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Nafion® and polyaniline composite modification with Li and Mg ions

Stanislavs Lozkins^{1,2}, Julija Hodakovska¹, Janis Kleperis¹ and Remo Merijs-Meri²

1 - Institute of Solid State Physics, University of Latvia, Latvia

2- Department of Polymer Materials Technology, Riga Technical University, Latvia
stanislavski@inbox.lv

Abstract.

Modification of Nafion®-based samples with polyaniline (PANI) and positive charged ions could potentially allow achieving good proton conductivity at higher working temperatures what is observed in typical polymer electrolyte membrane fuel cells.

In this work Nafion® polymer was modified with 1% polyaniline emeraldine salt and Li and Mg ions containing solutions. The influence of activation process and the type of ions on composites' proton conductivity was investigated. To define the best composition the physicochemical properties of synthesized materials were determined by the means of thermogravimetric analysis, impedance spectroscopy, determination of water absorption and its kinetics, and FTIR. From the original samples the best results of $\sigma=155$ mS/cm were shown by Nafion®/PANI membrane what was modified by Li⁺ reduction solution. This membrane also had better thermal characteristic compared to other researched samples: membrane degradation starts on higher temperature interval.

1. Introduction

Nowadays commercially available for applications in fuel cells are perfluorinated polymers, such as Nafion® made by DuPont Company. Many other materials were synthesized and tested, but till now Nafion® has shown better properties' relation. Main advantages of Nafion® are chemical and thermal stability, high proton conductivity, also mechanical stability. However, membrane's practical usage has been limited by Nafion® membrane's disadvantages, e.g. low proton conductivity at low humidity, high fuel (hydrogen or methanol) cross-over and finally high price of Nafion® [1]. The ways to eliminate this disadvantage is to synthesize new materials or modify existing ones, both could be done with a set of methods and could bring desirable improvements of exploitation values.

The focus of this paper is to synthesize and study the physical properties of Nafion®/PANI composite membranes, such as the water uptake, degradation and proton conductivity. Nafion®/PANI membrane was prepared by mixing Nafion® and PANI solutions and casting on glass and then treated by lithium and magnesium ions containing solution. Permeability and ionic conductivity of the modified membranes were measured using electrochemical impedance spectroscopy; the thermal stability was determined by thermogravimetric analysis, and the presence of ions in polymer matrix was determined with FTIR spectroscopy. The conductivity and thermal stability of all samples were compared with the unmodified Nafion® membrane as a reference.

2. Experimental

2.1. Materials

N-Methyl-2-pyrrolidone (NMP), 96% sulphuric acid (H₂SO₄), polyaniline emeraldine salt powder were supplied by Sigma-Aldrich. Nafion® (DuPont, equivalent weight of 1100 g/mol) was purchased as 10 w% water solution from Fuel Cell Store. All chemicals were used without further purification. Li⁺ and Mg⁺ ions containing reducing solutions were prepared from lithium or magnesium hydroxides accordingly by adding concentrated hydrogen chloride to get Li or Mg chloride water solution.

2.2. Membrane preparation



To prepare composite membrane Nafion® solution has been dried in air, than both polymers were separately dissolved in NMP and stirred for 24 h to obtain homogeneous solution. Solutions were mixed together to achieve polymer relation of Nafion®:PANI=99:1 and stirred for 24 h until homogeneous solution was obtained. The solution was cast on a glass plate, which was kept at temperature of 60°C, and after solvent evaporation a membrane was obtained. The membrane was washed in deionized water to remove residuals of solvent; membranes were activated by 4 steps: 1) samples were treated 1 hour by hydrogen peroxide on 80°C; 2) samples were treated 30 minutes by distilled water on 80°C; 3) samples were treated by sulfuric acid (96%) on 80°C; 4) membranes were washed in deionized water on room temperature. Then membrane was processed by reducing solution.

2.3. Methods

2.3.1. Impedance spectroscopy. The proton conductivities were determined using AC impedance spectroscopy with Becktech conductivity cell connected to potentiostat VoltaLab PGZ301 and self-made humidifying system. The samples in the cell were heated up to 70 °C with 100% humidity; frequency range was 2 mHz – 100 kHz. The conductivity values of the prepared membranes were calculated using the following equation: $\sigma=1/\rho$, where ρ - electrical resistivity, calculated from impedance spectrum.

2.3.2. Differential thermal analysis. Thermogravimetric analysis was performed with thermogravimetric analyser Shimadzu's DTG-60 in the region between 30 °C and 600 °C with heating speed of 10 °C/min in argon flow 20 ml/min.

2.3.3. Water uptake. The membranes were cut into samples with equal area, dried, weighted and then placed in deionized water at room temperature for a chosen time. The water uptake values of the prepared membranes were calculated using the following equation: $Water\ uptake\ (\%) = \frac{w_s - w_d}{w_d} \cdot 100\%$, where w_d and w_s are weight of dry and swollen membrane respectively.

2.3.4. FTIR spectroscopy. FTIR spectroscopy analysis of dried samples was performed with Infrared Fourier Vacuum Spectrometer Vertex 70 in 590 – 3500 cm^{-1} range.

3. Results and discussion

3.1. FTIR analysis

Experimentally acquired FTIR spectra of all samples (Figure 1.) shows several peaks that are related to Nafion® structure: e.g., at 806 cm^{-1} , what characterized S-H deformation vibrations; at 1210 cm^{-1} to C-F asymmetric vibrations; at 1152 cm^{-1} to C-F symmetric vibrations; at 1056 cm^{-1} to -SO₃ vibrations; at 983 cm^{-1} to C-O-C vibrations. Non-activated Nafion®/PANI sample shows 4 additional peaks compared to Nafion® sample: at 1310 cm^{-1} , 1508 cm^{-1} , 1590 cm^{-1} , 1722 cm^{-1} , which corresponds to C-N and C=C vibrations, benzenoid and quinoid forms respectively. It proves that in this sample the PANI is in emeraldine form [7]. The peak at 1643 cm^{-1} characterize C=O amide vibrations, 3500 cm^{-1} - NH²⁺ vibrations in PANI. Membranes with more intensive 1508 cm^{-1} peak designate that composite polymer has more reduced fragments (influence of hydrogenation) and vice versa. An increase of intensity of peaks at 1643 and 3500 cm^{-1} proves the fact that

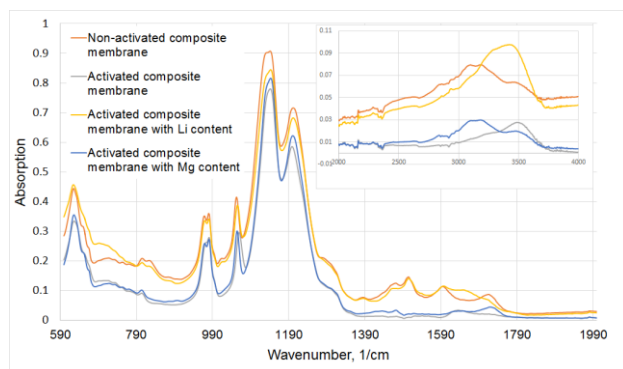


Figure 1. Composite membrane Nafion/PANI FTIR spectrum: non-activated and activated.

polyaniline had changed its structure: these peaks are characteristic to pernigraniline form of PANI, so some of the fragments of emeraldine salt form have hanged to non-conductive fragments [5,7]. Non-activated membrane has double peak at 806 cm^{-1} and 827 cm^{-1} and peak at 1390 cm^{-1} ; vibrations at 827 cm^{-1} and 1390 cm^{-1} belongs to NO_3^- anion.

Composite sample with magnesium content has additional peak at 1482 cm^{-1} what proves the presence of PANI in emeraldine form. Non-activated membrane with lithium content has peak at 1510 cm^{-1} what characterized NH_3^+ or N-H deformation vibrations in PANI.

Activated membrane doesn't show PANI additive because after activation process, there was a hydrogenation, what has influence on PANI state; also, hydrochloric acid can dissolve polyaniline. Some additional researches is needed to determine significance of influence of all the mentioned factors.

Comparing non-activated membranes FTIR results in the range of $2700\text{--}3700\text{ cm}^{-1}$ with Nafion®/PANI composite samples that have been treated with reduction ions, sample which include Li^+ ions part shows emeraldine form, but sample with magnesium ions has the similar line as non-activated membrane.

3.2. Water uptake

According to observed water absorption dynamics (Figure 2.) it is evident that 2 days is enough to reach water absorption maximum for all membranes, since obtained results after 2 and 6 days (2880 and 8660 minutes respectively) are the same.

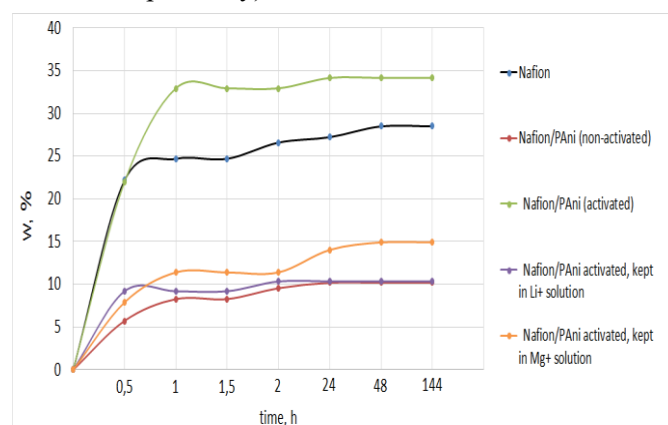


Figure 2. Water absorption kinetics results.

Compared to pure Nafion® the highest absorption ability was shown by activated Nafion®/PANI composite polymer - it absorbed 6 w% more water compared to pure Nafion® and 24 w% more than inactive composite sample. Compared to non-activated membrane samples which were treated in lithium and magnesium ion solutions, absorbed about the same and slightly more water (by 0.5 w% and 4.9 w% respectively). This could lead to increase mechanical stability due to less swollen membrane and geometrical size increase, but could cause proton conductivity decrease.

3.3. Thermal analysis

According to TGA/DSC results for pure Nafion® membrane during heating three obvious processes can be distinguished: evaporation of absorbed water which lasts to 110°C ; elimination of linked water what lasts to 205°C ; degradation interval $\sim 210\text{--}360^\circ\text{C}$ designate destruction of sulfonic group; Nafion®'s full degradation is observed before 500°C ; glass transition temperature on DSC curve is observed at $\sim 117^\circ\text{C}$.

Even though PANI degradation happens at higher temperatures compared to Nafion®, all obtained composite membranes with polyaniline content degrade at lower temperatures. Only for lithium sample degradation starting interval was shifted to higher temperature side, but it has faster speed of degradation with nearly vertical drop of mass to nearly fully degraded sample (Figure 3). Activated and non-activated samples shows endothermic peak at $\sim 140\text{--}145^\circ\text{C}$ on DSC curve, what mean that has started glass transition process into polymer. Although, membranes that were treated in reducer's solution show improved results compared to pure Nafion® membrane: for the composite membrane glass transition temperature is at $\sim 140^\circ\text{C}$.

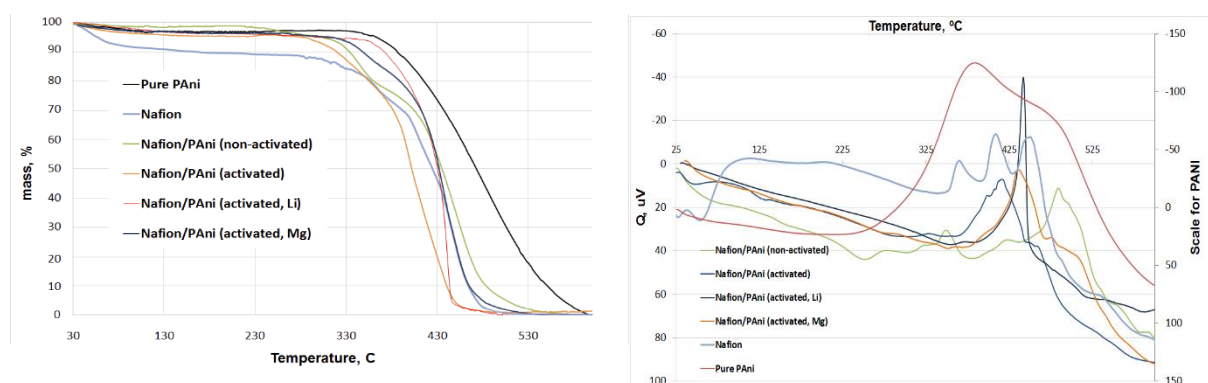


Figure 3. Composite sample TGA/DSC results.

Composites containing PANI significantly differs from pure Nafion®'s destruction. Process is characterized by noticeable decrease in losses of weight at stages of degradation of sulfonate groups and their destructions. Also end of stages is displaced in the range from 25 to ~ 40 °C. Results of membranes that were treated in reducing solution are more positive than those in which reducing agent is not active.

From obtained results it appears that in fuel cell where risk is possible when temperatures can rise above operating temperature of fuel cells, Nafion®/PANI composite membrane that is modified with lithium solution is best suited for use. It has ability to hold water in wide range of temperatures (up to ~ 120 °C) and “survive” for some time at elevated temperatures, what provide PANI content into composite polymer.

3.4. Proton conductivity

Results of original membranes were compared to results of pure Nafion® membrane. Conductivity of each sample at 100% humidity varies considerably. Adding PANI to the Nafion® causes material to loose in conductivity, but activation process allows achieving conductivity values that are comparable to the ones of the Nafion®.

Treating composite membrane with Li ions containing solution lead to the best results observed

Table 1. Conductivity of pure Nafion® and composite membranes - non- and activated.

Samples	σ , mS/cm
Pure Nafion®	118
Nafion®/PANI non-activated	69
Nafion®/PANI activated	145
Nafion®/PANI activated with Li ⁺	155
Nafion®/PANI activated with Mg ⁺	29

between measured samples. On the opposite, treating with Mg ions containing solution decreased proton conductivity; this sample showed the lowest conductivity value from the all samples. Probably this is caused by one or several ion's properties, because Li ion properties (size, nucleus charge etc.) are closer to the one of the hydrogen that participates in proton conductivity. Smaller size could lead to deeper Li ion impregnation; causing more homogeneous distribution in membranes volume. Reducing ions reduce quinone diimide to p-phenylenediamine on PANI and reduce number of electrostatic bonds between Nafion and PANI, what increases protons conductivity.

During several measurements that lasted two hours, no membrane showed any reduction in conductivity and no visible damage was observed after measurements that would indicate low mechanical or chemical durability in short time interval.

4. Conclusions

The modification of Nafion® membranes by PANI and reduction ions shows better properties than pure Nafion® sample and composites Nafion®/PANI without treatment by reduction ions. These modified membranes were characterized by impedance spectroscopy and TGA to confirm the ions positive

influence on composite. Impedance spectra data demonstrated that composite modify with Li^+ ions increase proton conductivity, FTIR shows that reducing ions have influence on PANI oxidation degree. It is believed that the polyaniline particle mostly occurs in membrane's volume and has influence on water absorption because formed polyaniline particle size in Nafion® matrix isn't limited to pore size. We conclude that composite Nafion®/PANI modification with positively charged ions is an effective way to reduce the rate of water transport through the membrane. Because of the physical electrostatic interaction between the positively charged polymer and negatively charged sulfonated groups in the membrane, the pore size shrunk.

In order to improve conductivity results for samples that were treated in reducing solution, experiments should be performed to determine optimum concentration of reducing agent (Li or Mg ion concentration in given solution) for known geometric parameters of the membrane and to find optimal elongation times to prevent such problem that ions can bind to sulfonate groups.

The results demonstrate that the content of polyaniline in a composite polymer matrix is suppressing degradation and destruction processes of sulfonate groups. Lithium ions in composite are improving membrane conductivity. This both component combination allows to get composite Nafion®/PANI with better options than the ones of the pure Nafion® polymer.

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