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Behavior of Nafion membrane at elevated temperature and pressure

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ABSTRACT

Nafion membrane was studied as a potential electrolyte for a polymer electrolyte membrane (PEM) reactor operating at temperatures in the range of 100–160°C. An attempt was made to avoid the well known problem of the decrease in the conductivity of Nafion at elevated temperatures caused by its insufficient humidification. Elevated pressure was applied. In the first instance the influence of elevated temperature and pressure on the ion exchange capacity of a Nafion membrane, one of the main characteristics, was tested in selected environments. One environment tested was 14.7 M H_3PO_4 used nowadays generally for the high temperature proton conducting polymer electrolytes. 0.5 M H_2SO_4, demineralized water and an open atmosphere represent the remaining environments under study. The most significant deterioration of the ion exchange capacity of the membrane was observed in 0.5 M H_2SO_4. In contrast to this, 14.7 M H_3PO_4 and an open air atmosphere left the membrane properties almost unchanged. Subsequently Nafion's conductivity was determined in the temperature range of 110–150°C at pressure up to 0.65 MPa. As anticipated, it was found that Nafion also exhibits sufficient conductivity above 100°C at 100% relative humidity of the environment. The conductivity decrease was observed during prolonged experiments. Surprisingly enough, no related changes in the structure of Nafion were indicated by IR spectroscopy, one exception being the sample stored in an autoclave for a prolonged time in 0.5 M H_2SO_4.

Keywords: Polymer electrolyte; Perfluorosulfonic acid; Membrane conductivity; Elevated temperature; IR analysis

1. Introduction

During the last decades, increased attention is being paid to the exploitation of renewable energy sources to secure mankind's energy needs. A typical example of this approach is the increasing percentage of overall energy production originating, for example, from wind turbines and photovoltaic cells. This trend will continue progressively in the future [1,2]. Despite the environmental point of view, the dependency of these technologies on actual weather conditions represents their crucial disadvantage. Therefore, today reliable technology is sought allowing for compensation of fluctuations in energy production and consumption intensity in time. To attain this target, means of rapid energy storage in the period of production excess are sought with the option of its efficient recuperation. Hydrogen, as an energy vector, offers an effective solution to this problem. It is available on earth in large quantities in the form of water [3,4]. Additionally, it

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is an environmentally benign compound with a high specific energy content. The chemical energy involved can be efficiently converted to electrical power by fuel cell technology or by combustion in the engines connected to electricity generators. Water electrolysis, as a direct hydrogen production method utilizing renewable energy sources, is the logical choice.

Water electrolysis can be realized both on alkaline or acidic way. Alkaline water electrolysis represents a well established industrial process [5,6]. For intermittent operation, however, an acidic polymer electrolyte membrane (PEM) reactor is more suitable [5]. The PEM electrolyzer exhibits several additional advantages, making this technology favorable for this type of application. The main advantages are high process intensity (i.e. high current densities and a small inter-electrode gap) and utilization of demineralized water as the process media.

On the other hand, PEM water electrolysis suffers from several significant problems. A platinum metal catalyst with a high loading probably represents the one of the most important. The most promising method of reducing catalyst loading is to raise the cell operational temperature to well above 100°C, preferably to 180–200°C. The enhanced electrode kinetics connected with the temperature increase results in reduced overpotentials at both electrodes and thus reduced catalyst loadings needed. At the same time, the heat generated by the process is of higher potential and thus better utilizable.

An increase in the operational temperature makes new demands on the materials used. This concerns both the construction materials as well as the proton-conductive membrane. Today, perfluorinated sulphonated membranes of the Nafion type represent the most frequently used polymer electrolyte in conventional PEM-type fuel cells and electrolyzers. At elevated temperatures of over 100°C at atmospheric pressure, the problem of Nafion drying out and thus the decrease in its conductivity is widely known. In the case of PEM-type fuel cells, H_3PO_4-doped PBI-type membranes are used to overcome this problem. In the case of water electrolysis, however, this approach raises several important issues. The first is that, in the case of electrocatalysis, concentrated H_3PO_4 acts as a catalytic poison [7]. Another issue is its significant corrosion aggressiveness. In the case of water electrolysis, however, it is possible to operate under such conditions, i.e. pressure, that water is present in the system in liquid form even at the desired temperatures above 100°C [8]. Under such conditions, the membrane drying out no longer represents an obstacle. The utilization of perfluorinated sulphonated material as a polymer electrolyte would thus avoid the above-mentioned problems.

Unfortunately, as reported by Alberti [9–11], the Nafion membrane exhibits significant deterioration of conductivity when exposed to elevated pressure and temperature (120°C, up to 28.5 MPa). One explanation proposed by Gebel [12] is that high temperature and pressure lead to extensive membrane swelling. As Nafion is a non-crosslinked polymer this results in an increased distance between the individual polymer chains and, at certain level, in the formation of colloidal dispersion of rod-like particles. The membrane thus loses its mechanical compactness and electrochemical properties. The aim of this study is to reveal more information on the Nafion degradation process at elevated pressure and temperature and to assess the possibility of its future utilization in this type of application.

2. Experimental

2.1. Membrane activation

Nafion 117 (Ion Power, USA) was used in all experiments performed. All samples were activated in an identical way prior to use. The activation procedure proposed in [13] was used: storage for 60 min in demineralized water at a temperature of 80°C, followed by leaching in 30% H_2O_2 for 25 min at 60°C, protonization in 0.05 M H_2SO_4 for 25 min at 60°C and finally washing in demineralized water for 120 min at 60°C. The activated membrane was stored in demineralized water.

2.2. Influence of the environment

A sample of Nafion membrane was placed in a PTFE autoclave filled with demineralized water; 0.5 M H_2SO_4 or 14.7 M H_3PO_4 (85 wt%). The last sample was exposed to the open atmosphere at a given temperature. The autoclaves were placed in a drying oven for 140 h at 170°C. The ion exchange capacity of the samples being an important indicator of potential change in properties, it was determined prior to and post-treatment. The method of ion selective electrode reported previously [14] was used for this purpose.

2.3. Conductivity measurement

Membrane conductivity was measured in longitudinal direction by means of electrochemical impedance spectroscopy (EIS) in a four-electrode arrangement. A Solartron SI1260 impedance analyzer in combination with a Solartron SI1287 Electrochemical Interface was used for this purpose. Membrane conductivity was evaluated on the basis of its determined resistivity and sample dimensions using Eq. (1).

$$\sigma = \frac{l}{R \cdot A} \quad [\mathrm{S/m}] \tag{1}$$

where σ stands for conductivity (S/m), l represents the distance between sensing electrodes (m), R membrane resistance (Ω) and A the membrane cross-section area (m^2).

The strip of membrane in approximate dimensions of 1 × 5 cm^2 was clamped into the conductivity cell. The assembly was placed in a drying oven and heated up to the desired temperature. The cell was connected to the supply of demineralized water pressurized by a HPLC pump. The pressure in the cell was controlled by a back-pressure valve. Membrane conductivity was measured in a temperature range of 110–150°C and at pressure up to 0.65 MPa. Preheated demineralized water with a conductivity lower than 0.7 μS/cm was pumped through the cell during measurements (0.5 mL/min) in order to keep the pressure constant and to wash out potential degradation products.

2.4. IR spectroscopy

The membrane structure was analyzed prior to and post exposure to elevated temperature and pressure by means of IR spectroscopy. Before analysis all samples were treated in 0.1 M HCl for 24 h and subsequently in demineralized water for 24 h at room temperature. IR spectra were obtained using a Perkin Elmer Paragon 1000 PC, ATR technique, equipped with a single reflection diamond crystal.

3. Results and discussion

3.1. Influence of the environment

In an ideal case, the water electrolyzer is fed just by demineralized water. This process arrangement is possible if the gas diffusion electrode is appropriately constructed, allowing for the frequent occurrence of three-phase contact on the catalyst surface. In order to enhance process performance, and thus improve catalyst utilization, a conductive electrolyte can be used as well. H_2SO_4 and H_3PO_4 solutions were chosen as the prospective electrolyte. In order to obtain information on Nafion stability in this environment autoclave experiments were performed at 170°C. The ion exchange capacity of all samples was determined prior to and after exposure as an important indicator of the potential deterioration of membrane characteristics. The results are summarized in Fig. 1. As it is clearly visible, the ion exchange capacity decreased most significantly in the case of the H_2SO_4 solution (by 85%) followed by pure water (by 50%). Significantly less pronounced changes are related to the sample's exposure to H_3PO_4 and to the open air atmosphere at the given temperature. The reason for such behavior results from the different environment properties. One of the obvious differences between the individual media is the equilibrium pressure achieved in each autoclave at the experiment temperature, i.e. 170°C. In the case of the H_2SO_4 solution and water, the pressure in the autoclave was close to 0.8 MPa. In the case of concentrated H_3PO_4, the pressure increase was limited. This is due to the low equilibrium pressure of this medium at this temperature. Higher pressure leads to more extensive structural changes resulting in a drop in ion exchange capacity. These changes cause blocking or decomposition of the Nafion ion exchange sites. Only a minimal decrease in ion exchange capacity in the case of the sample exposed just to the open air atmosphere confirms the importance of pressure for the stability of Nafion. There is one discrepancy between this theory and the experimental results. Pressure in the autoclave filled with demineralized water and 0.5 M H_2SO_4 is close for both media, for the former one being potentially slightly higher. Nevertheless, a significant drop in ion exchange capacity was observed just for the sample exposed to the H_2SO_4 solution. This was most probably caused by acidic catalysis of the Nafion desulfonation reaction.

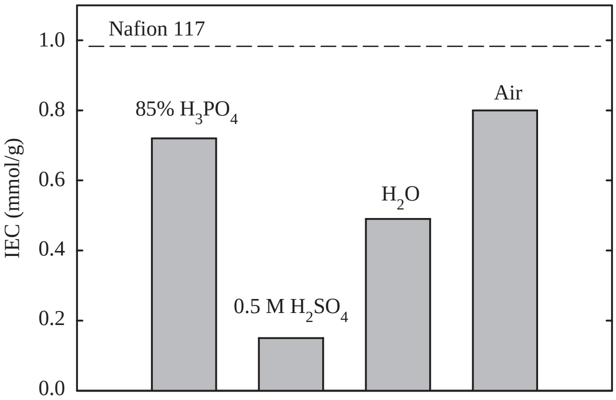

Fig. 1. Ion exchange capacity of Nafion 117 membrane samples after 140 h treatment at 170°C in autoclaves filled with: 85% H_3PO_4; 0.5 M H_2SO_4; demineralized water and air (exposed to the open atmosphere). Line in graph indicates ion exchange capacity of activated Nafion membrane.

3.2. Conductivity of Nafion

Direct evidence of the applicability of Nafion in elevated temperature and pressure water electrolysis is provided by the dependence of its conductivity on time. In the present case, the aim was to verify mid-term stability of the conductivity of Nafion in liquid water at temperatures up to 150°C. In the first

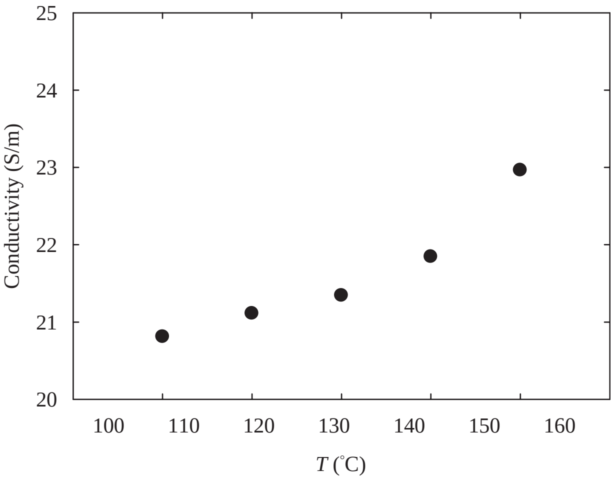

Fig. 2. Conductivity of Nafion 117 membrane at various temperatures under a pressure of 0.5 MPa and at 100% RH.

step, the influence of temperature on the conductivity of Nafion at constant pressure of 0.5 MPa was determined. The results are summarized in Fig. 2. The fit of the measured data to the Arrhenius plot exhibits a slight deviation from linear trend. This is caused by the conductivity decrease in the time between the start of the experiment and the achievement of a reliable resistivity value. This effect is especially important at the top limit of the temperature range studied.

The results of the stability of the membrane's conductivity in time are summarized in Fig. 3 which shows the time dependence of the conductivity for three temperatures in the range of 110–150°C at a pressure of 0.6 MPa over a period of 850 h. It is well visible that, in the entire temperature range under study, the conductivity of Nafion is not stable and it deteriorates in time. The kinetics of the deterioration is enhanced by the increasing temperature. This is documented by the fact that, whereas at 150°C the conductivity deteriorated during the first 100 h of the experiment by approximately 50% of its original value, at 110°C over the same time period the decrease only amounted to 15%. At the highest temperature studied, i.e. 150°C, the dependence was also determined for the pressure of 0.48 MPa in order to verify the influence of the pressure. As expected, at reduced pressure, the deterioration of membrane conductivity was less progressive. Deterioration by only 20% during the first 100 h was observed. The most interesting observation, however, was the conductivity behavior at the times close to the end of the experiment. Here a clear trend towards reaching the limiting conductivity value can be observed. This observation is in agreement with the results of Alberti et al. [9].

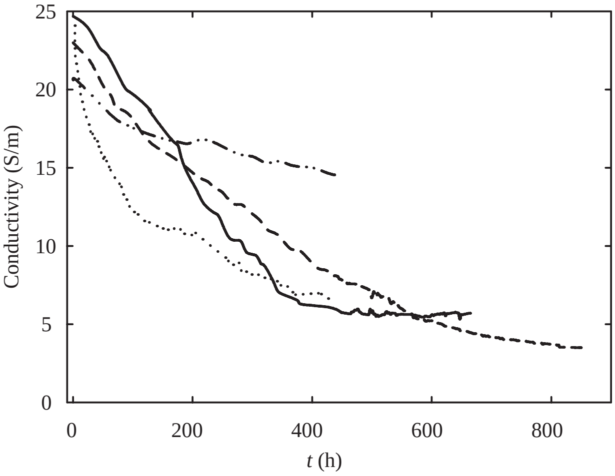

Fig. 3. Conductivity of Nafion 117 membrane at various pressures, temperatures of 110–150°C and at 100% RH conditions: —— 150°C, 0.48 MPa; ·········· 150°C, 0.6 MPa; - - - - - - - - 130°C, 0.6 MPa; -··-··- 110°C, 0.6 MPa.

At this stage it is difficult to explain the behavior observed. According to the literature [11], the crucial factor influencing the stability of Nafion is its degree of hydration. At elevated temperature and pressure, the degree of hydration increases and gradually changes the internal structure of the membrane. This results in decreasing membrane conductivity and at the same time it allows the degradation of the functional groups. Furthermore, this second aspect influences membrane conductivity and, additionally, its ion exchange capacity.

Even more challenging is the explanation of the limiting value of the decrease in membrane conductivity. It is also interesting that this trend is similar for all conditions under study. There may be several reasons. The first one is the possibility that only part of the membrane ion exchange sites is degraded. The remaining part ensures continuous membrane conductivity. A second explanation is the possibility that the long-term exposure of the membrane sample to the water flowing continuously through the cell results in a partial or complete change in the membrane cycle, which is obviously connected with the change in its conductivity. The source of the ions for the exchange can only with difficulty be ascribed to the demineralized water used (conductivity <0.7 μS/cm). The corrosion products of hydraulic circuitry are one option. In such a case, it would be difficult to predict the stability of the membrane, because it is known that the Nafion membrane is most unstable in the proton cycle [15]. In other ion cycles its stability substantially increases.

3.3. *Structure analysis by IR spectroscopy*

To validate a possible explanation for the degradation mechanism of Nafion, information about the

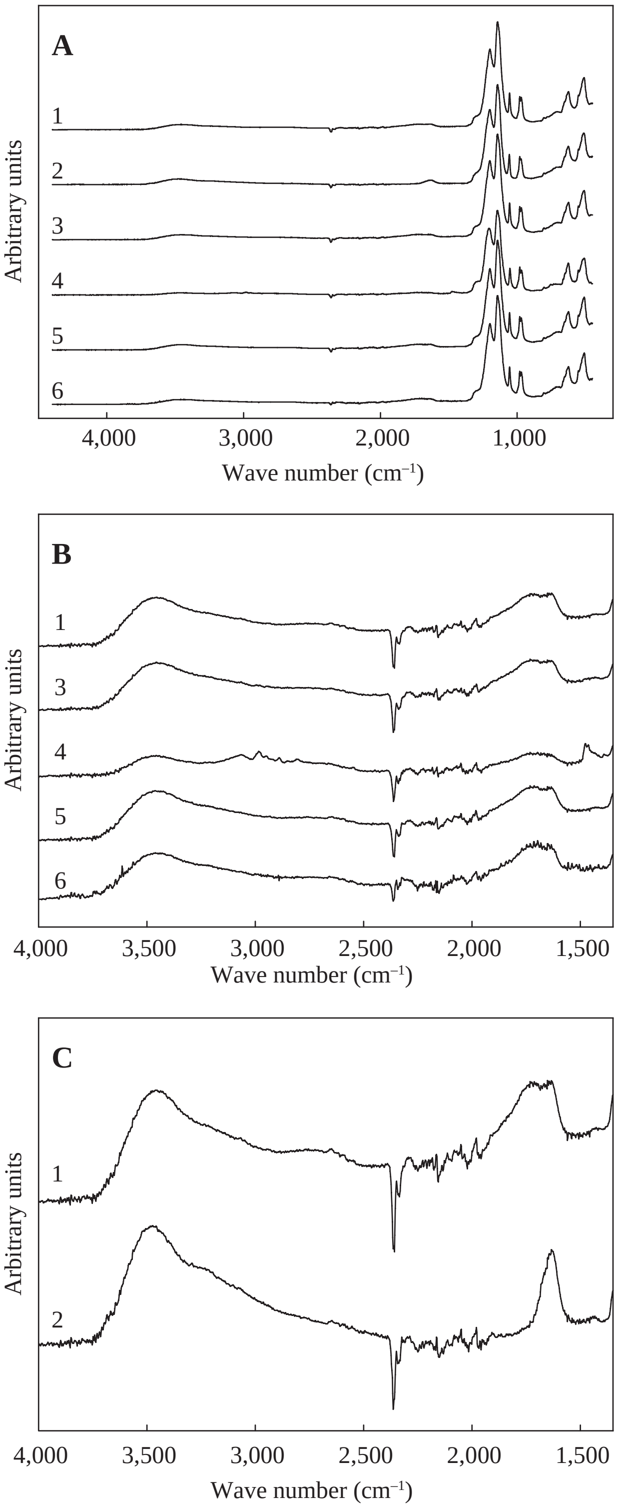

Fig. 4. IR spectra of Nafion 117 samples: A. Full range all samples; B. 1,300–4,000 cm^{-1} area detail of sample after 140 h treatment at 170°C in autoclaves and C. 1,300–4,000 cm^{-1} area detail of sample after midterm conductivity stability test. 1: ''fresh'' Nafion 117; 2: after 450 h 150°C 0.6 MPa; 3: autoclaved in 85% H_3PO_4; 4: autoclaved in 0.5 M H_2SO_4; 5: autoclaved in demineralized water; 6: exposed to air.

structural changes related to the sample's exposure to the individual environments and conditions is necessary. IR spectroscopy was proven by various authors to be a suitable method to obtain relevant information [16–21]. This technique can provide an answer to the question whether the changes observed are related only to the morphological changes of the membrane or to the degradation of the polymer. IR spectra for the entire wave number range measured are shown for all samples tested in Fig. 4A. Fig. 4C shows details of the IR spectra of the sample after the mid-term conductivity stability test. Fig. 4B then summarizes the spectra of samples treated in the autoclave. In all figures, the spectrum of the freshly activated Nafion 117 sample is shown for reference.

The spectra of the samples autoclaved in water and H_3PO_4 and exposed to the open air atmosphere are identical with freshly activated Nafion. Therefore, only morphological changes are responsible for the decrease observed in their ion exchange capacity. This is particularly interesting in the case of water, where a 50% drop in ion exchange capacity was observed. In the case of the sample autoclaved in 0.5 M H_2SO_4, the situation is different. Here the most evident difference in the IR spectra is the band at 1,484 cm^{-1}, see Fig. 4B. This band is attributed to the vibrations of SO_2–O–SO_2 bonds, which are a product of the degradation of the functional groups of Nafion. In the literature, the occurrence of such vibrations was typically observed for membranes exposed to the Fenton test [18,20,21]. This confirms that, at high temperatures, H_2SO_4 catalyses a degradation mechanism similar to that taking place during the Fenton test. Besides a decrease in ion exchange capacity, the loss of hydrophilic sulfonic groups also causes an increase in membrane hydrophobicity. Therefore, the intensity of the bands corresponding to the water present in the sample at 1,600–1,800 and 3,500 cm^{-1} is reduced.

In the case of the sample after mid-term exposure to the elevated temperature and pressurized water during the conductivity stability test, Fig. 4C, the main difference with respect to the activated Nafion membrane structure consists in the absence of a band at 1,770 cm^{-1}. This feature is typical of Nafion in an Na^+ or K^+ [16,17] cycle or of Nafion after the Fenton test [18]. According to Laporta [19], this band corresponds to the presence of H_3O^+ in the membrane structure. Furthermore, in the region of 2,700–2,900 cm^{-1}, the wide band assigned to H_3O^+ [18] is significantly weakened. Therefore, one possible option to consider is the contamination of the Nafion measured by traces of ions from the demineralized water or by corrosion product from the experimental cell. In such a case, the different course of the decrease in membrane conductivity over time can be explained by the ion exchange kinetics being influenced by the experimental conditions or by the different rate of the corrosion products penetration to the water from the experimental setup. Significantly more work is needed to understand this behavior more comprehensively.

4. Conclusion

As a membrane material, Nafion offers unique properties advantageous to the broad range of its application. Although it is an extremely stable ion-conductive polymer, its utilization is limited by the elevated pressure and temperature in the water environment. The latter aspect was the subject of this study. It was proven that elevated pressure and temperature cause a decrease in the membrane's ion exchange capacity and conductivity. Both increasing temperature and pressure promote the degradation process. One interesting feature is that the decrease in membrane conductivity clearly tends towards a limiting value different from zero. Although several explanations were suggested, the true reason is not yet clear.

Another interesting aspect is that, despite the significant drop in ion exchange capacity and in ionic conductivity, no related structural changes of the membrane were identified by the IR analysis. The changes in the membrane properties must thus be related mainly to morphological changes blocking the accessibility of the functional groups in the Nafion membrane. The main question to be clarified remains the reversibility of such changes. One exception to the previous statement is the sample autoclaved in 0.5 M H_2SO_4. In this case, the degradation of the functional sulfonic acid group was confirmed by IR analysis.

It is possible to conclude that, on the basis of the presented data, the application of Nafion as a polymer electrolyte for processes at temperatures above 100°C under fully humidified conditions can, under specific conditions, not be excluded. To obtain a clearer understanding of the phenomenon observed, however, further study is required.

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