Effects of irradiation on sulfonation of poly(vinyl fluoride)

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Preparation and analyses of directly sulfonated poly(vinyl fluoride), PVF, membranes have been performed. Electron beam or proton irradiation was used for the production of reactive sites. Ion-exchange capacity, sulfonation efficiency and ion conductivity were analysed. Increases in the absorbed dose and in the linear energy transfer were found to have a promoting effect on the sulfonation rate and sulfonic acid content. In addition, compared with commercial ion-exchange materials, quite high ion-exchange capacities were achieved. The highest measured ionic conductivity of the materials was 20 mS cm^{-1}, which was achieved with proton-irradiated samples after long sulfonation times. On the basis of the results the proton irradiation is believed to cause the formation of channels with higher sulfonic acid content than those found in other domains of the matrix. The presence of these channels increases the ionic conductivity.

Polymer electrolyte membrane fuel cells are of interest as potential sources of energy. The fuel cell converts free energy of reaction directly to electric current with a conversion efficiency of 60–80%. Among fuels at least hydrogen, methane, natural gas and methanol have been considered. Thus, energy production is more effective and has lower emissions than with conventional power sources.[1,2]

In small-scale energy production, *e.g.* power sources for vehicles, low-temperature fuel cells, such as the polymer electrolyte membrane fuel cell, are considered to be one of the most promising alternatives. One of the essential parts of the low-temperature fuel cell is the proton conducting polymer electrolyte membrane. High chemical stability and ion conductivity, as well as good barrier properties against the permeation of fuel and oxygen are required of the membrane. Commercial membranes of perfluorinated polymer electrolytes filling these requirements are available, *e.g.* Nafion® (Du Pont), Asahi and Dow developmental membranes, but the prices of these are high.[3] A new type of reinforced composite membrane, Gore-Select™ (W. L. Gore & Assoc.), which is available as very thin membranes, has recently been tested.[4]

The relation between the structure and the properties in ionic conducting polymer electrolytes is not very well known. The interaction between hydrophobic and hydrophilic regions, and the aggregation of ions and water in various polyelectrolytes have not been studied systematically in many cases. The correlation between ionic conductivity and ion-exchange capacity is not very clear. Nafion® is among the few proton conducting membranes which has been studied in detail. However, Nafion® has a very specific structure, therefore investigations on different materials for better knowledge of structure–properties relations are needed.

Generally, proton conducting polymers have been prepared from special monomers,[1] or by inclusion of acidic components in polymer matrices.[4–10] Both aliphatic and aromatic polymers have been investigated as matrix materials for the preparation of sulfonated polyelectrolytes for use either in electrochemical cells or as ion exchange membranes.

The preparation of aliphatic polymer electrolyte membranes has been carried out by polymerisation of functionalised monomers followed by film processing,[1] or by irradiation-induced polymer grafting, preferably of fluorine containing polymers, followed by sulfonation. Such membranes have been widely used for many applications.[11–19] In order to obtain proton conducting membranes, styrene is usually grafted onto a fluoropolymer, and the graft copolymer is subsequently functionalised by sulfonation.[11]

A third alternative method is the direct sulfonation of a polymer, whereby the functional group is linked directly to the matrix polymer. In aromatic matrices sulfonation can easily be done.[20] In contrast, the sulfonation of aliphatic polymers requires special techniques or several steps of modification to achieve the functionalised structure. In addition, the material must be in the form of a thin film. The direct sulfonation of aliphatic polymers for fuel cell applications has not been reported, but other applications are well known. Richards has studied the sulfonation of poly(vinylidene fluoride) films for the preparation of ion exchange membranes.[21] Chlorosulfonic acid or oleum was used as sulfonating agent. Ihata investigated the sulfonation of polyethylene films with sulfur trioxide[22] while Dimov and Islam used chlorosulfonic acid for the sulfonation.[23] In both cases the aim was hydrophilisation of the polymer film surface. Sulfonation has also been used to improve the conductivity of polyethylene.[24] The improvement in ion conductivity was almost ten orders of magnitude, but the ion conductivity was still too low (100 nS cm^{-1}) for most applications.

Direct sulfonation is considered an alternative method to prepare proton conducting membranes. The possibility to increase reactivity by irradiation of the polymer films is taken into account. Direct sulfonation after irradiation is simpler than the method of irradiation, grafting and sulfonation. The synthesis contains only three stages: irradiation, sulfonation and dissolution of sulfonating agent and solvents. Thus, the main cost of the direct sulfonation can be expected to be due to the irradiation. In comparison, the synthesis of grafted membrane includes, in addition, the purification of monomer, grafting, and dissolution of monomer and homopolymer after grafting.[8,9]

Here we report the preparation of ionic conducting membranes by direct sulfonation of poly(vinyl fluoride), PVF. Irradiation was used to increase the reactivity of the matrix. Electron beam (EB) or high-energy proton irradiation was used, and the effects of the masses of the projectiles (effect of linear energy transfer, LET) on the ion exchange capacities

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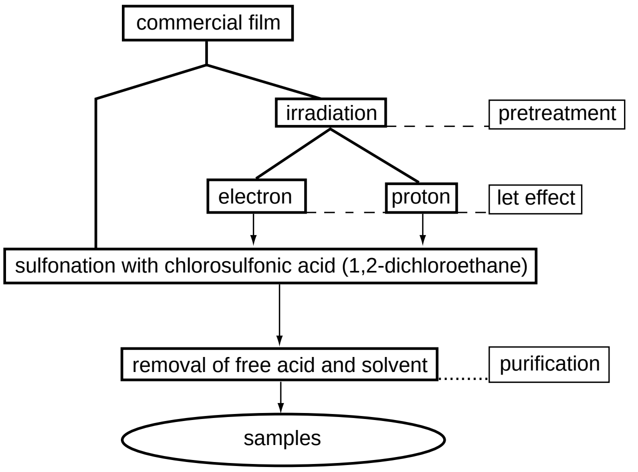

Fig. 1 Schematic diagram of sample preparation

and the ion conductivities of the membranes are compared. In all these measurements we have used Nafion® 117 as the reference.

Experimental

A general presentation of membrane preparation is presented in Fig. 1. Commercial PVF film (Tedlar, Du Pont) was generously supplied by Fluoroplast Oy and used as received. The film thickness was 31 µm and density 1.42 g cm^{-3}.

Irradiation with an electron beam

EB irradiation was performed at the Department of Polymer Technology of the Åbo Akademi University, with a CB-150 Electrocurtain® electron accelerator (Energy Sciences) with an acceleration voltage of 175 kV under a nitrogen atmosphere (<200 ppm O_2). All samples were irradiated several times to reach the total dose by cycling under a nitrogen atmosphere. Absorbed doses varied between 100 and 1000 kGy. To achieve total doses of 100 and 200 kGy, the samples were irradiated twice or four times, respectively, with 50 kGy single doses. Correspondingly, single doses of 100 kGy were used to achieve a total dose of 400 kGy, three single doses of 200 kGy and one of 100 kGy for a total of 700 kGy, and single doses of 200 kGy were used to achieve a total dose of 1000 kGy, respectively. The total overall irradiation time for all the samples was 5 min. Since the maximum penetration depth of the electrons is greater than the film thickness[25] all samples were irradiated in stacks of several films to avoid high energy losses with respect to absorbed doses. After irradiation the samples were immediately sulfonated.

Proton irradiation

The irradiation of sample films was performed at the Accelerator Laboratory of the University of Helsinki. The 2.5 MeV proton beam was supplied by the 2.5 MV van de Graaf accelerator.

The lateral uniformity of the proton beam at the sample film was accomplished by letting the forward scattered beam from 2.14 µm thick Havar foil hit the PVF film. The Havar foil was positioned in the beam line tube 1050 mm before the PVF films as shown in Fig. 2. The size of the collimating aperture defining the irradiated area at the sample was 1.5 or 9 cm^2. During irradiation the PVF films were under high vacuum (<10 µPa).

The sample film holder was grounded *via* a current integrator to enable direct beam current and collected charge measurement. The current measuring system and the integrator were calibrated by comparing the simultaneous measurements of the ion current and the yield of the backscattered ion beam from the PVF film and the reference Al target. A conventional Rutherford backscattering apparatus[26] with a 50 mm^2 silicon surface barrier detector at a distance of 60.0 mm from the PVF film was used. The solid acceptance angle of the detector aperture was 7.85 mSr.

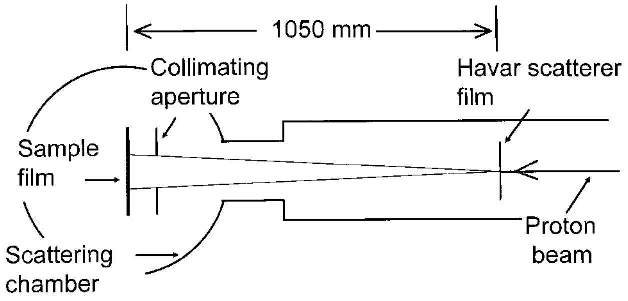

Fig. 2 A schematic diagram of the experimental apparatus for proton irradiation

The slowing down of the incident protons in the Havar scatterer foil and the PVF film was calculated by the SRIM-96 Monte Carlo code.[27] The energy lost in the Havar foil was 0.135 MeV with an energy spread of 0.015 MeV (standard deviation), resulting in an irradiation beam energy of 2.37 ± 0.02 MeV. The absorbed energy in the PVF film was calculated to be 0.685 MeV.

Each of the sample films was irradiated to the total dose in one single irradiation. The ion current was between 20 and 400 nA and irradiation time 30–160 s both depending on the total absorbed energy and area with different samples. The absorbed dose was between 100 and 1000 kGy. The average lateral distance of ion tracks was, for example, 50 Å with 100 kGy and 16 Å with 1000 kGy.

Sulfonation

All the irradiated samples were immediately transferred to the sulfonation mixture. Chlorosulfonic acid (Merck, reagent grade) was used as a sulfonating agent with 1,2-dichloroethane (Merck, reagent grade) as solvent. The acid content was 2.5% by volume. The sulfonation was performed separately both in untreated solutions of chlorosulfonic acid, and in solutions which had been purged with nitrogen prior to the sulfonation. The volume of sulfonation solution was kept constant in relation to the mass of the film to be sulfonated. The total amount of chlorosulfonic acid in each sulfonation container was high enough to keep the decrease of the free acid during the sulfonation to $<10\%$. The sulfonation time was varied between 1 and 70 h with EB irradiated samples and 1–28 h with proton irradiated samples, respectively. After the sulfonation the samples were washed with deionized water.

Mass increment

Mass increment analysis was done as the first analysis for the non-irradiated and EB-irradiated samples. Washed samples were dried in an oven at 70 °C to constant mass. This was compared to the initial mass of the film:

$$m(\%) = \frac{(m_{\text{sulfonated}} - m_{\text{original}}) \times 100\%}{m_{\text{original}}}$$

IR analysis

IR analysis of the materials after different stages of preparation was performed with a Nicolet 205 FTIR spectrometer in transmission mode at a resolution of ± 2 cm^{-1}. Sulfonated samples were dried as described, ground with potassium bromide and spectra measured from pellets in the usual way.

Ion exchange capacity

The ion exchange capacity (Q) was analysed 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. In addition, several parallel analyses were done with all samples. On basis of this the accuracy of the analysis was estimated to be 0.3 mequiv. g^{-1} when the residual water after drying in an oven at 70 °C is taken into account. In addition seven samples were boiled for 1 h in water prior to the analysis. Boiling did not, however, have any effect on mass or ion exchange capacity.

All membrane weighing steps were carried out by rapidly transferring the membrane to a weighing bottle and weighing by difference. Establishment of the water content in the membranes after drying at 70 °C (residual water) was done by thermogravimetry (TG). TG thermograms were measured with a Mettler Toledo TA800 instrument. 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^{-1} to 250 °C. We found a maximum mass loss attributable to the evaporation of water of *ca.* 4% at around 105 °C, and total loss (7%) at 150 °C in the sulfonated membranes. This mass loss was measured for a membrane with $Q = 5.1$ mequiv. g^{-1}, membranes with lower values of Q had lower amounts of residual water. 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 in ref. 28 and references cited therein.

We believe that our low-temperature drying method is preferable since exposure of the polymers in acid form to elevated temperatures can lead to degradation of the sample. The total water uptake was estimated gravimetrically from samples which were kept in water vapour in a closed jar for 4–7 days. Values of the total water uptake are included in Table 1.

Ionic 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 1 to 100 kHz. The conductivity cell was constructed with two 6.0 mm diameter steel electrodes, between which the sample was placed and pressed slightly. The cell was connected to a Solartron 1270 frequency response analyser and a microcomputer. The membrane resistance was obtained by extrapolating the data to the real axis of the impedance plot. The ion 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. The humidity in the cell was maintained at saturation level by continuously purging the cell with humidified nitrogen. The temperature of the cell was controlled by circulating water from a thermostat, and maintained at 20 °C. This procedure is described in detail elsewhere.[29]

Results and Discussion

PVF was chosen as matrix material for the sulfonation because it is commercially available, and it was shown in preliminary experiments to react with sulfonating agents after irradiation. Such membranes can be useful as ion exchangers and separators, and we will test them in a fuel cell. PVF is known to be chemically stable in demanding applications. Therefore good stability could be expected for the sulfonated structure with the sulfonic acid groups linked directly to the polymer backbone.[30]

PVF is very hydrophobic, and therefore difficult to substitute directly with hydrophilic groups such as the sulfonic acid group. Thus the introduction of reactive sites to promote the rate of substitution of sulfonic acid groups into PVF has been attempted by EB and proton irradiation. The direct sulfonation of non-irradiated PVF under identical conditions has been used as the reference in the present investigation.

Absorption of energy from ionising particles proceeds mainly as a consequence of interaction of the radiation with electrons in the irradiated matter. Accelerated particles (e^- or H^+) and some of the free electrons formed in the collisions of the accelerated particles with the irradiated material have high enough energy to cause cleavage of chemical bonds.[10,31,32] Owing to this high incident energy, radicals, ions and excited states can be formed, which in turn cause chain scission, crosslinking, and formation of low molar mass volatiles and double bonds. Small amounts of oxygen in contact with the polymer during irradiation and subsequent reactions can cause the formation of oxy radicals, peroxy radicals and hydroperoxides, which can be intermediates in the formation of carbonyl and hydroxy groups. The effect of radiation on polymers has been extensively studied.[10,18,33,34] In carefully done experiments in the absence of oxygen the radical centres and possibly ions can be used for substitution in the polymer matrix.

In this work care was taken to avoid reactions with oxygen. EB irradiation was performed in an atmosphere of nitrogen with <200 ppm of oxygen while proton irradiation was carried out under high vacuum. The irradiated films were instantly transferred to the sulfonation mixture. The formation of functional groups in the irradiated films, and, after sulfonation, of groups other than sulfonic acid groups in the sulfonated membranes, was evaluated from IR spectra. In the irradiated films only minor traces of carbonyl groups could be seen even after storage in ambient atmosphere for two weeks. All the absorptions of the original PVF film could be found unchanged in the irradiated films, both with respect to intensity and wavenumber. For example, in a proton-irradiated sample with an absorbed dose of 700 kGy a very weak carbonyl peak at 1730 cm^{-1} can be observed after two weeks of storage (Fig. 3). The intensity of this carbonyl peak is considerably less than

Table 1 Ion conductivities of the non-irradiated, electron irradiated (EB) and proton irradiated (H^+) sulfonated samples. For Nafion 117 a value of 52.2 mS cm^{-1} was obtained. All samples were analysed at room temperature and constant humidity

irradiation	absorbed dose/kGy	sulfonation time/h	ion exchange capacity/mequiv. g^{-1}	water uptake/g g^{-1}	water uptake $N(H_2O)/N(SO_3H)$	ion conductivity/ mS cm^{-1}
—	—	70	4.2	0.4	6	3.4
EB	400	70	4.5	0.3	4	1.9
EB	1000	5	3.1	0.3	6	2.2
EB	1000	70	5.1	0.3	4	5.3
H^+	400	5	3.1	0.5	10	20.8
H^+	1000	7	—	—	—	19.6

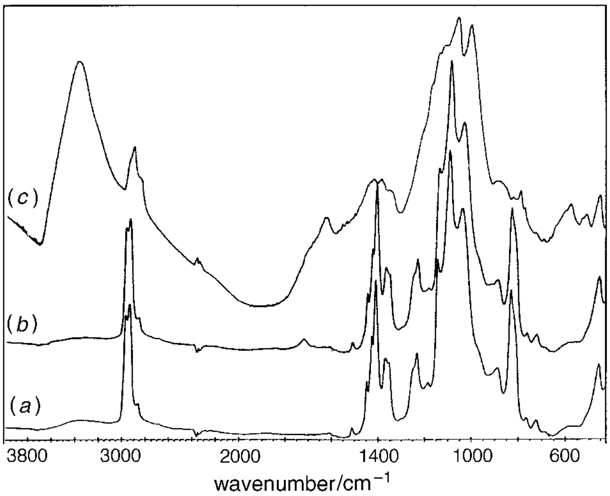

Fig. 3 IR spectrum of (*a*) original PVF film, (*b*) proton-irradiated sample (600 kGy), and (*c*) proton-irradiated and sulfonated (1 h) PVF sample

5% of the strong ν(CF/CC) absorptions around 1100 cm^{-1} (three maxima: 1140, 1100, 1050 cm^{-1}).[35] Also the strong absorption of ν(CC)/δ(CF) at 830 cm^{-1} is seen in spectra of irradiated samples.[35] Hence the conclusion is drawn that the irradiated films are not very sensitive to attack by oxygen under the experimental conditions used. No traces of hydroxy groups or double bond formation can be seen in the IR spectra. On the other hand the films are extremely sensitive to the sulfonation conditions. In membranes sulfonated in untreated mixtures very extensive formation of carbonyls (strong and broad absorption at 1730 cm^{-1}) and hydroxy groups (2800–3400 cm^{-1}) can be seen, in addition to the formation of sulfonic acid groups. The formation of the sulfonic acid group is seen as a very broad band around 1230 cm^{-1}.[34] In addition the broad hydronium ion absorption appears at 1680 cm^{-1}.[36] When the sulfonation was carried out in a mixture which had been carefully purged with nitrogen before sulfonation, the carbonyl absorption was missing from the IR spectrum, Fig. 3. On the other hand the PVF absorptions around 1100 and at 830 cm^{-1} are clearly seen. We therefore conclude that the main reaction induced by the irradiation is sulfonation under conditions excluding oxygen from the sulfonation mixture. The mechanism of the sulfonation reaction of the irradiated membranes is probably complex, including at least both radical and ionic reactions. These mechanisms will be further investigated.

Changes in mass of the polymer during the sulfonation were analysed both for EB irradiated and non-irradiated samples. These changes are shown in Fig. 4. The mass of the polymer film decreases in the early stages of sulfonation both for irradiated and for non-irradiated films. The decrease is probably due to dissolution of low molar mass chain fragments close to the surface of the film which are soluble in the sulfonating mixture. Part of the increase in mass at longer sulfonation times is due to increasing amounts of ionically bound water in the matrix, which does not evaporate under the drying conditions used in the present case.

The mass decrease is larger in irradiated samples than in non-irradiated ones. This is to be expected due to chain scission during the irradiation.[33,34,37] After sulfonation times of >1 h the solubility of the polymer decreases to a negligible value, the decrease being considerably faster for irradiated samples than for non-irradiated samples. The decrease in solubility with increasing time of sulfonation is probably caused by crosslinking of the chains in the polymer matrix. In EB irradiated samples the reactive sites are formed randomly throughout the film.[25] The crosslink density is therefore higher inside the matrix than close to the surface since radical coupling is more probable inside the film. The largest decrease in mass is observed after 1 h of sulfonation for the sample with the highest absorbed dose, 1000 kGy, in which sample the chain scission at the surface can be expected to be most effective, see Fig. 4.

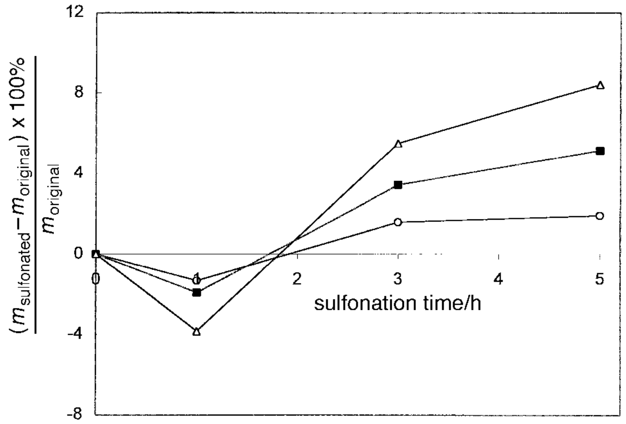

Fig. 4 Mass change of non-irradiated and electron-irradiated samples during the sulfonation with different absorbed doses (○, 0 kGy; ■, 400 kGy; △ 1000 kGy). The lines combining the points are only guides for the eye.

After *ca.* 1 h of sulfonation the decrease in mass turns to an increase with the increase in mass being larger in the EB irradiated samples than in the non-irradiated ones. The largest increase in mass is observed for samples with highest absorbed dose at longer times of sulfonation than 1 h. Thus, it is concluded that as the density of reactive sites increases with absorbed dose the rate of sulfonation increases, and hence the hydrophilicity of the reaction environment increases and facilitates further reactions of chlorosulfonic acid in the already formed hydrophilic regions of the polymer matrix.

The change in mass in proton-irradiated samples could not be determined because the ion beam was focused on only a part of the film. The basic characteristics of the behaviour of high-energy protons in irradiated PVF lead us to believe that the mass change during the sulfonation of the proton-irradiated samples resembles that of the non-irradiated samples. In this work the evenly irradiated area of the proton irradiated portion of the film was relatively small, <9 cm^2. Technical solutions are known where much larger areas can be subjected to evenly distributed proton irradiation, *e.g.* in the manufacture of Millipore™ membranes. Hence the use of proton irradiation for the production of proton conducting membranes is not limited to small areas.

Proton and EB irradiation affect the polymer matrices in different ways. With an energy less than a few MeV the path of accelerated electrons is random.[25] The distribution of energy absorption sites, and thus, the sites of reaction is also random. In contrast, the ionisation sites and the mechanical trajectory of high-energy nuclear particles form an essentially rectilinear path through the sample film.[31,38] This has been verified for polymers by *e.g.* Albrecht *et al.*,[39] and it implies the formation of cylindrical tracks of active centres through the film. These tracks can be used in the preparation of organised membranes.[40] For instance, highly oriented cylinder shaped polystyrene domains are formed in high-energy Kr irradiated poly(vinylidene fluoride) upon grafting.[41] In contrast to this, in EB irradiated grafted materials, as well as in materials prepared with other methods, the conducting paths are randomly distributed without orientation with respect to the surface.

Protons penetrate the polymer matrix more efficiently than EB irradiation with formation of cylindrical tracks through the film.[39] Track visualisation for proton penetration of PVF in this work is shown in Fig. 5 which shows the tracks of 100 protons passing the 31 µm PVF film as calculated by the Monte Carlo program SRIM-96.[27] A parallel beam of particles incident on a point at the film surface at the left is assumed. The gradual transverse deflection of the particles with increasing film thickness is mainly caused by electronic interaction. The average deviation of a large number of transmitted particles leaving the film is 0.36 µm from the line defined by the direction of the incident particles. Hence chain scission at the surface of the film is unlikely and crosslinking and radical scavenging preferably takes place along these tracks. The crosslink network thus formed prevents the dissolution of polymer into the sulfonation mixture.

The active sites for sulfonation of the proton-irradiated PVF samples are thus mainly located along the formed cylindrical tracks. The distribution of sulfonic acid groups is therefore very different in EB- and proton-irradiated samples, respectively. Along the cylindrical tracks in the proton-irradiated samples the concentration of reactive sites is locally very high.

The ion exchange capacity, Q, of the sulfonated, and the irradiated and sulfonated samples, respectively, are shown in Fig. 6 as a function of sulfonation time. The value of Q increases with increasing sulfonation time and is >1 mequiv. g^{-1} for all the samples. The increase in Q is highest with the highest absorbed doses, and higher for proton- than EB-irradiated samples with the same dose and sulfonation time. The highest values of Q were *ca.* 5 mequiv. g^{-1} achieved with 1000 kGy EB irradiation and 70 h sulfonation. (The apparent disagreement of the last two sentences is owing to the difference in the longest sulfonation times; 70 h with EB and 28 h with high-energy proton-irradiated samples.) Under the same analysis conditions Nafion® 117 gave an ion exchange capacity of 0.9 mequiv. g^{-1}.

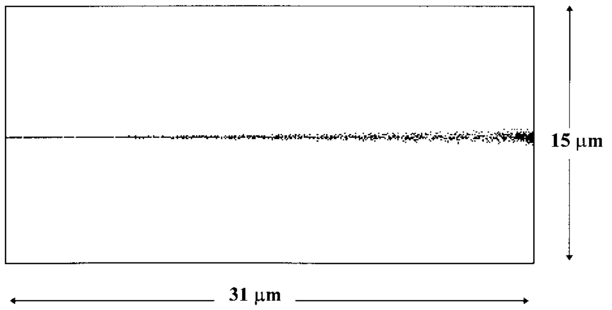

Fig. 5 Calculated tracks of protons penetrating through the PVF film. A parallel beam of particles enters the film from left. The tracks of 100 particles are shown.

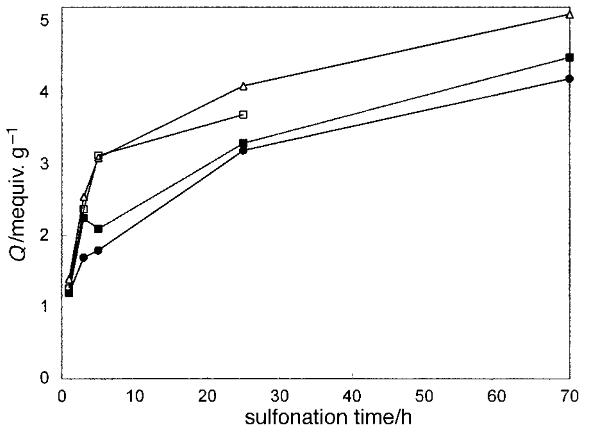

Fig. 6 Dependence of ion-exchange capacity, Q, on absorbed dose and irradiating particle (●, 0; ■, EB 400 kGy; △, EB 1000 kGy; □ H$^+$ 400 kGy). The lines combining the points are only guides for the eye. A value of 0.9±0.15 mequiv. g^{-1} was obtained for Nafion 117.

The efficiency of sulfonation of the different samples is shown in Fig. 7. Values in these plots are calculated by comparing values of Q of samples with different times of sulfonation $(Q_{t2}-Q_{t1})$. In addition, the values for irradiated samples are divided by the respective values of non-irradiated samples. Thus, if the value of this relation is higher than unity then the efficiency of sulfonation is higher in the irradiated samples. It is seen from Fig. 7 that the sulfonation rate is faster with increasing absorbed dose. In addition, proton irradiation promotes the sulfonation more effectively than EB irradiation, with sulfonation times up to 5 h. With longer sulfonation times the efficiency of sulfonation is more or less independent of irradiation. The sulfonation is probably promoted by the increasing hydrophilicity of the reaction environment with long sulfonation times.

Results of the ion conductivity measurements are presented in Table 1. Since the surfaces of the films are intrinsically rough, and the process of irradiation and sulfonation further increases the roughness, the contact between the electrodes and the polymer film in the measuring chamber is not very efficient. Hence the accuracy of the conductivity measurement is about ±20%. Thus we find that the ion conductivities in the sulfonated non-irradiated films and in sulfonated EB-irradiated films are of the same order of magnitude. The conclusion is therefore drawn, that the EB irradiation does not increase the ion conductivity of the sulfonated films, but it increases the efficiency of sulfonation considerably in the beginning of the reaction. The sulfonic acid groups are randomly distributed through the film in both the non-irradiated and EB irradiated samples, and enough pores for efficient ion transport are not formed. This conclusion is in accordance with the high values of Q achieved. The situation is different in the proton irradiated samples. In these the sulfonic acid groups are preferably attached along the cylindrical tracks, which can lead to the formation of proton conducting pores through the film. This is reflected in the higher values of ion conductivity in the proton irradiated films than in the EB irradiated or non-irradiated films. The rate of sulfonation is increased considerably by proton irradiation, see Fig. 7. Conductivities in proton irradiated films are 10–20 mS cm^{-1} with absorbed doses 400–1000 kGy. The ion conductivity of Nafion® 117 under the same conditions was *ca.* 50 mS cm^{-1}.

The differences in proton conductivities between Nafion 117 and the proton-irradiated sulfonated PVF membranes can be explained by differences in the mobility and relaxation of the

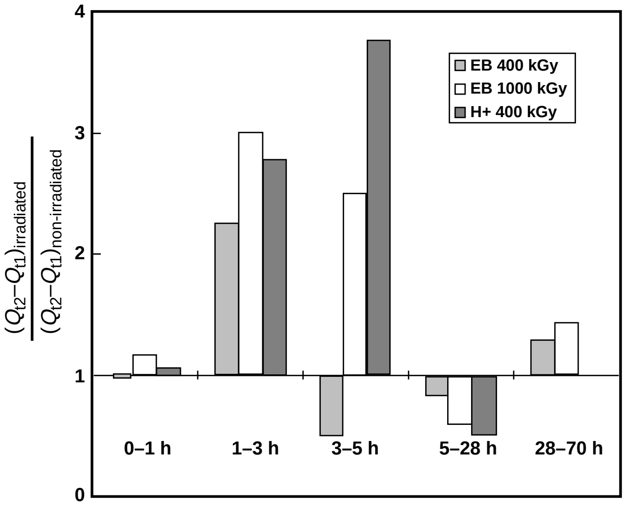

Fig. 7 Dependence of the efficiency of sulfonation on absorbed dose and irradiating particle at different time intervals, expressed as the ratio of change in ion-exchange capacity, Q

polymer matrices, and differences in the solubility and the interaction of gases and water in the membranes. Further investigations are in progress.

Conclusions

Sulfonation of PVF after irradiation with an electron beam or high-energy protons, respectively, has been performed with the aim of producing new ion conducting materials. Ion-exchange capacities of the prepared samples were comparable to those of commercial ion exchangers. The absorbed dose and the mass of the irradiating particle have been shown to influence the sulfonation. The rate of sulfonation is increased both with EB and with proton irradiation at short sulfonation times. With long sulfonation times the increasing hydrophilicity in the sulfonated regions governs the rate of sulfonation. The proton irradiation, and thus increase in LET, promotes the formation of pores in the membrane in which the sulfonic acid density is high, and which form conducting channels. The presence of these channels increases the ion conductivity to around 20 mS cm^{-1}. These membranes will be further tested in electrochemical applications. The microstructure and the state of water in the sulfonated membranes, as well as gas permeability studies and tests for technical applications are in progress.

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