Effect of crosslinking on the physicochemical properties of proton conducting PVDF-g-PSSA membranes

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Abstract

Poly(vinylidene fluoride) (PVDF) membranes, radiation-grafted with styrene and sulfonated, were studied as a candidate material for polymer electrolyte fuel cell (PEFC). In particular the effect of the use of crosslinkers in the polymer structure was investigated using bis(vinyl phenyl)ethane (BVPE) and divinylbenzene (DVB) as reagents. Water uptake in the H^+ form, proton conductivity and ion exchange capacity of the PVDF-g-PSSA membranes, as well as transport properties of oxygen and hydrogen were determined at room temperature. Crosslinking with DVB resulted in a more pronounced decrease in the properties; the use of BVPE had no significant influence. Even on the permeation of oxygen and hydrogen the BVPE had little effect: the diffusion coefficient and solubility remained at the same level as for the non-crosslinked membranes. Increasing the membrane thickness was found to be at least as effective in reducing the oxygen permeation rate as using crosslinkers.

1. Introduction

The polymer electrolyte fuel cell (PEFC) has attracted considerable attention as a potential nonpolluting power source, in particular for vehicles [1, 2]. Several problems with the PEFC need to be solved in order to achieve a practically useful system.

Our research has been directed to the study of a new type of membrane for use in the PEFC. These membranes are produced by pre-irradiation grafting of poly(vinylidene fluoride) (PVDF) films with styrene and subsequent sulfonation [3]. The PVDF-g-PSSA membranes have shown interesting physical and structural properties [4]. Proton conductivity, for example, which at room temperature exceeds $0.1\,S\,cm^{-1}$ [5], corresponding to area resistance below $0.2\,\Omega\,cm^2$, offers the possibility to regard the material as a candidate for low temperature fuel cells.

For radiation-grafted FEP-polystyrene membranes, Büchi et al. [6] have shown that crosslinking of the membrane decreases gas crossover in a fuel cell, which

improves the stability of the membrane and fuel cell performance. Therefore, PVDF-based membranes with two different crosslinkers have been synthesized [7]. Here we present results on the physical and electrochemical properties including ion exchange capacity, proton conductivity, water uptake as well as solubility and diffusion coefficient of oxygen and hydrogen in the membrane. In particular, the influence of crosslinking on the properties of the PVDF-g-PSSA membranes is discussed.

2. Experimental details

2.1. *Materials*

The matrix PVDF films of $80\,\mu m$ thickness were purchased from Goodfellow. Irradiation was carried out using an Electrocurtain electron accelerator (Energy Sciences, Inc) under nitrogen atmosphere (<200 ppm O_2) at an acceleration voltage of 175 kV. The

irradiated (100 kGy) films were immediately immersed in the monomer solution containing styrene (Fluka) and the crosslinker (BVPE and/or DVB, see below) at 2.5, 5 and 10 mol %, respectively. The volume ratio of monomers to solvent (toluene) was in all cases 1:1. Divinylbenzene (DVB) was purchased from Fluka and distilled prior to use. Bis(vinyl phenyl)ethane (BVPE), see Figure 1, was prepared according to the method of Li et al. [8]. The details of the preparation process have been published elsewhere [7]. The degree of grafting was determined gravimetrically. Finally, the grafted membranes were sulfonated with $0.5 \, mol \, dm^{-3}$ chlorosulfonic acid in 1,2-dichloroethane at ambient temperature, ending up with about 95% degree of sulfonation for membranes with high degrees of grafting (above 40%), whereas unexpectedly low degrees of sulfonation were observed in the characterization of the membranes with low degrees of grafting.

Commercial Nafion® 117 (DuPont) was used as reference material.

2.2. Water uptake

The water uptake of the membranes, defined as the ratio of the mass of the absorbed water to that of the dry membrane, was determined by equilibrating the membranes separately with water vapour and with liquid water. The dry weight of a sample was obtained after drying it over P_2O_5 in a desiccator for one week at room temperature.

2.3. Proton conductivity

Prior to conductivity measurements the membranes were equilibrated with water vapour in a closed vessel for a minimum of three days. The ionic conductivity of the membranes was determined by the impedance method using a frequency range of 5–50 kHz. The measurements were done in a solid two-electrode cell with a heating jacket, the cell being connected to a

Fig. 1. Structure of the two crosslinkers, bis(vinyl phenyl)ethane (BVPE) and divinylbenzene (DVB).

Solartron 1170 frequency response analyser and a microcomputer. The membrane resistance was obtained by extrapolating the linear part of the spectrum to the real axis of the impedance plot. The conductivity was calculated from the electrode area of the cell ($0.283 \, cm^2$) and the thickness of the membrane, which was measured with a micrometer. During the measurements the cell was continuously purged with humidified nitrogen to maintain constant humidity in the sample. The temperature of the cell was kept constant at 20 °C by circulating water from a thermostat.

2.4. Ion exchange capacity

The ion exchange capacity (IEC) was determined by back titration. A known amount of aqueous NaOH was added to the weighed samples. The sample containers were shaken occasionally and after equilibration the excess of NaOH was titrated with standard HCl solution. The pH was recorded with a MetLab PHM210 pH-meter. Blanco and Nafion® 117 samples were used as internal and external references. Several parallel analyses were done with all samples. On the basis of this the accuracy of the analysis was estimated to $0.1 \, meq \, g^{-1}$ when the residual water after drying in a vacuum desiccator at 70 °C is taken into account.

2.5. Solubility and diffusion of gases in the membrane

The solubility and diffusion coefficient of oxygen and hydrogen were determined using the electrochemical monitoring technique [5, 9]. Using a two-compartment cell with the membrane between the compartments a membrane/electrode combination was prepared by coating the membrane on one side with platinum. This was accomplished by a chemical method [10], where one cell compartment was filled with acidic platinum salt solution and the other with a solution of a reducing agent, in this case a 3% aqueous solution of sodium borohydride $NaBH_4$ (Merck). The reducing agent diffuses through the membrane, and platinum is deposited on the platinum solution side of the membrane.

During the actual measurement the electrode compartment was filled with $0.5 \, mol \, dm^{-3}$ sulfuric acid while the other one was flushed with gas, that is with oxygen or hydrogen during the measurements and nitrogen between them. The membrane was supported by a platinum mesh which served as a current collector for the working electrode. A saturated calomel electrode was used as a reference and a platinum foil as a counter electrode. As a potentiostat, Amel model 553 with a function generator Amel 567 was employed. The tem-
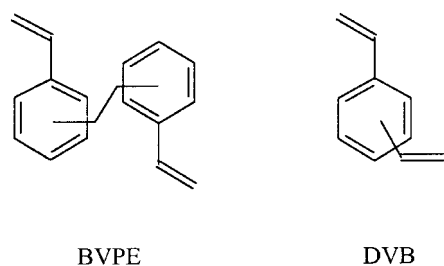
perature was controlled by immersing the cell in a constant temperature water bath. The diffusion coefficient and solubility of oxygen in the membrane were obtained by recording the diffusion-limited current of oxygen reduction reaction as a function of time after switching the gas flow from nitrogen to oxygen or hydrogen, and subsequently fitting the curve to the equation of limiting current [5].

3. Results and discussion

Four different types of PVDF-g-PSSA membranes in the H^+ form were investigated:
(i) PVDF-g-PSSA without crosslinker
(ii) PVDF-g-PSSA crosslinked with bis(vinyl phenyl) ethane, BVPE
(iii) PVDF-g-PSSA crosslinked with divinylbenzene, DVB
(iv) PVDF-g-PSSA crosslinked with BVPE and DVB
The crosslinker content of the grafting solution was 5 mol %. For membrane type 4 the content was 2.5 mol % BVPE and 2.5 mol % DVB. It would have been of interest to know the crosslinker content in the membranes in addition to the content in the solution, but unfortunately such a determination by IR or Raman spectroscopy was found to be very difficult and to fail to give even semiquantitative results [11]. Solubility and diffusion of oxygen was investigated for types 1 and 2 with crosslinker contents 2.5, 5 and 10 mol % for the latter. For all the membrane types the water uptake, proton conductivity and ion exchange capacity were determined.

When exposed to an aqueous phase the PVDF-g-PSSA membranes swell considerably. As seen in Figure 2, depending on the degree of grafting and the type of crosslinker used the membranes absorb water, which leads to variation in the membrane thickness and surface area whenever humidity in the surrounding gas phase changes. The greatest swelling is observed in the case of noncrosslinked membranes; crosslinking reduces the amount of water absorption. For membranes crosslinked with BVPE the water uptake is approximately twice the uptake for membranes crosslinked with DVB. The absorption for samples containing both crosslinkers was found to have values between the ones for samples containing only one of the two crosslinkers at the same degrees of grafting. All in all, at high degrees of grafting the water uptake for PVDF-g-PSSA membranes is considerably higher than for the Nafion® 117 membrane for which a value 0.28 gg^{-1} has been measured [5] for the absorption from saturated vapour phase.
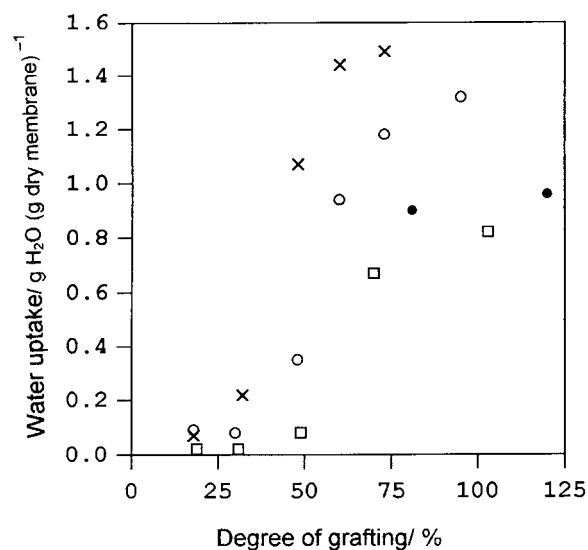

Fig. 2. Water uptake from saturated vapour phase for different PVDF-g-PSSA membranes as a function of degree of grafting; (×) no crosslinker, (○) crosslinked with BVPE, (□) crosslinked with DVB, (●) crosslinked with BVPE and DVB.

With radiation-grafted PVDF-g-PSSA membranes it is possible to achieve proton conductivities that even at room temperature are higher than 0.1 S cm^{-1} which is often considered to be a critical limit for a useful fuel cell electrolyte material although the practically more important area resistance depends on membrane thickness. In a way similar to the water uptake the proton conductivity is strongly enhanced by increasing the degree of grafting for the membrane material. Around 40% degree of grafting there is a substantial increase of many orders of magnitude in the proton conductivity (Figure 3a). This undoubtedly follows from the membranes becoming throughout grafted and sulfonated, which for noncrosslinked, BVPE crosslinked and DVB crosslinked membranes occurs at about 30% , 50% and 60% degree of grafting, respectively.

The highest conductivity was achieved when no crosslinker was used. The use of BVPE as a crosslinker resulted in a higher conductivity than in the case of DVB-crosslinking. Again, as a result of using a mixture of two crosslinkers in the grafting solution, the conductivity at high degrees of grafting was determined to be between the values for membranes for which only one type of crosslinker was applied. This result was expected; a similar pattern was reported by Büchi et al. [12] who successfully used DVB and triallyl cyanurate (TAC) as crosslinkers in their 'double crosslinking' experiments with FEP-based membranes. It remains to be seen in further studies if such a favourable compro-
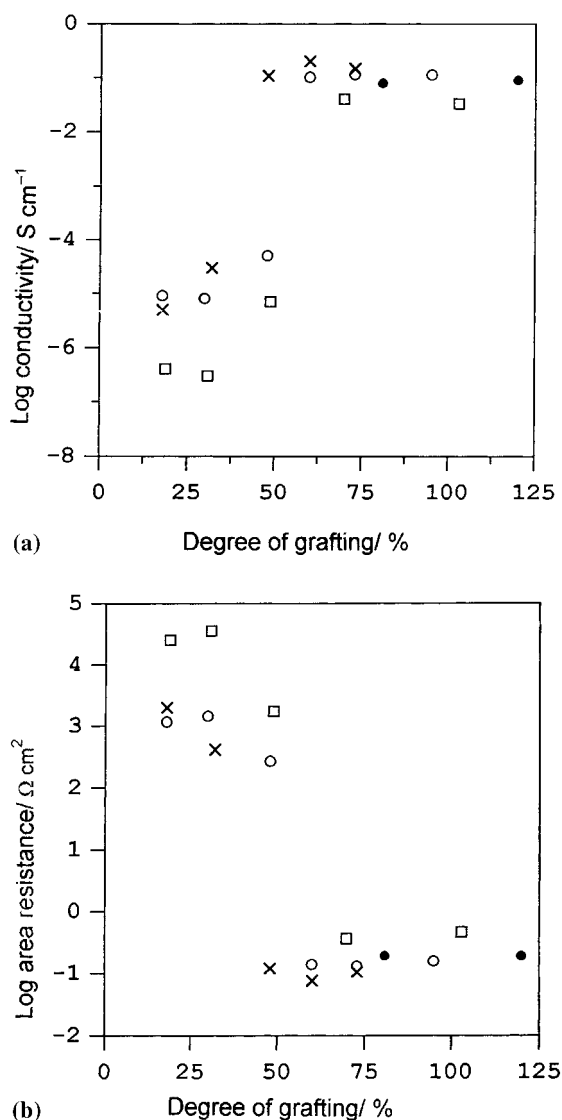
(a)

Degree of grafting/ %

(b)

Degree of grafting/ %

Fig. 3. (a) Proton conductivity and (b) area resistance of different PVDF-g-PSSA membranes at 20 °C as a function of degree of grafting; symbols as in Figure 2.

mise in membrane conductivity and stability can also be achieved with DVB and BVPE.

The thickness of the membranes in equilibrium with water vapour varied from 100 to 175 μm increasing with the degree of grafting. When the thickness of the membrane samples is taken into account and the conductivity transformed into area resistance, the data shown in Figure 3b are obtained. There is little change in the relative positions of the data points; the highest resistance is obtained for the membranes crosslinked with DVB while the lowest values belong to the noncrosslinked membranes. However, the area resistance values verify that it may not be advantageous to

produce membranes with degrees of grafting as high as possible when the application in fuel cells is anticipated. The resistance of the electrolyte increases with its thickness which in turn increases with degree of grafting. On the other hand, a thick electrolyte membrane may be a better gas separator than a thinner one. The water content of the membrane also evidently affects the gas permeability.

In Figure 4 the results on the measurements of the ion exchange capacity (IEC) of the PVDF-g-PSSA membranes are presented. Now the differences between the different types of membrane are smaller than in the case of water absorption and proton conductivity. At high degrees of grafting (above 50%) the IEC values exceed $2 \, \text{meq} \, \text{g}^{-1}$, corresponding to equivalent weights below 500. In this regime the ion exchange capacity of the DVB crosslinked membranes is at least as high as the IEC of the other membrane types. However, the proton conductivity and water uptake of membranes crosslinked with DVB are only about 50% of the values for membranes crosslinked with BVPE and membranes without any crosslinkers.

The reason for the lower proton conductivity of the membranes containing DVB as a crosslinker is apparently related to the different microstructures of the materials. When DVB is used as a crosslinker, a highly crosslinked surface layer is formed because of the faster reaction rate of DVB as compared to styrene [7]. For the membranes with high degrees of grafting the diffusion-controlled grafting reaction has also occurred in the inner parts of the membranes. In the dense surface
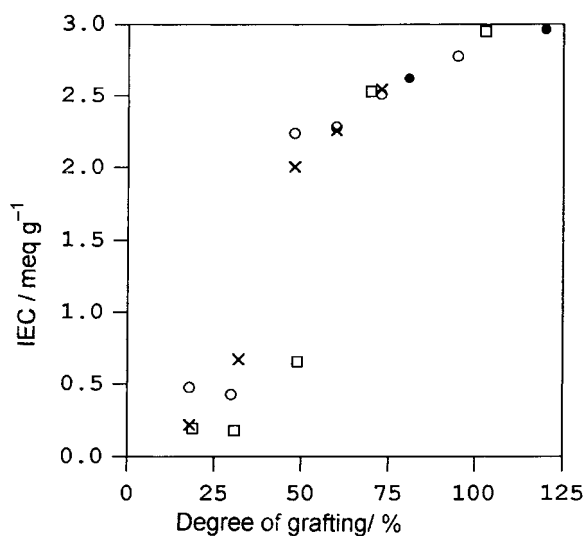

Fig. 4. Ion exchange capacity of different PVDF-g-PSSA membranes at 20 °C as a function of degree of grafting; symbols as in Figure 2.

layers, however, the proton mobility may be reduced, leading to a suppressed overall conductivity in the membrane. In contrast to this, crosslinking with BVPE results in a more homogeneously and randomly cross-linked membrane. These membranes swell more in water and obviously provide a more favourable environment for the proton conduction.

A common feature for both types of the crosslinked membranes is the reduced increase in water uptake, conductivity and ion exchange capacity below about 35% degree of grafting. There might even exist a minimum in the values, whereas for the non-crosslinked membranes there seems to be a monotonic increase in the corresponding properties up to high degrees of grafting. The same phenomenon in these membranes was observed earlier in the swelling due to sulfonation and boiling in water [7]. In the Raman studies [13] it was found that at low degrees of grafting especially the crosslinked membranes suffer from incomplete sulfonation, that is, a major part of the styrene groups remain unsulfonated. It was further suggested that, at low degrees of grafting, the solvent used in the sulfonation is incapable of swelling the grafted and crosslinked structure sufficiently for complete reaction of the chlorosulfonic acid [14]. It is evident that such a failure in the sulfonation is reflected as a decrease in ion exchange capacity, water uptake and proton conductivity of membranes with low degrees of grafting.

The solubility (c, mol cm^{-3}) and diffusion coefficient (D, cm^2 s^{-1}) of oxygen in the membranes were determined using the electrochemical monitoring technique [5, 9]. Because of the lower proton conductivity and brittleness of the DVB-crosslinked membranes only samples containing BVPE as a crosslinker or no crosslinker at all were chosen for the gas permeation studies.

From the data in Table 1 some conclusions may be drawn. The diffusion coefficient of oxygen in the membrane increases with the degree of grafting and membrane water content. At the same time the solubility tends to decrease. Especially at low degrees of grafting the crosslinking seems to reduce the oxygen diffusion coefficient somewhat. On the other hand, the solubility of oxygen in the membrane is connected rather to membrane water content than to the amount of the BVPE crosslinker used. This is to say, if slow diffusion and low solubility of oxygen are the desired membrane properties, membranes with high degree of grafting and heavy crosslinking, or no crosslinker at all, are preferred. Based on studies with different membranes Büchi et al. [15] have suggested that the optimal solubility and permeation rate of oxygen in the electrolyte depends on whether the fuel cell cathode is operated under kinetic-ally controlled or diffusion limited conditions. However, as far as the pure electrolyte membrane between the catalysed active layers of the electrodes is concerned, a low permeation rate is highly desirable.

The diffusion coefficient and solubility of oxygen in the membrane both affect the total permeability (Dc) in PVDF-g-PSSA membranes as shown in Table 1. When the thickness of the membrane (L) is taken into account and the permeability presented as a flux (Dc/L), the differences between crosslinked samples with different degrees of grafting are emphasized. The benefit of using a thick membrane can be easily visualized as the increasing degree of grafting means increasing thickness. The most significant conclusion, however, is that the use of BVPE as a crosslinker in the PVDF-g-PSSA membranes does not have any preventive effect on the oxygen permeation. At high degrees of grafting it is the membrane water content, not the extent of crosslinking, that seems to be the dominating factor in determining the permeation rate of oxygen.

The total oxygen permeability for PVDF-g-PSSA membranes is close to that obtained for Nafion® 117 even though the D and c for Nafion® are very different from those for the PVDF-g-PSSA membranes. This difference is probably due to the different structure and smaller water content of the Nafion® material. The result for Nafion® 117 in the H$^+$ form is in accordance with that reported by Parthasarathy et al. [16] who used choronoamperometry. The permeability value 9.1×10^{-12} mol cm^{-1} s^{-1} agrees well with the result from gas chromatography measurements by Broka and Ekdunge [17].

In the studies of the permeation of hydrogen through the membranes, PVDF-g-PSSA membranes with no crosslinker and with 10 mol% BVPE were used. The results in Table 2 show that in the PVDF-g-PSSA membranes, as well as in Nafion® 117, hydrogen permeates through the material in larger quantities per unit time than oxygen. This is solely due to the high diffusion coefficient of hydrogen since the solubility of hydrogen in the membranes is low compared to that of oxygen. This may be related to the difference in solubility of the gases in water: for hydrogen in water $c \approx 0.8 \times 10^{-6}$ mol cm^{-3} whereas for oxygen $c \approx 1.4 \times 10^{-6}$ mol cm^{-3} at 20 °C [18]. Furthermore, in the more extensive studies of hydrogen permeation through PVDF-g-PSSA membranes [19] it was stated that the increase in permeability was closely related to the increase in the water uptake of the membranes while crosslinking had little effect. The results obtained here do not contradict this conclusion.

The lower conductivity of the membranes crosslinked with DVB compared to the other membrane types may

Table 1. Water uptake from liquid phase and diffusion coefficient, solubility, permeability (Dc) and diffusive flux (Dc/L) of oxygen for different proton exchange membranes at 20 °C

Sample	Degree of grafting /%	BVPE crosslinker /%	Water uptake /gg^{-1}	10^6 D /cm^{2}s^{-1}	10^6 c /mol cm^{-3}	Permeability 10^{12} Dc /mol cm^{-1} s^{-1}	Flux 10^{10}Dc/L /mol cm^{-2} s^{-1}
PVDF-g-PSSA	36	–	0.29	0.5	8.2	4.1	3.6
	61	–	1.26	2.9	2.3	6.7	4.9
	75	–	1.44	2.7	2.9	7.8	5.0
	100	–	1.99	1.8	2.8	5.0	3.1
	60	2.5	1.20	1.5	7.6	11.4	9.7
	100	2.5	1.56	2.7	3.0	8.1	4.9
	72	5	1.14	1.2	8.0	9.6	7.2
	115	5	1.75	1.4	3.6	5.0	2.8
	70	10	1.92	2.1	3.0	6.3	4.4
	121	10	1.32	3.3	2.3	7.6	4.3
Nafion® 117	–	–	0.37	0.7	13.0	9.1	4.6

not be an sufficient reason to exclude this crosslinker from further studies. It has been shown recently that by carefully adjusting the parameters in the membrane preparation much of the brittleness caused by the DVB crosslinker can be avoided, especially at not too high degrees of grafting [7]. Therefore studies with all these types of membranes are continuing.

4. Conclusions

In ion exchange membranes the ion exchange capacity, water uptake and proton conductivity are interrelated. This was also found to be the case with radiation-grafted, sulfonated PVDF-based membranes. As a result of irradiation and subsequent grafting with styrene and sulfonation the originally hydrophobic and nonconducting PVDF is turned into a water absorbing, ion conducting material. The proton conductivity of the PVDF-g-PSSA membranes is of particular interest because of its relevance to the performance of the polymer electrolyte fuel cell where a PVDF-g-PSSA membrane might be used as proton conducting electrolyte.

At high degrees of grafting the PVDF-g-PSSA membranes exhibit high proton conductivity around 0.1 S cm^{-1} at 20 °C, high water uptake and ion exchange capacities above 2 meq g^{-1}. The conductivity is sufficient for fuel cell use. Another important issue in this respect is the gas separation capability of the membrane. Mainly to decrease the gas permeation in the PVDF-g-PSSA membranes these were crosslinked using two different crosslinkers, divinylbenzene (DVB) and bis(vinyl phenyl)ethane (BVPE). The use of DVB resulted in decreased conductivity and water uptake. The ion exchange capacity on the other hand was affected only at low degrees of grafting. Smaller changes in the properties were found when BVPE was employed as a crosslinker. No significant decrease in the solubility and diffusion coefficient of gases was observed. Thus the efforts to crosslink the membranes with BVPE appeared to be quite ineffective in improving the gas separation properties of the PVDF-g-PSSA membranes. It remains to be investigated whether this is due to low extent of crosslinking in the membrane or to the nature of the BVPE crosslinker itself.

The determination of physicochemical properties such as proton conductivity gives valuable information about the suitability of the membranes for fuel cell use. However, it is difficult to draw any straightforward conclusions about the fuel cell performance without testing the membranes in an actual cell. The fuel cell tests with PVDF-g-PSSA membranes with and without additional crosslinker are in progress.

Table 2. Diffusion coefficient, solubility, permeability and diffusive flux of hydrogen for different proton exchange membranes at 20 °C

Sample	Degree of grafting /%	BVPE crosslinker /%	10^6 D /cm^2 s^{-1}	10^6 c /mol cm^{-3}	Permeability 10^{12} Dc /mol cm^{-1} s^{-1}	Flux 10^{10} Dc/L /mol cm^{-2} s^{-1}
PVDF-g-PSSA	61	–	5.0	1.8	9.0	6.6
	75	–	4.2	2.4	10.2	6.4
	70	10	4.5	2.2	9.9	7.1
	121	10	4.6	2.4	11.0	6.4
Nafion® 117	–	–	1.8	6.4	11.5	5.8

Acknowledgements

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