

Gas permeation properties of radiation grafted and sulfonated poly-(vinylidene fluoride) membranes

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Abstract

The helium and hydrogen gas permeabilities through proton exchange membranes, poly(vinylidene)-graft-polystyrene sulfonic acid membranes (PVDF-*g*-PSSA), were studied using a mass spectrometric leak detector. The membranes were prepared by electron beam irradiation followed by grafting with styrene and subsequent sulfonation. In order to separately evaluate the effect of grafting and sulfonation the unsulfonated membranes (PVDF-*g*-PS) were also studied. The permeability was found to increase with increasing graft content of the unsulfonated membranes. The PS grafts are likely to phase separate from the PVDF matrix during grafting because of the incompatibility of the polymers. Hydrogen and helium permeabilities of PS are higher than of PVDF. Thus the increase in gas permeabilities is most likely due to gas permeation through phase separated polystyrene domains. The gas permeabilities of the dried PVDF-*g*-PSSA membranes were considerably lower than the values for the unsulfonated membranes. The gas permeability of the dried PVDF-*g*-PSSA membranes decreased around d.o.g. 35% which is the graft penetration limit. Similarly the ion exchange capacity of the membranes increased at this point. In the water saturated state the permeabilities increased with increasing water content of the membrane. The gas permeability of the water saturated PVDF-*g*-PSSA membranes reached a plateau value at the graft penetration level. The gas permeation in the water saturated state is mainly governed by the diffusion of the gas in water. The highest permeabilities for PVDF-*g*-PSSA membranes were of the same order of magnitude as for the commercial Nafion® 117 membrane. These permeabilities were measured for membranes with d.o.g. ~ 70%. Thus the PVDF-*g*-PSSA membranes are good candidates for the use as electrolytes in electrochemical cells. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte membranes; Gas permeability; Characterisation

1. Introduction

Membranes with high protonic conductivity are potentially useful as separators and electrolytes in electrochemical cells including fuel cells. Poly(perfluorosulfonic acid) membranes are the polymeric materials most commonly used in such applications. Such membranes, e.g. Nafion® and the Dow Developmental membranes, have suitable chemical and physical properties for use in demanding electrochemical applications [1–4]. However the price of these membranes is very high and other membrane materials are being sought.

One way to produce new less costly materials is by functionalisation of a preformed polymer film. Among many techniques, radiation initiated grafting is one of the most useful and has been extensively studied [5–13]. Usually a fully fluorinated polymer (for example poly(tetrafluoroethylene), PTFE, or poly(tetrafluoroethylene-*co*-hexafluoro-

propylene), FEP) is chosen as the matrix material because of the stability requirements. The most commonly used grafting agent is styrene together with divinylbenzene (DVB). In order to obtain proton conducting membranes grafting is followed by sulfonation. These materials have been tested in fuel cells and they show promising performance and stability [6].

The preparation and the characterisation of proton conducting membranes based on poly(vinylidene fluoride), PVDF have been reported [13–17]. The three step preparation procedure involves the irradiation of the PVDF matrix with electron beam, grafting to varying degrees with styrene, styrene with divinyl benzene (DVB) or styrene with bis-(vinyl phenyl) ethane (BVPE) and sulfonation. The membranes have been characterised by several methods, including mechanical testing [15], swelling tests [13], differential calorimetry [14], small and wide angle X-ray diffraction [14] (SAXS, WAXS, respectively) and ac impedance spectroscopy [13,17].

The introduction of the styrene grafts and of the

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hydrophilic sulfonic acid groups into the strongly hydrophobic PVDF matrix produces a very complex structure. Also the structure and the physical properties of the matrix are changed drastically in the preparation steps. The gas permeability is a measure of the combined effect of gas solubility and diffusion in a particular material. Permeability data can thus be used to compare membranes at different stages of preparation and with different characteristics. In this study we have tried to relate gas permeabilities to changes in membrane graft content, ion exchange capacity and water content. Another aim has been to test the suitability of the membranes for fuel cell applications with respect to gas permeation. In a fuel cell the fuel gas crossover from either electrode side to the other results in “chemical short circuiting”. To minimise this, the membrane should have sufficient barrier properties for the gases used. As hydrogen is used as a fuel for low temperature solid polymer electrolyte fuel cells and has been studied extensively for Nafion [2], hydrogen permeability coefficients of water saturated poly(vinylidene fluoride)-*graft*-polystyrene sulfonic acid, PVDF-*g*-PSSA membranes were compared with Nafion 117 membrane measured in a similar manner. Helium is frequently used as a permeability test gas in polymers [18]. In addition the helium permeability coefficients were measured.

2. Experimental

2.1. Materials

Fifteen different membranes were prepared by the three step method described in a previous communication [13,15]. In this method commercial PVDF membrane (Goodfellow, 80 μm), was irradiated with electron beam, producing radical sites which initiate grafting onto the PVDF chain. The grafting of the membranes was carried out immediately after irradiation in:

1. 50/50 V/V styrene/toluene mixture (“noncrosslinked”);
2. 5/45/50 V/V bis(vinyl phenyl)ethane/styrene/toluene mixture (“BVPE crosslinked”);
3. 5/45/50 V/V divinylbenzene/styrene/toluene mixture (“DVB crosslinked”).

for varying periods of time. BVPE was synthesised as described elsewhere [15]. DVB (Fluka, 65% isomeric mixture in ethylvinylbenzene) was distilled prior to use. Styrene (Fluka) and toluene were reagent grade and used as received. BVPE and DVB were used to obtain crosslinking of the grafted material. The membranes were then extracted in a Soxhlet apparatus with chloroform over night and dried to constant mass. The degree of grafting (d.o.g.) was

$$\text{d.o.g.} = \frac{m_1 - m_0}{m_0} * 100\% \quad (1)$$

where m_0 is the original mass of the sample and m_1 the mass of the grafted sample. The resulting material is at this stage called poly(vinylidene fluoride)-*graft*-polystyrene (PVDF-*g*-PS).

The membranes were sulfonated by 0.5 M chlorosulfonic acid (Merck, reagent grade) in 1,2-dichloroethane (Merck, reagent grade) for 24 h [19]. The sulfonation takes place mostly to the *para*-position of the styrene rings [13]. Following the sulfonation the PVDF-*g*-PSSA membranes were washed first with dichloroethane and then with distilled water to neutrality. In the measurements the membranes were in the fully protonated form.

Nafion 117 (Du Pont de Nemours) membrane was boiled in 10% H_2O_2 solution for 30 min, boiled in distilled water for 30 min, boiled in 1 M H_2SO_4 for 30 min and finally, boiled in distilled water for 30 min [20]. The samples were air dried and stored in sealed bottles at ambient temperature.

2.2. Water uptake of the membranes (WU)

The water uptake [WU/g/g] from liquid water was determined as follows. Membranes were boiled for 1 h in distilled water. The surface of the membrane was blotted dry with filter paper and the membrane was weighed. The membranes were dried 12 h in vacuo at 70°C, weighed immediately and the WU was determined

$$\text{WU} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \quad (2)$$

where w_{dry} is the mass of the dried sample and w_{wet} the mass of the wet sample. The residual water content of the membranes bound to sulfonic acid groups in the membrane after drying at 70°C in vacuo was evaluated with thermogravimetric analysis (TA) with a Mettler-Toledo 8000 TA thermobalance. The predried sample was kept in the sample chamber at 70°C for 10 min, and subsequently heated at a rate of 10°C/min to 250°C. The maximum weight loss attributable to the evaporation of water from 70°C to 150°C was found to be 7%. Such an amount of water (7%) corresponds to approximately one molecule of water per sulfonate. Similar drying procedures and results for sulfonated membranes have been described [21].

2.3. Ion exchange capacity (Q)

The ion exchange capacity Q [meq/g] of the membranes was determined titrimetrically. The mass of the dried membrane sample was recorded and the sample was soaked in excess of aqueous sodium hydroxide and equilibrated for ten days. The solution was then titrated with hydrochloric acid using cresol red as an indicator. Q was calculated from

$$Q = \frac{n_1 - n_0}{m_{\text{dry}}} \quad (3)$$

where n_1 is moles of hydroxide ions originally present, n_0 moles hydrochloric acid consumed and m_{dry} the mass of the

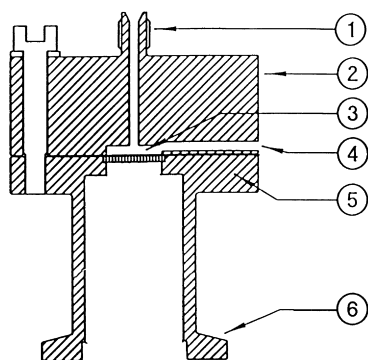


Fig. 1. Schematic drawing of the gas permeation cell. (1): Gas inlet, (2): Stainless steel housing, (3): Membrane on porous stainless steel support, (4): Gas outlet, (5): Lower housing, (6): Standard vacuum connection.

dried sample. The accuracy of the measurement is affected by residual water in the dried samples as described for the WU measurement.

2.4. Permeability measurements

The gas transmission through the samples was recorded with a Leybold-Heraeus UL-100 gas leak detector. The detector is based on mass spectrometric detection and can be used to detect hydrogen, deuterium and helium, respectively. Hydrogen (99.8%) and helium (99.996%) gases were used in the measurements. The values given by detector were corrected for both gases by a volumetric method. A vessel of known volume was evacuated, hydrogen or helium was let in by an adjustable valve, and the pressure rise in the vessel with respect to time was compared with the detector response for the same leak. Other leak rates were calculated assuming a linear response from the detector. The stability of the leak detector was checked with dried Nafion 117 membrane during the measurements and found stable. The lowest gas flows which could be used for the calibration were higher than the gas flows for the actual membranes. This means that the values of the permeability coefficients were determined from extrapolated calibration data and they should therefore be interpreted with care, but that they are comparable with each other. A schematic drawing of the measuring cell is shown in Fig. 1. The cell is made of stainless steel with a porous stainless steel support in the gas inlet. The area of the circular support is 1 cm^2 . During

measurements a vacuum in the order of 10^{-2} bar was applied on the mass spectrometer side of the membrane, while on the other side of the membrane was purged with gas of atmospheric pressure. The gas inlet pipe was a few mm from the membrane surface. The gas transmission through the membranes was measured under dry and wet conditions. Under dry conditions membranes of PVDF, PVDF-*g*-PS and PVDF-*g*-PSSA were measured by cutting a circular piece of membrane and placing it in the measuring cell. The cell was sealed, helium gas purged into the cell and the helium leak rate was recorded after reaching a stable value. The detector was turned to hydrogen detection and the hydrogen background was recorded while helium was purged. After this the gas was changed to hydrogen and the hydrogen leak rate was recorded. Finally the helium background was measured with hydrogen gas purging. Each measurement was continued until stability. After each set of measurements the thickness of the membrane sample was determined with a micrometer.

Typically the samples were measured 2–3 times. The reproducibility of the measurements was found to be within 15%.

For the measurements under wet conditions the PVDF-*g*-PSSA membranes were swollen in liquid water. In order to avoid drying of the membranes during measurements, a silicon rubber membrane (SR, D606, 25 μm , Radiometer Copenhagen) was placed between the porous support and the membrane in the measuring cell. The cell was filled with water. Excess water was blown from the cell by applying the gas flow to the cell. Each value of the leak rate was then measured in a similar manner as with the dried membranes. After measurement the thickness of the wet membrane was determined. A commercial Nafion 117 membrane was used as a reference material in the permeability studies.

The permeability coefficient P [$\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s}^{-1}\text{Pa}^{-1}$] was calculated for both hydrogen (P_{H_2}) and helium (P_{He}) from

$$P = \frac{(Q_1 - Q_0) \cdot l}{A \cdot \Delta P} \quad (4)$$

where Q_1 is the gas leak rate, Q_0 is the gas background, l is the thickness of the sample, A is the area of permeation and ΔP is the pressure difference (Pa) between the different sides of the membrane. The leak rate of the silicon rubber

Table 1
Hydrogen and helium permeability coefficients of different polymers

	H_2 $P/10^{13} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$	He $P/10^{13} \text{ cm}^3 \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$
PVDF	0.2	1.0
PS [25]	17.0	14.0
Dried Nafion 117	3.2	18.4
Dried Nafion 117 [20]	3.5	
Water saturated Nafion 117	18.3	24.9
Water saturated Nafion 117 [26]	45	

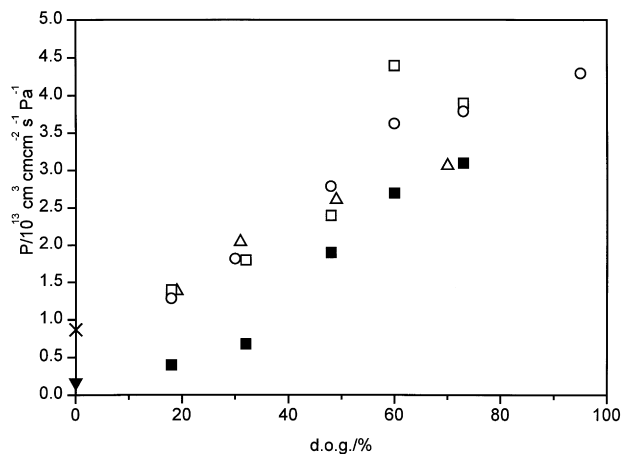


Fig. 2. Hydrogen, P_{H_2} , permeability coefficients of (▼) original PVDF film and (■) noncrosslinked PVDF-*g*-PS membranes. Helium, P_{He} , permeability coefficient of (X) original PVDF, (□) noncrosslinked, (O) 5% BVPE cross-linked and (△) 5% DVB crosslinked PVDF-*g*-PS membranes as a function of d.o.g.

membrane was more than 20 times the leak rate of the membranes for both helium and hydrogen and was thus not considered in the calculation of the permeability coefficients.

3. Results and discussion

The results of the measurements and literature values of the hydrogen and helium permeabilities through Nafion 117

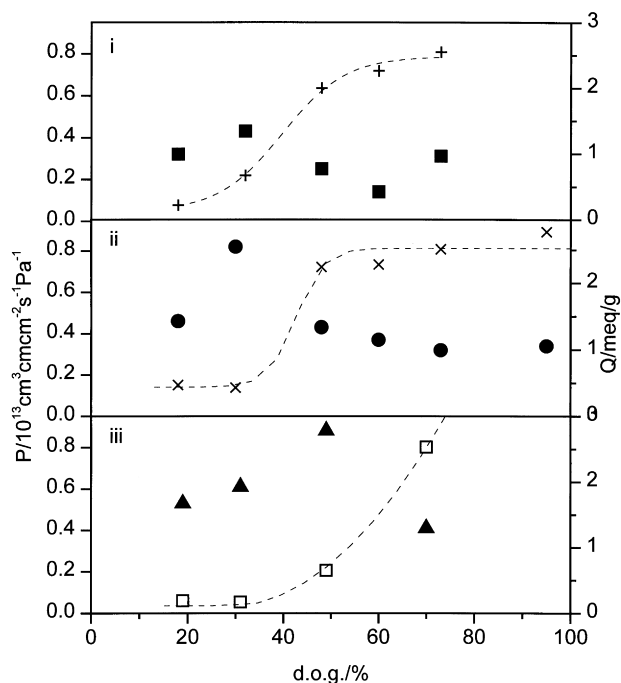


Fig. 3. Hydrogen, P_{H_2} , permeability coefficients of dried PVDF-*g*-PSSA membranes and Q values as a function of d.o.g. (i) P_{H_2} (■) and Q (+) of noncrosslinked samples. (ii) P_{H_2} (●) and Q (×) of 5% BVPE crosslinked samples. (iii) P_{H_2} (▼) and Q (□) of 5% DVB crosslinked samples.

and PVDF are collected in Table 1. The P_{H_2} and P_{He} values of a series of PVDF-*g*-PS membranes as a function of d.o.g. are shown in Fig. 2. Both P_{H_2} and P_{He} of the PVDF-*g*-PS membranes show similar increase with respect to d.o.g. Styrene grafting clearly increases both P_{H_2} and P_{He} coefficients compared with the original PVDF membrane.

The reproducibility of the measurements was found to be satisfactory. However, since the calibration was done with Nafion (see Table 1.) the permeability of which differs from our samples by one order of magnitude, the values measured for our sample should be comparable to each other, but not necessarily accurate on an absolute scale.

Myers et al. [22] and Huang and Kantz [23] have studied the nitrogen and carbon dioxide permeability of styrene grafted polyethylene films. They found decreasing values of the gas permeability with a minimum for gas permeability at low grafting levels, d.o.g. $\sim 20\%$ – 30% , compared to the gas permeability of pure polyethylene. The conclusion was drawn that this is due to filling of the free volume in polyethylene. Increasing permeability for gases was found at higher d.o.g. ($>$ d.o.g. $\sim 30\%$). They conclude that the increased permeability was caused by crystal disruption owing to growing polystyrene chains.

In the case of the PVDF-*g*-PS membranes a decrease in crystallinity [14,15] takes place at d.o.g. 30% – 50% . In this d.o.g. range no dramatic change in P_{H_2} and P_{He} can be seen.

We have found [14] that the grafting of styrene into PVDF results in a complex phase separated structure with polystyrene microdomains in the amorphous part of the PVDF matrix. The crystallinity decreases only slightly in the grafting reaction. It has been shown [25] that the P_{H_2} and P_{He} of polystyrene is larger than P_{H_2} and P_{He} measured for PVDF membranes. Thus it is likely that the increase in the content of the more permeable polystyrene is the main source of the increased permeability. The simultaneous slight decrease in the crystallinity of the matrix PVDF polymer further increase the permeability for hydrogen and helium gases.

The conclusion is drawn that the increase in gas permeability is not an effect of filling of the free volume in the PVDF matrix, in contrast to the results reported for the styrene grafted polyethylene membranes [22,23]. Our results may not, however, be completely comparable. Nitrogen and carbon dioxide were used in the studies of styrene grafted polyethylene. The molecular dimensions of these gases are very different from the molecular dimensions of hydrogen and helium used in this study.

The PVDF-*g*-PS crosslinked with DVB or BVPE had nearly the same permeabilities as the noncrosslinked ones with respect to d.o.g., see Fig. 2. In these membranes it was shown that the crystallinities measured by DSC and WAXS are very similar to each other and to noncrosslinked PVDF-*g*-PSSA membranes [15]. However some properties of the membranes, for example the ion exchange capacity and water uptake, of the crosslinked membranes are different as we will discuss later in this paper.

Table 2
Ion exchange capacity (Q) and water uptake (WU) of PVDF-*g*-PSSA membranes

d.o.g./%	Q /meq/g	WU/g/g
Noncrosslinked		
18	0.22	0.06
32	0.67	0.79
48	2.00	1.00
60	2.26	1.68
73	2.55	1.57
5% BVPE		
18	0.47	0.06
30	0.43	0.15
48	2.24	1.03
60	2.28	1.16
73	2.51	1.29
95	2.77	1.48
5% DVB		
19	0.19	0.06
31	0.17	0.05
49	0.65	0.06
70	2.53	0.73

The P_{H_2} values of PVDF-*g*-PS and dried PVDF-*g*-PSSA membranes at low d.o.g. are same within the error limits of the measurement. However, at high d.o.g. (over 35%) the P_{H_2} values of the dried PVDF-*g*-PSSA are significantly lower than the values for unsulfonated PVDF-*g*-PS

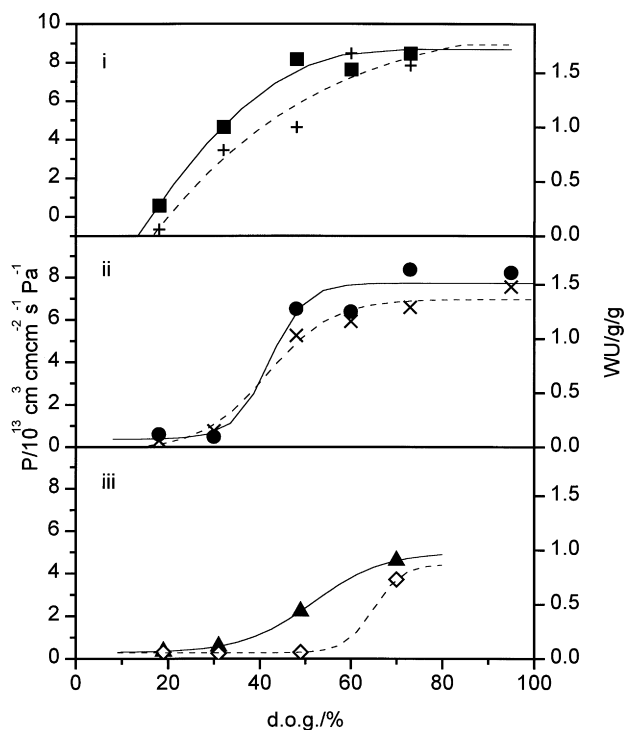


Fig. 4. Hydrogen, P_{H_2} , permeability coefficients of wet PVDF-*g*-PSSA membranes and WU values plotted as a function of d.o.g. (i) P_{H_2} (■) and WU (+) of noncrosslinked samples. (ii) P_{H_2} (●) and WU (×) of 5% BVPE crosslinked samples. (iii) P_{H_2} (▼) and WU (◇) of 5% DVB crosslinked samples.

membranes (see Figs. 2 and 3). In contrast to the increasing P_{H_2} values of the PVDF-*g*-PS with d.o.g., the P_{H_2} values of the PVDF-*g*-PSSA are increasing at low d.o.g., but begun to decrease around d.o.g. 35%, see Fig. 3. At this d.o.g. the ion exchange capacity, Q , of the PVDF-*g*-PSSA membranes also increases as shown in Table 2 and in Fig. 3. Very recently we have been able to show that the efficiency of sulfonation in the membranes is low in the membranes below the graft penetration limit [24], and therefore the conclusion is drawn that the presence of the sulfonic acid groups dramatically affects the solubility and diffusion of hydrogen in the membranes.

It has been shown that increasing sulfonic acid content decreases the permeation of hydrogen and oxygen in some commercial proton conducting membranes [20,25,26]. Our results for the dried PVDF-*g*-PSSA membranes are in good agreement with these conclusions, as for the samples with higher Q the hydrogen permeability decreases.

The crosslinked membranes have significantly lower Q values at d.o.g. less than 50%. The P_{H_2} values are clearly higher than for the noncrosslinked membranes. The difference between the two crosslinking agents, BVPE and DVB, is very small. Hence we conclude that the sulfonic acid groups in the dried membranes hinder the gas permeation, and possibly this is because of the decrease of solubility of gas into the membrane [20].

No dramatic change in the crystallinity of the PVDF is observed because of sulfonation [14,15]. Therefore we conclude that the changes in crystallinity have only minor effect on the change in P_{H_2} and P_{He} of the membranes. The P_{He} in the dried PVDF-*g*-PSSA membranes shows again similar structural dependence as the hydrogen permeability.

The P_{H_2} of the water saturated PVDF-*g*-PSSA membranes in relation to the WU values as a function of d.o.g. are presented in Fig. 4. The P_{H_2} values are now almost one magnitude higher than for the dry PVDF-*g*-PSSA membranes and are increasing with increasing d.o.g. The increase in permeability values follows very closely the increase in WU. A large increase in permeability takes place at the graft penetration limit at d.o.g. around 35% and thereafter reaches a plateau value.

Increasing gas permeabilities with increasing hydration have been reported for other polyelectrolytes of different Q and correspondingly different WU, namely for Nafion types 117 and 125 [20,26]. In Nafion membranes the increase in the hydrogen permeability coefficients is connected to the increasing water cluster size caused by the increasing hydration. The route of permeation is also changed from permeation through the matrix polymer in the dry state to permeation through water clusters in the hydrated state. In hydrated Nafion membranes the gas permeability is increased by an increase in the diffusivity of the gas, while the solubility of the gas is decreased. Although the water cluster model of Nafion membranes does not apply exactly to PVDF-*g*-PSSA membranes as such, it is likely that the increased permeability of gases in the PVDF-*g*-PSSA

membranes is also as a result of increased gas diffusivity in water clusters.

The swelling characteristics of DVB and BVPE cross-linked PVDF-*g*-PSSA membranes are different from the noncrosslinked membranes, as shown in Table 2 and Fig. 4. However, the BVPE and DVB crosslinked PVDF-*g*-PSSA membranes show similar changes in P_{H_2} and P_{He} as noncrosslinked membranes, as the permeability seems to be mostly dependent on the WU of the membrane.

The measured P_{H_2} for water saturated Nafion 117 membrane and the literature values for Nafion 117 [20,24] are shown in Table 1. The P_{H_2} of the water saturated PVDF-*g*-PSSA membranes is lower than that of the water saturated Nafion membrane. However, the gas permeation through a membrane naturally depends also on the thickness of the membrane. As the P_{H_2} values are normalised against thickness, it is important to know the actual gas transmission rate through membrane, q , which determines the gas permeation quantitatively for a membrane of certain thickness. The thickness of the water saturated PVDF-*g*-PSSA membranes (100–175 μm , increasing with d.o.g.) is comparable with the water saturated Nafion 117 ($\sim 220 \mu\text{m}$) membrane. Thus the q is nearly the same for the water saturated PVDF-*g*-PSSA membranes of highest d.o.g. and the Nafion 117 membrane. Although the conditions used in the gas permeation studies (room temperature, liquid water) do not correspond to conditions used in a working fuel cell ($T > 50^\circ\text{C}$, water in vapour phase), the hydrogen gas permeation through the membrane should not be problematic for testing of the PVDF-*g*-PSSA membranes in a fuel cell. The gas permeation tests together with the ion conductivity measurements [17] are promising and the investigation is continued with tests of thermal stability and tests in a model fuel cell.

4. Conclusions

Hydrogen and helium permeabilities of PVDF-*g*-PS and PVDF-*g*-PSSA membranes were measured and related to structural features of the membranes. It was observed that grafting of PVDF with styrene with or without crosslinker increased the permeability of the hydrogen and helium gases through the PVDF-*g*-PS membranes. This increase depends mainly on increased graft content and on the graft penetration of the matrix. To a lesser degree it depends on the decreased crystallinity of the matrix PVDF. The sulfonation decreased the permeability of dried PVDF-*g*-PSSA membranes compared to the PVDF-*g*-PS membranes. The permeability of the dried membranes decreased markedly at a d.o.g. which corresponds to the penetration limit of the graft in matrix polymer. In the crosslinked dried membranes the permeabilities were slightly higher than in the noncrosslinked membranes. The permeabilities of water saturated PVDF-*g*-PSSA membranes was found to increase from values similar to the dried membranes at d.o.g. $< 35\%$ to

the tenfold at d.o.g. $> 35\%$. The increase shows that the gas permeation is related to the diffusion of the gases in water, since the graft penetration barrier is around d.o.g. 35%. The commercial Nafion 117 membrane in the water saturated state had a similar gas transmission rate as the water saturated PVDF-*g*-PSSA membranes with the highest d.o.g.

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