Cross-Linker Effect in ETFE-Based Radiation-Grafted Proton-Conducting Membranes

I. Properties and Fuel Cell Performance Characteristics

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Cross-linking of styrene grafted and sulfonated fuel cell membranes is essential to obtain well-performing and durable membranes. In this study, the properties and fuel cell performance of radiation grafted membranes based on poly(ethylene-alt-hexafluoropropylene) (ETFE) (25 μm) with different extent of cross-linking, using divinylbenzene (DVB) as a comonomer to styrene, were investigated. The water uptake and proton conductivity decrease as a function of increasing the extent of cross-linking. Also, the membranes become more brittle. Fuel cell performance is limited by the high ohmic resistance of the membrane at high degrees of cross-linking, whereas at low degrees of cross-linking the membrane-electrode interface is of poor quality. Optimum performance is obtained at an extent of cross-linking corresponding to a styrene:DVB monomer ratio (v/v) of 95:5 in the grafting solution.

Substantial advances have been made in polymer electrolyte fuel cell (PEFC) power density over the past 15 years, the most important ones, regarding the membrane electrode assembly (MEA), being the decrease of the noble metal loading by introducing carbon supported catalysts, and reduction of the internal resistance through the use of thinner membranes. Presently, the PEFC technology is at a prototype or precommercial level. However, there are still technological barriers that hamper market introduction of fuel cell-based products: durability and cost. The cost of the proton exchange membrane is a major contributor to the cost of the MEA, in particular when using perfluorosulfonic acid-type membranes. The development of alternative membrane materials, which are partially fluorinated or even fluorine-free, is therefore of high interest. Among the promising alternative candidate materials are poly aromatic membranes (for an overview see Ref. 2) and radiation grafted membranes (see the review in Ref. 3).

The synthesis of proton exchange membranes through modification of a preformed polymer film by means of preirradiation-induced graft copolymerization (or, for short, “radiation grafting”) offers the prospect of tailor-made and cost-effective membranes for the PEFC. Radiation grafting allows the introduction of a functional property, in this case proton conductivity, into a preformed polymer film by grafting of a second component through radical polymerization onto activated centers in the base polymer, thereby forming a graft copolymer. The attractiveness of the technology lies in the versatility of the method, as the range of base polymers and graft monomers is virtually unlimited and the process parameters at hand allow adjustment and tuning of the membrane composition to specific requirements.

The preparation of radiation grafted fuel cell membranes at Paul Scherrer Institut has achieved a promising stage of development. Membranes based on styrene/divinyl benzene (DVB) grafted onto the perfluorinated base film poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) with 25 μm thickness and subsequent sulfonation have shown an attractive performance similar to Nafion 112, and stable operation for over 4000 h at a cell temperature of 80°C. The extent of cross-linking of the grafted membrane was found to be of paramount importance. Un-cross-linked membranes purely based on styrene as a grafting monomer and FEP as a base film are highly susceptible to degradation in the fuel cell, failing in the timeframe of around 50 h at a cell temperature of 80°C. In a study on the influence of the cross-linker on fuel cell performance and durability reported earlier, using FEP base film, the optimum ratio of styrene to DVB in the grafting solution was found to be 9:1 (v/v), i.e., 10 vol % DVB with respect to total monomer content.

Membranes prepared using a lower DVB content were chemically unstable and showed a rapid degradation in the fuel cell, whereas membranes prepared using a higher DVB to styrene ratio tend to be brittle and fail mechanically, either during MEA fabrication, cell assembly, or operation.

Although styrene has been widely used as a grafting monomer, because it readily polymerizes by the radical mechanism and the aromatic ring is easily sulfonated subsequently, the susceptibility of sulfonated polystyrene to chain degradation in the presence of radical species (HO•, HOO•) is well-known. Alternative monomers with suitable substituents at the α-position of styrene can yield membranes with a higher intrinsic chemical stability. Such an alternative monomer, which is also readily available, is α-methylstyrene (AMS). Membranes based on grafted AMS onto a 25 μm FEP-based film have been shown to exhibit excellent performance and considerably enhanced fuel cell durability compared to styrene grafted membranes.

These encouraging results notwithstanding, potential advantages of using poly(ethylene-alt-hexafluoropropylene) (ETFE) as a base polymer in comparison to FEP have been identified: (i) ETFE is readily available in higher molecular weights, yielding superior mechanical properties such as tensile strength and elongation at break, (ii) grafting onto ETFE is expected to proceed with enhanced kinetics due to improved monomer diffusion, and (iii) lower radiation-induced damage due to the propensity of ETFE to undergo less chain scission and more cross-linking reactions compared to FEP. Investigations of the fuel cell relevant ex situ properties and fuel cell testing of styrene/DVB grafted ETFE (25 μm)-based membranes with a fixed DVB monomer content of 10% in the grafting solution as a function of graft level have been published earlier. The choice of DVB content of 10% was based on earlier findings using FEP as a base film. It was found that the optimum degree of grafting was between 20 and 30 wt %. Lower grafted membranes showed a poor conductivity, hence resulting in poor fuel cell performance. Membranes with a graft level 30 wt % or higher were increasingly brittle, leading to crossover leak failure in the cell. The optimum cross-linker content for the preparation of ETFE-based membranes, however, does not necessarily have to be identical to the optimum 10% DVB monomer content found for FEP-based membranes. The grafting kinetics and diffusion of styrene and DVB may well be...
different in the matrix of ETFE compared to FEP, due to differences in the chemistry (partially fluorinated vs perfluorinated) and/or microstructure (crystallinity, molecular weight, orientation). In a recently published article, we investigated the effect of DVB on the grafting kinetics, dimensional changes during grafting and sulfonation, and thermal properties of the resulting membranes.\textsuperscript{11} In this study, the properties and fuel cell performance characteristics of styrene/DVB grafted ETFE 25 \mu m-based membranes with different extent of cross-linking are reported to find the optimum DVB monomer content in the grafting solution. Based on our earlier findings, the degree of grafting is kept constant at 25 wt \%.\textsuperscript{11}

### Experimental

**Membrane preparation.**— ETFE films of thickness 25 \mu m (Tefzel, DuPont, USA) were electron beam irradiated to a dose of 1.5 kGy and subsequently stored at \(-80^\circ\)C until used. Grafting was carried out in a stainless steel reactor at a temperature of 60°C. The grafting solution consisted of 20\% (v/v) monomer (mixture of styrene and DVB), 65\% (v/v) isopropanol, and 15\% (v/v) water.\textsuperscript{12} The DVB concentration, given as the volumetric ratio of DVB with respect to the total amount of monomer (styrene + DVB) in the initial grafting solution, was varied from 0, 2, 3, 4, 5, 6, 8, 10, 15, to 20\%. Thus, ETFE grafted films with a different extent of cross-linking were obtained. The graft level was adjusted to \(-25\%\) by adjusting the grafting time accordingly, as the grafting kinetics is a function of the DVB content in the grafting solution.\textsuperscript{12} Sulfonation of the grafted films to obtain proton-conducting membranes was carried out in a solution of 2\% (v/v) chlorosulfonic acid in dichloromethane at room temperature for 5 h, followed by hydrolysis in 0.1 M NaOH solution and reprotonation in 2 M H\textsubscript{2}SO\textsubscript{4} solution. Finally, the resulting membranes were swollen in deionized water at 80°C for 5 h. The thickness of the membranes in the swollen state was around 35 \mu m, with a slightly decreasing trend toward higher degrees of cross-linking (32 \mu m for the membrane prepared with 20\% DVB).

**Ex situ membrane characterization.**— The ion exchange capacity (IEC) of the membranes, i.e., the number of ionic sites per unit mass of polymer, was determined by cation exchange using 0.5 M KCl solution, followed by titration of the released protons and subsequent drying of the sample to determine the dry weight of the polymer. The water uptake was determined from the difference in weight of the water-swollen membrane and the dried membrane. The hydration number in the swollen state, i.e., the number of water molecules per sulfonic acid group, was calculated from the water uptake and the IEC. The proton conductivity in the fully hydrated state was measured at room temperature via ac impedance spectroscopy (Zahner IM6 or IM6e, Zahner-Elektrik, Kronach, Germany) in a through-plane two-electrode configuration on circular samples of 2 cm diameter using an in-house-built cell. Details on the experimental procedures used for ex situ membrane characterization can be found elsewhere.\textsuperscript{11}

**MEA preparation.**— The radiation grafted and sulfonated membranes based on ETFE with a graft level of around 25\% and different extents of cross-linking were prepared under identical conditions. Upon drying at room temperature for 5 h, followed by hydrolysis in 0.1 M NaOH solution and reprotonation in 2 M H\textsubscript{2}SO\textsubscript{4} solution. Finally, the resulting membranes were swollen in deionized water at 80°C for 5 h. The thickness of the membranes in the swollen state was around 35 \mu m, with a slightly decreasing trend toward higher degrees of cross-linking (32 \mu m for the membrane prepared with 20\% DVB).

**Single-cell testing.**— MEAs were assembled into single cells with an active area of 29.2 cm\textsuperscript{2}, comprising a serpentine flow field machined into graphite plates (Fig. 1). The membrane prepared with 20\% DVB content in the grafting solution could not be tested in the single cell because of its high brittleness, leading to fracture during handling. The cells were operated at a temperature of 80°C, using pure H\textsubscript{2} and O\textsubscript{2} in counterflow mode at a stoichiometry of 1.5 each as reactants with minimum flows of 60 (H\textsubscript{2}) and 30 (O\textsubscript{2}) mL min\textsuperscript{-1}, respectively, and ambient pressure. The H\textsubscript{2} feed stream was humidified at 80°C using bubblers; the O\textsubscript{2} was fed to the cell dry. The cells were operated at a constant current density of 0.5 A cm\textsuperscript{-2}. For performance characterization, polarization curves were recorded with online measurement of the ohmic resistance using our in-house-developed auxiliary current–pulse method.\textsuperscript{11}

**EIS.**— Electrochemical impedance spectroscopy (EIS) was previously shown to yield information on ohmic and interfacial resistances in an MEA.\textsuperscript{2} EIS spectra were recorded using a Zahner IM6 or IM6e system at a dc current density of 0.5 A cm\textsuperscript{-2} in pseudoglycolanostat mode with a perturbation signal of 3.4 mA cm\textsuperscript{-2} (100 mA absolute) amplitude, in a frequency range between 100 mHz and 25 kHz. The resulting spectra were semicircle-like, intercepting the real axis at the low and high-frequency end, respectively. As in our previous analysis, the high-frequency intercept was interpreted as ohmic resistance \(R_0\) of the MEA, which is governed by the resistance of the proton exchange membrane. The diameter of the semicircle was interpreted as polarization resistance \(R_p\).\textsuperscript{11} The analysis of various MEAs based on radiation grafted membranes showed that the polarization resistance is a measure for the quality of the membrane–electrode interface.\textsuperscript{3,21}

**Electrochemical platinum surface area.**— The electrochemical platinum surface area of the anode and cathode, respectively, was determined via CO stripping voltammetry at a cell temperature of 80°C (Fig. 2). In preparation of the experiment, fully humidified N\textsubscript{2} was fed to the working electrode and H\textsubscript{2} to the opposite electrode serving as reference and counter electrode, at a flow rate of 200 mL min\textsuperscript{-1} each. Both gases were fully humidified. After about 1 h, a stable equilibrium potential of around 0.1 V was reached. Impurities on the Pt catalyst surface were removed by cycling the potential of the working electrode between 0.050 and 1.000 V at a sweep rate of 100 mV s\textsuperscript{-1}. The potential was then set to 0.125 V and the working electrode feed gas changed from pure N\textsubscript{2} to N\textsubscript{2}/1% CO for 15 min to adsorb CO on the catalyst. Gas phase CO was subsequently removed by purging with pure N\textsubscript{2} for another 15 min. The CO stripping voltammetry was performed at a sweep rate of 10 mV s\textsuperscript{-1}, followed by voltammetry cycles between 0.050 and 1.000 V. From the area under the CO electro-oxidation peak the electrochemical platinum surface area was calculated, assuming a specific charge of 420 \mu A cm\textsuperscript{-2} (Pt). To obtain the specific electrochemical catalyst surface area, this value was divided by the catalyst loading of the electrodes (0.5 mg Pt cm\textsuperscript{-2}).

**H\textsubscript{2} permeation.**— The reactant permeability of the electrolyte membrane was assessed via in situ measurement of the hydrogen permeation flux.
crossover rate. The permeability of the membrane for reactant gases was found to be correlated with the rate of membrane degradation by various authors.14,17 For the measurement of the rate of H2 permeation through the membrane, the cell was operated in H2/N2 mode, as explained in the previous paragraph for the cyclic voltammetry experiment. The H2 crossover rate was measured by applying a cell voltage of 0.5 V. The measured current is the limiting current for H2 permeation through the membrane from the H2 to the N2 side. Therefore, the H2 crossover current density is a measure of the mechanical integrity of the membrane.

Results and Discussion

The principal parameter for the characterization of a radiation grafted membrane is the degree of grafting (also graft level). The higher the graft level, the more the properties of the resulting polymer will be determined by the properties of the graft component. In view of the known susceptibility of poly(styrenesulfonic acid) (PSSA) to oxidative attack under fuel cell conditions,9 excessive grafting is to be avoided to take advantage of the higher chemical and thermal stability of the base film, ETFE in our case. To obtain a continuous path for proton conduction in the sulfonated membrane, the grafting front has to reach the center of the film, i.e., a minimum graft level is required to enable proton conduction through the thickness of the membrane.

We have investigated the effect of the graft level on membrane properties and fuel cell performance characteristics of ETFE-based membranes with a fixed concentration on styrene to DVB of 9:1 v/v in the grafting solution.11 The degree of grafting range with interesting membrane properties was identified at 20–30%. At lower graft levels, conductivity was insufficient; above a graft level of 30% the membranes tend to be brittle, leading to low lifetimes in the fuel cell due to mechanical failure.11 Hence, for the investigations in this study, the graft level of the prepared membranes was adjusted to 25%. The styrene:DVB ratio in the grafting solution was varied from 100:0 to 80:20. As a consequence of the different grafting kinetics as a function of cross-linker content, the grafting times had to be chosen accordingly, ranging from 45 min (0% DVB) to 32 h (20% DVB).

The cografting of styrene and the cross-linker DVB is associated with several implications. The grafting process is controlled by the reactivity of the monomers and their diffusivity in the polymer undergoing grafting. Hence, the higher polymerization reactivity of DVB compared to styrene is expected to yield a higher concentration of DVB in the grafted film than in the grafting solution. The diffusivity of DVB in the film is likely to be lower than that of styrene, owing to its larger dimensions. In reality, a sizable gradient of the extent of cross-linking is observed in the grafted film, with higher DVB incorporation into areas close to the film surface, and lower DVB:styrene ratios in the bulk of the film. Therefore, we should keep in mind that we are talking about average properties of the material, yet knowing that the properties may well be different on a local scale in the thickness direction. For simplicity, the cross-linker content quoted in the following discussion will be the DVB content (v/v) with respect to the total amount of monomer in the grafting solution.

Ex situ properties.— The ex situ membrane properties of primary interest for application in the fuel cell are the IEC, water uptake, and conductivity (Table I, Fig. 3). The values for the ETFE-based membranes are compared against those of a standard FEP 25 μm-based membrane and Nafion 112. The sulfonation of the styrene units in the grafted film is a relatively uncritical reaction; only at high degrees of cross-linking of 10% DVB and more, is a notable drop in IEC observed (Fig. 3a). A degree of sulfonation of 100% corresponds to the introduction of one sulfonic acid group per styrene unit. The average degree of sulfonation up to a DVB content of 10% is 102 ± 2%. As the DVB derived units in the grafted film are more difficult to sulfonate, the degree of sulfonation drops markedly below 100% at DVB contents of 15 and 20%. Because the IEC is a mass-based quantity, one has to take into account the different density of ETFE and FEP-based membranes (in the dry state), estimated at 1.5 and 1.8 g cm−3, respectively. The volumetric IECs of the two types of grafted membranes then agree fairly well (2.5 mmol cm−3).

The water uptake, expressed as the number of water molecules per sulfonic acid site, decreases with increasing cross-linker content (Fig. 3b). Evidently, the increasing network density reduces the

**Table I.** Ex situ properties of selected membranes. “g-” stands for radiation grafted and sulfonated membranes. Base film thickness of FEP and ETFE is 25 μm. DVB cross-linker content is given with respect to total monomer content in the grafting solution (rest = styrene). A degree of sulfonation of 100% corresponds to one sulfonic acid group per styrene unit.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>DVB content in grafting solution [vol %]</th>
<th>Degree of grafting [wt %]</th>
<th>IEC [mmol/g]</th>
<th>Degree of sulfonation [%]</th>
<th>Water uptake [wt %]</th>
<th>Hydration number [H2O/14SO4H]</th>
<th>Proton conductivitya [mS/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-ETFE</td>
<td>0</td>
<td>25.6</td>
<td>1.74 ± 0.06</td>
<td>103 ± 4</td>
<td>33.9 ± 3.1</td>
<td>10.8 ± 0.8</td>
<td>102 ± 13</td>
</tr>
<tr>
<td>g-ETFE</td>
<td>5</td>
<td>25.8</td>
<td>1.74 ± 0.08</td>
<td>102 ± 5</td>
<td>21.7 ± 3.1</td>
<td>7.5 ± 0.7</td>
<td>62 ± 2</td>
</tr>
<tr>
<td>g-ETFE</td>
<td>10</td>
<td>24.1</td>
<td>1.71 ± 0.04</td>
<td>105 ± 2</td>
<td>14.1 ± 0.5</td>
<td>4.6 ± 0.1</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>g-ETFE</td>
<td>15</td>
<td>27.3</td>
<td>1.65 ± 0.05</td>
<td>93 ± 3</td>
<td>10.5 ± 3.2</td>
<td>3.5 ± 1.0</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>g-ETFE</td>
<td>20</td>
<td>24.9</td>
<td>1.45 ± 0.02</td>
<td>88 ± 1</td>
<td>7.8 ± 0.8</td>
<td>3.0 ± 0.7</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>g-FEP</td>
<td>0</td>
<td>18.0</td>
<td>1.33 ± 0.02</td>
<td>102 ± 2</td>
<td>70.7 ± 1.3</td>
<td>29.5 ± 0.7</td>
<td>72 ± 6</td>
</tr>
<tr>
<td>g-FEP</td>
<td>10</td>
<td>18.2</td>
<td>1.36 ± 0.06</td>
<td>103 ± 5</td>
<td>16.3 ± 1.5</td>
<td>6.7 ± 0.7</td>
<td>41 ± 1</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>—</td>
<td>—</td>
<td>0.91</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

a At room temperature in liquid water equilibrated state.
Also, the mechanical properties change with increasing the extent of cross-linking, the tensile strength of the membranes increases, whereas the elongation at the break decreases, rendering the polymer increasingly brittle. The water uptake of Nafion 112 (33.9%) and that of the un-cross-linked ETFE-based membrane (33.5%) are identical. Because the water uptake is a mass-based quantity, the volume-based water uptake is higher for Nafion 112 owing to its higher density. The lower water uptake of the un-cross-linked ETFE-based membrane compared to that of the un-cross-linked FEP-based membrane and Nafion 112 is also reflected in the lower amount of sorbed water per sulfonic acid site (hydration number) (Table I). This may be a consequence of the fact that the irradiation of ETFE also causes some cross-linking of the base polymer preventing excessive swelling, or a higher elastic stiffness of the polymer.

The lower water uptake of the ETFE-based membrane compared to the FEP-based one at the same DVB concentration could be related either, as already mentioned, to the cross-linking of the ETFE-based polymer upon irradiation, or an effective higher degree of DVB incorporation into the graft polymer. It is known that ETFE shows some swelling in the grafting solution, whereas FEP does not. Owing to the higher reactivity of DVB vs styrene, DVB could be preferentially grafted in ETFE. In FEP, diffusion of the more bulky DVB molecule compared to styrene could be limited.

The conductivity (Fig. 3c) follows the general trend of the water uptake data. As the ionic site density is roughly constant (Fig. 3a), the decrease in conductivity is attributed to a lower proton mobility at lower hydration levels. Between the conductivity and hydration level an approximately linear correlation is observed for the radiation grafted membranes (Fig. 3d). For Nafion membranes, a similar correlation is observed, yet with conductivity values shifted to higher hydration numbers. With the ETFE-based membranes, the conductivity of Nafion 112 (82 ± 6 mS cm⁻¹) is reached at a lower hydration level. This is most probably a consequence of the higher volumetric IEC of the radiation grafted membranes (2.5 mmol cm⁻⁻) compared to that of Nafion with an equivalent weight of 1100 (1.6 mmol cm⁻⁻).

**Fuel cell performance characteristics.**—For the characterization of fuel cell performance, polarization curves were recorded as a first test after cell conditioning at a constant current density of 0.5 A cm⁻² and obtaining stable performance. MEAs with membranes prepared with different cross-linker content, i.e., 0, 2, 3, 4, 5, 6, 8, 10, and 15%, were evaluated. The membrane with a DVB content of 20% could not be tested in the single cell; it was too brittle and cracked during cell assembly. Results for selected MEAs are presented in Fig. 4. The in situ membrane resistance was determined via the auxiliary current-pulse technique. The membrane resistance is notably higher for cross-linker concentrations of 10% (136 mΩ cm² @ 0.5 A cm⁻²) and 15% (188 mΩ cm² @ 0.5 A cm⁻²), with a concomitant decrease in cell performance, compared to the values for the un-cross-linked and 5% DVB cross-linked membrane, respectively (both 84 mΩ cm² @ 0.5 A cm⁻²).

The distinct increase in ohmic resistance toward higher current densities is most probably associated with partial drying of the anode side of the membrane and/or the anode–membrane interface. In this sense, highly cross-linked radiation grafted membranes, although having a thickness of only 35 μm, can exhibit resistance characteristics similar to those of thick Nafion membranes.

The lowest performance, however, is exhibited by the cell with an un-cross-linked membrane, despite the membrane resistance being the lowest in the series (84 mΩ cm² @ 0.5 A cm⁻²), which is puzzling at first. Yet, similar observations have been made for FEP-based radiation grafted membranes with varying extents of cross-linking. The phenomenon will be revisited shortly. The highest performance is obtained with the membrane prepared with 5% DVB. Compared to identical MEAs with optimized 25 μm FEP-based membranes (10% DVB) and Nafion 112, respectively, almost identical performance and membrane resistance is achieved (Fig. 4b).

Fuel cell performance at various current densities for MEAs with differently cross-linked membranes is shown in Fig. 5a. The open-circuit voltage (OCV) is markedly lower in the case of the uncross-linked and low cross-linked membranes, which is a consequence of higher reactant crossover, leading to a more pronounced formation of a mixed potential. At medium (0.82 A cm⁻²) and high (1.58 A cm⁻²) current densities, the higher performance losses at low and high degrees of cross-linking, respectively, become apparent. Maximum performance is obtained at intermediate cross-linking corresponding to around 5% DVB in the grafting solution. The relevant MEA performance loss terms will be discussed in the following sections.

<table>
<thead>
<tr>
<th>Crosslinker / v-%</th>
<th>Conductivity / mS cm⁻¹</th>
<th>Hydration / [H₂O] / [SO₃H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>120</td>
<td>33.5%</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>33.9%</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>34.0%</td>
</tr>
<tr>
<td>15</td>
<td>60</td>
<td>34.1%</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>34.2%</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>34.3%</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td>34.4%</td>
</tr>
</tbody>
</table>

**Figure 3.** Ex situ membrane properties of ETFE (25 μm)-based grafted and sulfonated membranes as a function of cross-linker monomer content in the grafting solution. (a) IEC, (b) water uptake, quoted as molecules of water per sulfonic acid site, (c) proton conductivity, and (d) proton conductivity plotted against water uptake. Conductivity and water uptake are for liquid water equilibrated membranes at room temperature. Data for a standard FEP (25 μm)-based membrane and Nafion 112 are given for comparison.
branes. The electrode performance is unaffected. It is clear, however, from Fig. 5 that the limited performance at low degrees of cross-linking is caused by another phenomenon. To gain further insight into prevalent loss mechanisms, ac impedance spectra were recorded at a current density of 0.5 A cm$^{-2}$ (Fig. 6). Quite clearly, the MEA with the un-cross-linked membrane exhibits the highest overall impedance, which agrees with the lowest observed performance (Fig. 4a). The spectra for the MEAs with higher cross-linked membranes appear to be similar in shape, yet gradually shifted toward higher values on the real axis. From the impedance spectra, the ohmic resistance $R_{\text{p}}$ and polarization resistance $R_{\text{p}}$ were extracted (for details on the method cf. the Experimental section) and plotted together with similar data obtained for FEP-based membranes (Fig. 7). The trends for both types of membrane are similar. A low degree of cross-linking, an ohmic resistance of around 100 m$\Omega$ cm$^2$ is measured, which increases with increasing the extent of cross-linking, and stronger so for the ETFE-based membranes. Contrariwise, the polarization resistance decreases with increasing cross-linking. For the ETFE-based membranes, the $R_{\text{p}}$ value decreases from around 400 m$\Omega$ cm$^2$ for the un-cross-linked membrane to a stable value of 192 m$\Omega$ cm$^2$ for membranes prepared with 5% DVB and above. Whereas the increasing $R_{\text{p}}$ is clearly associated with the decreasing membrane conductivity (Fig. 3c), correlating well with the ohmic resistance data determined via the current–pulse technique (Fig. 4a and 5b), the significance of $R_{\text{p}}$ in this context is less straightforward. It has been argued that $R_{\text{p}}$ is a measure for the quality of the membrane–electrode interface, based on the fact that the value appears to be influenced by MEA laminating conditions and membrane surface pretreatment. A decreasing $R_{\text{p}}$ with increasing the extent of cross-linking would mean that the membrane–electrode interface quality improves with cross-linking. The correlation with physico-chemical phenomena of the interface is inconclusive at this point. Our results are somewhat at variance with the finding, obtained via X-ray photoelectron spectroscopy (XPS) analysis of the membrane surface, that with increasing the degree of cross-linking, the membrane surface becomes more and more “FEP-like,” i.e., gradually lower amounts of PSSA moieties are detected.

This would contradict the insight that the ionomer in the electrodes (Nafion) and the PSSA domains in the membrane need to be well-connected to minimize interfacial proton transport losses. It has to be kept in mind, however, that the surface of the humidified membrane is likely to have different properties compared to the membrane surface in the ultrahigh vacuum environment used for XPS analysis.

One aspect that needs to be pointed out in this discussion is the poor chemical stability of the low cross-linked membranes, especially the un-cross-linked one. The results presented in Fig. 4–7 are based on measurements taken after 160 h of operation. This was to make sure the MEAs were properly conditioned. The membranes with a low extent of degradation, however, had already experienced some degradation at this point. The ac impedance derived ohmic resistance $R_{\Omega}$ of the un-cross-linked membrane increased from 70 m$\Omega$ cm$^2$ after 21 h of operation to 94 m$\Omega$ cm$^2$ after 160 h, and the polarization resistance $R_{\text{p}}$ increased from 277 to 411 m$\Omega$ cm$^2$. Despite the observed increase in resistance, even with the initial values for $R_{\Omega}$ and $R_{\text{p}}$, the trend of decreasing ohmic resistance and increasing polarization resistance toward lower extents of cross-linking remains the same.

Based on the results obtained so far, we conclude that, in terms of cell performance, the ETFE-based membrane prepared with 5% DVB in the grafting solution offers the optimum combination of ohmic resistance and membrane–electrode interface properties, yielding the highest MEA performance among all the samples tested with a varying degree of cross-linking. A comparison of MEA performance characteristics for an optimized ETFE (5% DVB) and FEP (10% DVB)-based membrane, respectively, and Nafion 112 is
Figure 6. AC impedance spectra in Nyquist representation recorded at a dc current density of 0.5 A cm\(^{-2}\) under the experimental conditions stated in the caption of Fig. 4. Frequency range: 0.1 Hz to 25 kHz.

Figure 7. Polarization and ohmic resistance values extracted from ac impedance spectra in Fig. 6 (for details, cf. the Experimental section). Data for FEP-based membranes are from Ref. 7.

Table II. Key performance data of selected MEAs with different membranes, tested in single cells.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>OCV</th>
<th>Cell voltage @ 1.58 A/cm(^2)</th>
<th>Ohmic (current–pulse) resistance(^a)</th>
<th>Ohmic resistance(^b)</th>
<th>Polarization resistance(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-ETFE (5% DVB)</td>
<td>919</td>
<td>443</td>
<td>84</td>
<td>95</td>
<td>184</td>
</tr>
<tr>
<td>g-ETFE (10% DVB)</td>
<td>898</td>
<td>425</td>
<td>97</td>
<td>113</td>
<td>166</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>914</td>
<td>465</td>
<td>88</td>
<td>86</td>
<td>138</td>
</tr>
</tbody>
</table>

\(^a\) Ohmic resistance determined via auxiliary current–pulse technique.

\(^b\) Ohmic and polarization resistance determined via ac impedance spectroscopy at a current density of 0.5 A cm\(^{-2}\).
over on MEA durability is currently being investigated. The effect of the concentration of DVB, used as a cross-linker in this series can only account for differences in membrane resistance and the available catalyst surface area. Based on 25\%/H20849, uptake and conductivity of the membranes decreases due to an increase in cross-linking. With increasing the extent of cross-linking, the water permeability of the membrane. In this experimental series, the in situ \( H_2 \) crossover was found to decrease with increasing the extent of cross-linking. Lower rates of gas permeation through the membrane are expected to yield a higher chemical stability of the membrane, owing to the lower amount of aggressive radical species (HO\(^-\), HOO\(^-\)) formed at the electrodes due to interaction of \( H_2, O_2, H_2O \) and the Pt catalyst.

### Conclusions

The effect of the concentration of DVB, used as a cross-linker and comonomer to styrene in the grafting solution, on the ex situ and in situ properties of radiation grafted and sulfonated membranes based on 25 \( \mu \)m ETFE with a constant graft level of 5\% DVB was investigated in this study. The incorporation of DVB into the film during grafting leads to the formation of cross-links within the polymer structure. With increasing the extent of cross-linking, the water uptake and conductivity of the membranes decreases due to an increased density of the polymer network. However, the distribution of the DVB-derived cross-links is not homogeneous over the thickness of the membrane, but the extent of cross-linking appears to be higher at the membrane surface compared to the bulk of the material, which is a consequence of the dissimilar diffusion and reaction properties of styrene and DVB in the film undergoing grafting.

Fuel cell performance shows a maximum using the membrane prepared with 5\% DVB in the grafting solution. Performance is nearly equivalent to that of a crosslinked radiation grafted membrane and Nafion N112. At higher extents of cross-linking (>5\% DVB), performance is limited by the increasing ohmic resistance of the membrane. Also, the membranes become more brittle when highly cross-linked. The membrane corresponding to 20\% DVB could not be tested because of crack formation in the membrane during cell assembly. Conversely, the MEAs with low cross-linked membranes are limited in performance due to the apparently poor membrane-electrode interfacial properties, as evidenced by ac impedance spectroscopy. The reason for this behavior is not clear at this stage. A partial explanation is the rapid degradation of membranes with a low extent of cross-linking, in particular the un-cross-linked one, which failed after 166 h due to excessive gas crossover. In comparison with a Nafion 112-based MEA, the higher interfacial resistance of radiation grafted membranes, both based on ETFE and FEP, indicates an inferior compatibility of the grafted membrane with the ionomer (Nafion) used in the electrodes.

A detailed investigation on the durability of these membranes is currently being carried out and will be reported in our subsequent article. An important property in this context is the reactant permeability of the membrane. In this experimental series, the in situ \( H_2 \) crossover was found to decrease with increasing the extent of cross-linking. Lower rates of gas permeation through the membrane are expected to yield a higher chemical stability of the membrane, owing to the lower amount of aggressive radical species (HO\(^-\), HOO\(^-\)) formed at the electrodes due to interaction of \( H_2, O_2, H_2O \) and the Pt catalyst.

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