFCs, scientists propose to add to Nafion membrane such inorganic additives as ZrP, SiO_2, TiO_2, BPO_4, H_3PO_4, $Sn_{0,95}Al_{0,05}P_2O_7$-P_xO_y or $CsHSO_4$ [e.g. 1,2,8–14] or the immersion of membrane in organic additives (imidazole, triazole, diethyl amine, triethylamine, polybenzimidazoles (PBI), vinylbenzyl substituted PBI, different salt forms of the Nafion ionomer, ionic liquid cation 1-butyl-3-methylimidazolium or/and phosphoric acid [e.g. 10,15–28]). The properties of Nafion membrane for PEMFCs may be influenced not only by the temperature, time of immersion, kind of solvent, and kind and amount of additives. For example, Ainla and Brandell [18], investigated the influence of the time and concentrations of immersion Nafion membrane in PBI and PBI and diethyl amine solution for Direct Methanol Fuel Cell (DMFC) applications. One of the best values of conductivity (75 mS/cm) relative to Nafion (71 mS/cm) was found in case of the membrane dipped for 15 min into a 0.1% PBI solution, repeating the procedure 4 times. In our work we have chosen relevant conditions. However, it was not a goal of our work to investigate the influence of concentration and time of immersion on the electrochemical parameters of the constructed single fuel cells. Nafion-212 membranes with vinylbenzyl substituted PBI showed proton conductivity (σ) values over 10 mS/cm under humidified environment [19], while Nafion-115 membrane with ionic liquid cation 1-butyl-3-methylimidazolium doped with phosphoric acid exhibited value of σ about 11 mS/cm at 160 °C without humidifying [20]. Phosphoric acid increased the working temperature of Nafion membranes above 100 °C without substantive decreasing of the strength of the membrane at elevated temperature [20]. Phosphoric acid doped Nafion membrane (by using different

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salt forms of the Nafion ionomer for electrolysis cell) was operated at 130 °C at ambient pressure with a current density (J) about 300 mA/cm^2 at 1.75 V [16]. 4,5-Dicyano-1H-[1,2,3]-triazole shows good electrochemical stability in the potential window and did not cause so strong poisoning effect on the Pt catalyst in comparison with imidazole [24].

As it was shown above acid-base blend membranes consisting of polymer with sulfonic groups and a basic compound with N-heterocycle groups are one of the most promising directions in the last decade to develop PEMFCs [22,29].

In this work, binary and ternary membranes based on Nafion-115 and BAPBI, Im and BAPBI-Im were obtained, activated in H_2SO_4 and studied as PEMFC single cells. The main idea was to form so called sub-network based on Nafion-115 and these additives in order to evaluate their influence on the fuel cell performance which is typically highly dependent on the presence of water in case of PEMFCs. Interactions between Nafion-115 and organic compounds were investigated by FTIR and TGA (DTA) analysis. Electrochemical properties of four constructed single PEMFCs were analyzed taking into account the kind of imidazole applied (BAPBI, Im), and temperature used (25 and 60 °C). The morphology and mechanical properties of membranes were analyzed by AFM method. BAPBI was synthesized and for the first time proposed in this subject matter as a new and good basic additive for PEMFCs based on Nafion membrane.

2. Experimental

2.1. Materials

Nafion-115 film was purchased from Quintech Brennstoffzellen Technologie. 3,3′-Diaminobenzidine, 4-aminobenzoic acid, imidazole and poly(phosphoric acid) (PPA) and N,N-dimethylacetamide (DMA) were obtained from Aldrich and used as received.

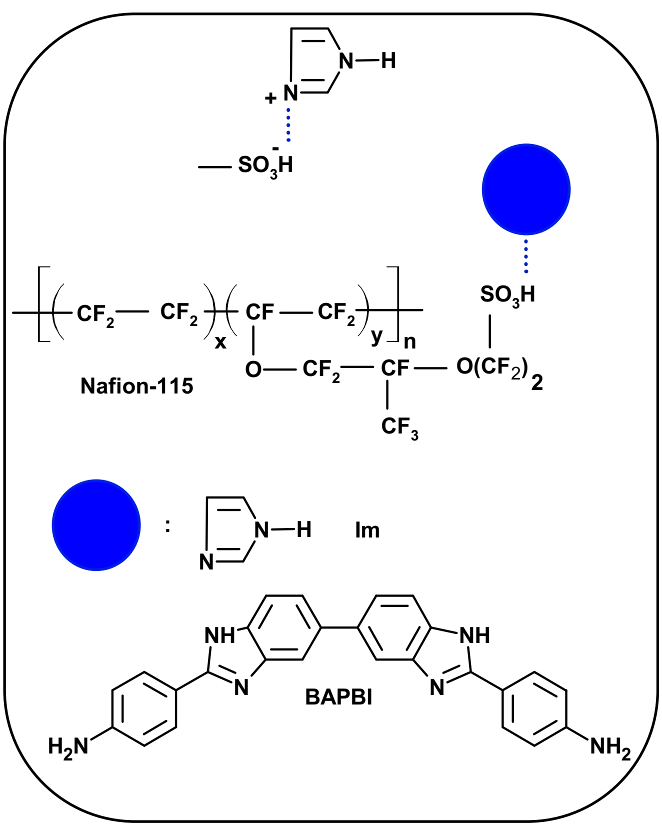

Fig. 1. Chemical structures of BAPBI, Im and Nafion-115 along with possible interactions between these compounds.

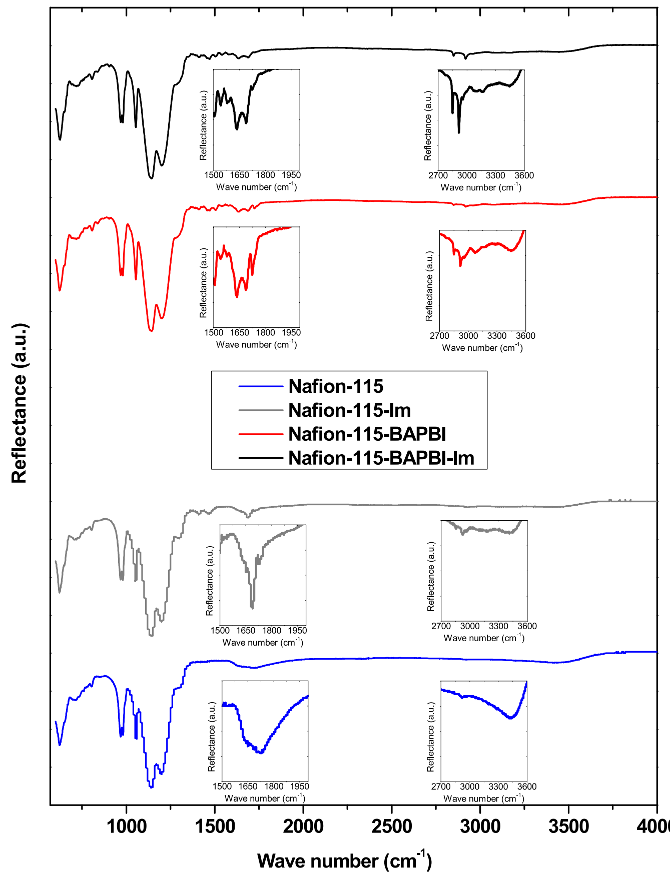

Fig. 2. ATR-FTIR spectra of Nafion-115 and binary and ternary membranes. (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

2,2′-bis(4-aminophenyl)-5,5′-bibenzimidazole (BAPBI) was obtained according to the synthesis described in [30]: yield 90%, m. p. 226 °C, ^{1}H NMR (300 MHz, DMSO-d$_6$), δ [ppm]: 12.50 (broad NH), 7.90, 7.87, 7.73, 7.57, 7.54, 7.46, 7.44, 6.71, 6.68, 5.63 (NH_2). ^{13}C NMR (75 MHz, DMSO-d$_6$), δ [ppm]: 153.65 (—C=N—), 151.14 (NH_2—C_{Ar}), 135.73, 128.31, 121.56, 117.75, 116.42, 115.45, 114.12, 113.53, 113.21. FTIR (KBr pellet), ν [cm^{-1}]: 3728, 3702 and 3628, 3597, 3337, 3205, 3155, 3019 (N-H stretching of imidazole rings), 1620 (C—N stretching), 1607 (N—H bending or stretching in the aromatic rings), 1486, 1437, 1387, 1358 (stretching in the aromatic rings), 1276 (C—N stretching), 1176, 834, 800, 759, 737, 722, 687.

2.2. Preparation of binary and ternary Nafion-115 membranes

In the first step, Nafion-115 membrane was purified by boiling in deionized water for one hour. Next, Nafion-115 membranes were dipped for 15 minutes into Im, BAPBI or Im-BAPBI DMA solution (0.1% solution), and next dried at temperature of 105 °C for 3 minutes. This procedure was repeated four times. In the third step all membranes were cleaned by boiling in deionized water for one hour and then rinsed in 3.75% H_2O_2 for an hour and finally activated in boiling 0.2 M H_2SO_4 solution during one hour. All membranes were also rinsed several times in fresh distilled water to remove any residual contaminants.

2.3. Construction of single PEMFCs

Single PEMFCs with area of 1 cm^2 were constructed based on prepared membranes, commercial gas diffusion electrodes (SLGDE 0.5 mgcm^{-2}, FuelCellsEtc) and graphite single-serpentine plates.