

Novel covalently cross-linked poly(etheretherketone) ionomer membranes

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Abstract

Sulfonated PEEK was synthesized via reduction of sulfochlorinated PEEK. The degree of sulfonation was determined by redox titration. By partial reduction of sulfochlorinated PEEK, PEEK carrying both SO₂Cl and sulfinate groups could be obtained. From these polymers, covalently cross-linked ionomer membranes were prepared by reaction with the cross-linker diiodobutane and subsequent hydrolysis of the sulfochloride groups by aqueous post-treatment. The membranes show strongly reduced swelling connected with good H⁺-conductivity. Moreover, due to the fact that in these membranes all macromolecules are integrated into the covalent network, no leaching out of soluble substance took place during immersion in 90 °C hot DMAc for 5 days. One of the membranes was tested in a DMFC and exhibited stable performance up to $T = 130$ °C.

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1. Introduction

Hydrogen fuel cells based on a polymer electrolyte (proton exchange membrane fuel cell, PEMFC) are considered a promising alternative technology to the internal combustion engines in cars. Furthermore, PEMFC as well as direct methanol fuel cells (DMFCs) are currently being developed to substitute batteries in mobile applications, such as laptops, PDA's and cellphones. During the last decade, fuel cell research and development has been a fast growing research field both in academia and industry. Ion-exchange membranes are at the heart of PEMFC and DMFC systems enabling the most important fuel cell functions, however, they are also responsible for a considerable share of the fuel cell system costs. The Nafion[®] membrane family from DuPont is the most common and best known commercial

fuel cell membrane because of their long-standing availability and chemical stability. On the other hand, Nafion is very expensive, and shows in the DMFC application an unacceptable high methanol and water permeability. Therefore, the research and development of alternative, low-cost, non-fluorinated ionomer membranes is currently an intensively pursued topic [1]. Mainly the novel membrane developments are based on modifications of poly(sulfones) (PSU), poly(etheretherketone) (PEEK) and poly(benzimidazoles) (PBI), also some cross-linked blends or inorganic/organic composites.

PEEK as a thermal stable polymer has been widely studied [2]. PEEK can be homogeneously sulfonated with sulfonic acid or chlorosulfonic acid from 30 to 100% sulfonation degree, referring to repeating unit. Unfortunately, the conductivity of directly sulfonated PEEK (sPEEK) having an ion-exchange capacity (IEC) of 2.2 meq g⁻¹ is only 0.01 S cm⁻¹ at 20 °C, while 0.1 S cm⁻¹ can be reached at 140 °C [3], but the extremely high water sorption limits the mechanical stability. Therefore, in order to get high conductivity and good mechanical stability, sPEEK can be blended with basic

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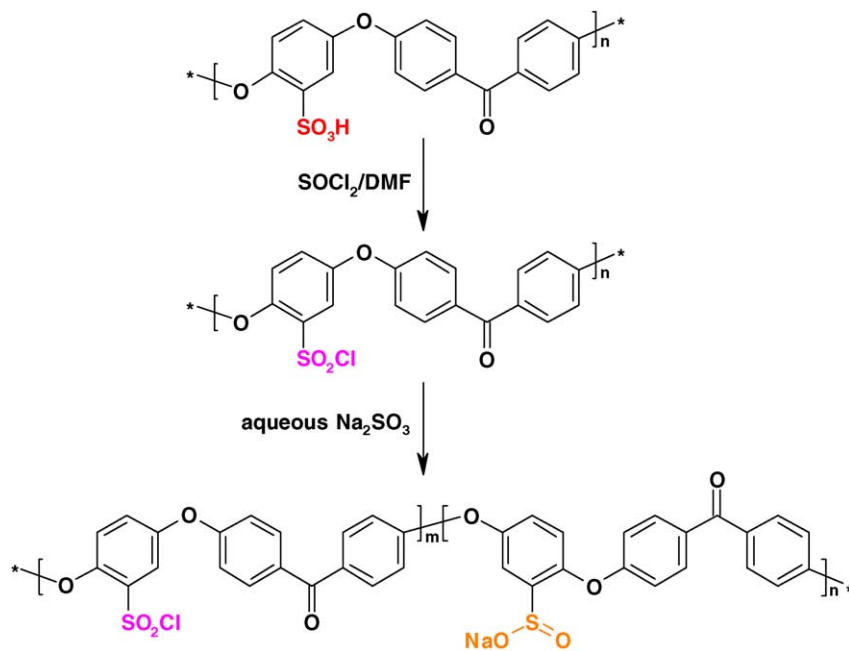


Fig. 1. Schematic of the route from PEEK- SO_3H to PEEK- SO_2Na .

polymers, such as PBI to form some ionically cross-linked membranes having a very good performance in fuel cells [4]. However, the ionic bonds are not very stable at high temperatures which makes the use of such membranes at $T > 80\text{--}100\text{ }^\circ\text{C}$ in fuel cells questionable. The inorganic material composite with sPEEK is still under investigation [5].

For reduction of swelling of PEEK ionomeric membranes, PEEK- SO_3H can be converted into PEEK- SO_2Cl by reaction with thionylchloride, followed by reaction with 4,4'-diaminodiphenylsulfone, forming $\text{--SO}_2\text{--NHR}_2\text{--}$ cross-links, as reported in [6]. However, the swelling of such membranes amounts to 1800% at $85\text{ }^\circ\text{C}$, therefore it can be concluded that the stability of $\text{--SO}_2\text{--NHR}_2\text{--}$ cross-links is insufficient at high temperatures. Our approach to covalently cross-linked PEEK ionomers is deduced from the fact that from low-molecular organic chemistry it is known that sulfochloride groups can be reduced to sulfinate groups [7]. We have shown earlier that sulfinate groups can be used as cross-linking group by reaction with α,ω -dihalogenoalkanes [8]. The cross-linking process is very simple and thermally and mechanically stable membranes having reduced water uptake can be obtained by this method. Sulfinated PEEK has not been reported yet. For reduction of sulfochloride groups of low-molecular organics, reducing agents, such as zinc dust, LiAlH_4 and Na_2SO_3 , are suitable [9]. For an efficient polymer reduction, the reaction of the reduction reagents with the polymer backbone has to be avoided. In preliminary experiments, we have found out that reduction of PEEK-sulfochloride to PEEK-sulfinate is possible by stirring a PEEK- SO_2Cl suspension in aqueous Na_2SO_3 solution. The procedure has advantages such as being easy-to-perform, and being inexpensive. Moreover, the reaction product can be eas-

ily purified. The obtained sulfinated-sulfochlorinated PEEK was cross-linked with α,ω -dihalogenoalkanes, ending up in covalently cross-linked ionomer networks where all macromolecular chains take part in cross-linking. The obtained membranes from this method showed very good properties and are very promising when applied to DMFC. The synthesis procedure from sulfochlorinated to sulfinated PEEK is presented in Fig. 1. In Fig. 2, the procedure for the preparation of the covalently cross-linked PEEK ionomer membranes is shown.

2. Material and experimental methods

2.1. Materials

Poly(etheretherketone) (PEEK) was supplied from Victrex Company. 99.95% tetrahydro-furane (THF) from Fisher, methanol and 97% H_2SO_4 was purchased from Merck. 97% SOCl_2 , 99.95% THF, 98% dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and LiCl from Fluka and Na_2SO_3 , NaOCl (4% active hypochlorite) solution from Aldrich.

2.2. Synthesis of the polymers

2.2.1. Synthesis of sPEEK

An amount of 100 g poly(etheretherketone) PEEK is dissolved in 2 L 96% H_2SO_4 and heated at $80\text{ }^\circ\text{C}$ for 6 h. Subsequently, the solution is poured onto ice. The formed precipitate is sucked off and washed until most of sulfuric acid is removed from the sulfonated polymer.

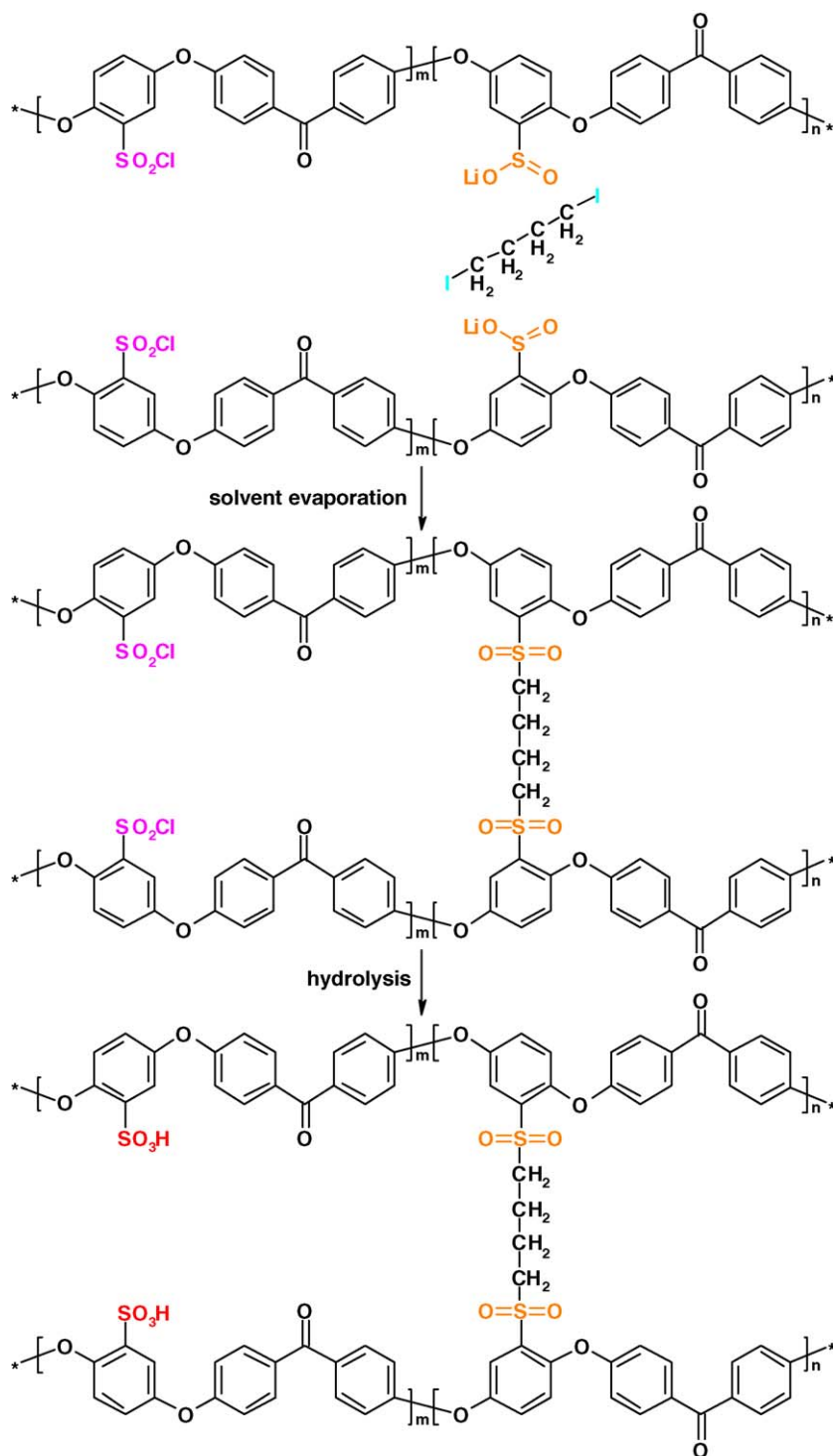


Fig. 2. Preparation route for the cross-linked PEEK ionomer membranes.

The precipitate is dissolved in water via heating to 90 °C. The polymer solution is dialyzed, followed by evaporation of water at 90 °C. Then the polymer is dried to constant weight at 90 °C in the oven. Sulfonated PEEK having an ion-exchange capacity (IEC) of 2.7 meq g⁻¹ is obtained.

2.2.2. Synthesis of PEEK-SO₂Cl

The sulfonated poly(ether ether ketone) has been transformed into sulfochlorinated poly(ether ether ketone) using the following procedure. An amount of 60 g of the sulfonated poly(ether ether ketone) are dissolved in 1 L thionylchloride. Then 15 mL of *N,N*-dimethylformamide are added to the

solution to start the sulfochlorination, which is indicated by a strong HCl and SO₂ development. Then the mixture is heated to 60 °C under stirring. During this time, the polymer dissolves in thionylchloride. After 3 h, the gas development is finished, which indicates that the reaction is completed. Then the solution is heated to 85 °C, 90% of the SOCl₂ is distilled off. Subsequently, 100 mL THF are added to the mixture under stirring to dilute the solution. The polymeric sulfochloride is then precipitated in 2 L *iso*-propanol. The sulfochlorinated polymer is filtered off and dissolved in 200 mL THF. Then it is again precipitated in 2 L *iso*-propanol and filtered. Finally, the polymer is dried under vacuum at RT overnight.

2.2.3. Partial reduction of PEEK-SO₂Cl

In a 500 mL three neck glass vessel, 40 g PEEK-SO₂Cl was added to 300 mL of 2 M Na₂SO₃ solution under stirring and heated to 70 °C. The solution was allowed to heat 20–24 h. During this time, a white suspension formed, which was separated in a separation funnel. The polymer was then exchanged into Li⁺ form using 10% LiCl solution. The polymer was filtered, suspended in deionized water, and dialyzed to remove residual LiCl and excess Na₂SO₃. Finally, the partially reduced polymer was filtered and dried at 40 °C under vacuum.

2.3. Membrane preparation

An amount of 2 g PEEK-SO₂Li-SO₂Cl was dissolved in 20 mL NMP. Diiodobutane was added to the degassed polymer solution with a syringe under strong stirring. The solution was cast onto a plate glass with a doctor knife to form a film. Then the NMP solvent was removed in an oven at 90 °C for 1 h and then 120 °C under vacuum overnight. The obtained membrane was removed from the glass surface in a water bath and hydrolyzed in 7% NaOH solution at 90 °C for 1 day and then in 10% H₂SO₄ solution at 90 °C for 1 day and finally in water at 90 °C for 1 day.

2.4. Characterization of polymers and membranes

The FT-IR spectra (KBr pills or ATR with membranes) were recorded with a Bio FTS155 spectrometer at ICVT, University Stuttgart. The ¹H and ¹³C spectra were recorded at the Institute for Organic Chemistry of the University Stuttgart. Solvent was D₆-DMSO or CDCl₃.

The elemental analyses were performed at the Institute for Organic Chemistry of the University Stuttgart. The water uptake of membranes was measured in the following way. The membranes were equilibrated in water at ambient temperature for 1 day and carefully cleaned with tissue paper and weighed to get the water uptake weight. Then the membranes were dried at 90 °C in a airflow oven for 1 day to constant weight and then weighed. The water uptake is calculated with the following formula:

$$SW(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where the W_{wet} is the weight of the swollen membranes and W_{dry} is the weight of the dried membranes.

The membrane electric resistance was measured via impedance spectroscopy (IM6 impedance measurement system, Zahner Elektrik, with two gold-plated copper electrodes, electrode area 0.25 cm²). The membrane was equilibrated in 0.5 N H₂SO₄ solution for 1 day before it was measured. Then the membrane was placed between two Nafion 117 membranes and pressed between two electrodes at 25 °C. Also the electrodes were immersed in 0.5 N H₂SO₄ solution during the measurement. Then the resistance of the three-membrane stack Nafion117-measurement membrane-Nafion117 was determined. Then the measurement membrane was removed, and the resistance of the two Nafion membranes was determined. The membrane resistance was obtained by subtraction of the three-membrane stack resistance from the two-membrane stack resistance.

The ion-exchange capacity (IEC) was determined by acid–base titration. About 0.5–1.0 g dried polymer or membrane in H⁺ form was stirred in a saturated NaCl solution to release the H⁺ ions. Then the mixture was titrated with a 0.1 N NaOH solution.

The thermal stability of the membranes was determined by thermal gravimetric analysis (TGA) method with Netzsch Jupiter 490 STA machine. The measurement was performed under heating rate 10 K min⁻¹ for membrane and 20 K min⁻¹ for polymer, under air flow, starting mass of samples being about 10–20 mg.

The sulfinate group content of the polymers was determined via a redox back titration. The sulfinated polymer was oxidized with NaOCl to obtain a corresponding sulfonated polymer [8]. The details of the redox back titration of the PEEK-sulfinate is given in the following. An amount of 0.5 g sulfinated PEEK polymer was stirred in 150 mL deionized H₂O. Then about 5 g NaOCl (4% active Cl) was added to the solution via syringe, the solution being subsequently heated at 40 °C for 4 h. Then the solution was cooled to room temperature, and about 1.5 g KI was added to the solution. Then, 10 mL acetic acid (HAc) was added, the solution turning to black color which indicated free I₂ released by reaction of NaOCl with KI. Then the solution was titrated potentiometrically with 0.1 N Na₂S₂O₃ solution to determine the amount of free, unreacted NaOCl.

The membrane cross-linking extent was determined by an extraction experiment. The weighed dried membrane was extracted in a DMAc solution at 90 °C for 3 days. The undissolved membrane part after the extraction was washed with methanol, dried at 90 °C under vacuum and weighed. The undissolved weight percent was considered the cross-linking extent of the membrane.

2.5. Membrane-electrode assembly (MEA) preparation and DMFC experiment

2.5.1. MEA preparation

The catalyst inks are prepared by dispersing unsupported catalyst in Suprapure Millipore water. Then Nafion[®] solution is added to obtain the wanted content in the ink. Nafion[®] is necessary both for the binding of the electrode as well as for providing proton conductivity to the active layer. Although the Nafion binder in the electrode is better suited for perfluorinated membranes in comparison to polyarylene membranes it was used also for the investigated membranes because high electrode activity and superior catalyst utilization is obtained with Nafion ionomers as the preparation conditions of the electrode have been optimized. Details of the preparation have been published elsewhere [10]. Summarizing the procedure, the gas diffusion electrodes are prepared by a spraying directly onto the membrane. The preparation of the catalyst ink for the spraying consisted in stirring it for at least 3 days. The wet membrane is fixed in a frame before being coated with catalysts. After fabricating the electrodes by spraying, a tempering step at 135 °C for >25 min in an oven follows. The catalyst loading is calculated by comparing the weight of the MEA after drying with the weight of the membrane and the catalyst content of the ink.

2.5.2. DMFC experiment

The MEA is introduced in a dry state into a home-made graphite cell with an active area of 25 cm² and a serpentine flow field with one channel of 1 mm × 1 mm. As gas diffusion layers teflonized carbon papers are used (Toray TGP-120, 25% PTFE). The test station for the single cell DMFC measurements controls the important parameters for fuel cell application like cell temperature, humidification of gases, pressure in the anode and cathode chamber, mass flow, etc. The pressure is measured at the outlet of cathode and anode compartment. The aqueous methanol solution is used in a single flow through the cell without recirculation into a reservoir in order to maintain a constant methanol concentration. Temperatures of cell, humidifiers and other components are regulated by an eight-channel Watlow controller. The cell temperatures are established with the help of four heating cartridges which are introduced into aluminium endplates of the cell. Performance curves were obtained using an electronic load from ITS GmbH (model ITS 7141–2) at constant currents. At the cathode exhaust, a CO₂ sensor from Fisher–Rosemount with a detection limit of 1% of CO₂ in the cathode exhaust gas is used [10]. The methanol cross-over is determined by monitoring the CO₂ flux in the cathode affluent gas using the optical IR CO₂ sensor. The method is based on the condition that methanol permeating through the membrane is completely oxidized to CO₂. This can be achieved in a simple way by introducing an afterburner in front of the sensor. The catalytic afterburner (with Pt–Al₂O₃ catalyst) is operated at 160 °C and it was checked that all unconverted methanol at the cathode is reacted to CO₂.

3. Results and discussion

3.1. Characterization of sulfonated, chlorosulfonated and sulfinated PEEK

The IEC of the starting – water-soluble – sulfonated PEEK polymer is 2.68 meq g⁻¹ which means 98.24% degree of substitution (DS = 0.98 group –SO₃H). The substitution degree can also be determined by ¹H NMR, yielding a DS of about 0.94 per group/repeating unit, see also the NMR part of this paper. PEEK-SO₂Cl and PEEK-SO₂Li have nearly the same chemical shifts in NMR as PEEK-SO₃H. Therefore, in mixed substituted PEEK containing SO₂Cl, SO₃Li and SO₂Li groups these groups cannot be distinguished from each other by NMR analysis.

However, the –SO₂Cl group can be found in FT-IR spectra. Normally the –SO₂Cl peak can be detected at 1385–1365 cm⁻¹ [11], see also the FT-IR characterization part of this paper. The theoretical elemental analysis results of 1.0 group PEEK-SO₂Cl are: C 59.06, H 2.85, S 8.29, Cl 19.07. The experimental elemental analysis results are: C 57.43, H 3.07, S 8.32, Cl 19.54. From this results can be concluded that the sulfochlorination conversion of sPEEK is about 100%.

3.1.1. Determination of the substitution degree via NMR

The protons assignment in modified PEEK repeat unit in the aromatic ring is shown in Fig. 3. The quantitative determination of substitution degree (DS) can be calculated from the peak intensity or peak area (symbol A_H) based on H_E peak by the following formula [12]:

$$\frac{n}{12 - 2n} = \frac{A_{H_E}}{\sum A_H} \quad (0 \leq n \leq 1) \quad (3)$$

$$DS(\%) = n \times 100 \quad (4)$$

The peaks of protons H_A and H_{A'} are found at high chemical shifts around 8.0 ppm (four protons). H_{B'} is placed at low chemical shift 7.0 ppm (two protons). H_B, H_C, and H_D are around 7.1–7.3 (four protons). H_E is the position which indicates the DS of the neighboring aromatic proton (X position), whose chemical shift is around 7.5 ppm. Here H_E is treated as the reference for the DS.

The ¹H NMR spectra of PEEK-SO₃H (sPEEK) and PEEK-SO₂Cl show the same chemical shifts for the aromatic range, see Fig. 4. The DS of sPEEK, which can be calculated from the H integrals, is about 0.91 which fits well with the DS value (DS = 0.98) determined by acid–base titration.

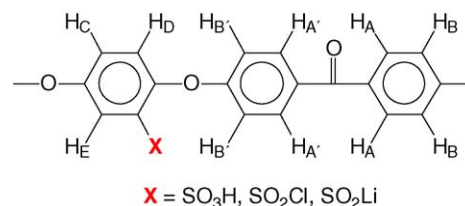


Fig. 3. Assignment of the aromatic protons of modified PEEK.

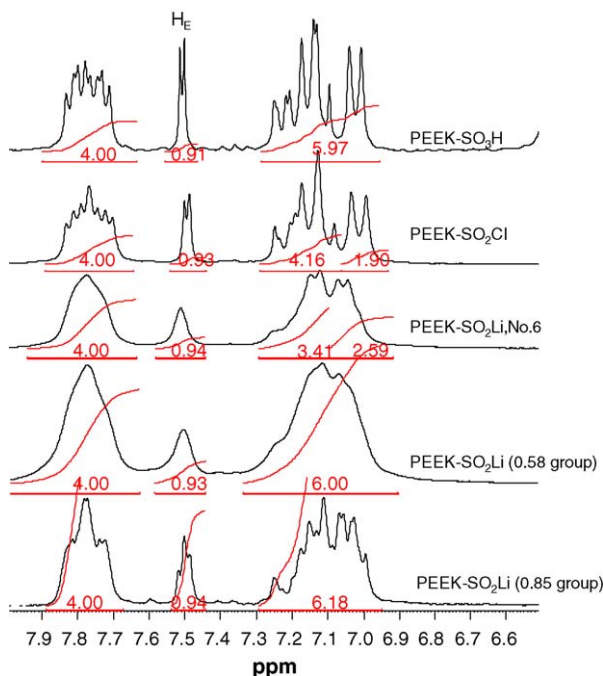


Fig. 4. ^1H NMR spectra of sPEEK, PEEK- SO_2Cl and of three PEEK- (SO_2Li) (SO_2Cl) polymers having different sulfonation degrees.

The corresponding PEEK- SO_2Cl DS value determined by ^1H integral analysis is 93.6%. The overall DS of the PEEK- (SO_2Cl) (SO_2Li) polymer obtained by partial reduction is 0.95, as determined by ^1H NMR integral analysis. In Fig. 4, the ^1H NMR spectra of the polymers PEEK- SO_3H , PEEK- SO_2Cl , and three different partially reduced PEEK- SO_2Cl (SO_2Li) are shown. Fig. 4 indicates clearly that it is not possible to distinguish between the different functional groups being attached to the PEEK backbone. Therefore, for determination of the DS of the different functional groups redox-titration was used (see below).

3.1.2. Determination of the sulfonation degree via redox titration

The reduction of the SO_2Cl to the SO_2Li group is a slow reaction, as observed for low-molecular compounds [13]. A maximum conversion rate of SO_2Cl to SO_2Li of 80% has been determined [13]. No work has been done so far on the reduction of high-molecular sulfochlorides with Na_2SO_3 . In Table 1, the results of the determination of the sulfinate group degree of different partially reduced PEEK- (SO_2Cl) (SO_2Li) polymers, which have been treated for different

Table 1
Sulfonation degree as a function of reaction time

Polymer (No.)	Reaction time (h)	Sulfinate content per RU ^a by titration (groups/repeat unit)	Conversion (%) ^b
PS-1	24	0.85	86.7
PS-2	20	0.58	59.2
PS-3	19	0.51	52
PS-4	17	0.304	31
PS-5	7	0.216	22

^a RU, repeating unit.

^b Based on PEEK $(\text{SO}_3\text{H})_{0.98}$.

time with Na_2SO_3 , via redox titration are presented. After 24 h, the conversion is about 86.7%, as determined by redox titration.

3.2. Membrane characterization results

3.2.1. Polymer sulfinate content and IEC of covalently cross-linked ionomer membranes made from these polymers

From the polymers having different sulfinate group content covalently cross-linked membranes have been prepared by addition of 1,4-diiodobutane to the NMP solutions of the polymers. After casting of the membranes and during solvent evaporation, the cross-linking reaction takes place. From Table 2, it can be seen that in most of the cases a good correspondence between calculated (from the sulfinate group content of the polymers) and experimental IEC of the membranes was found, assuming high yield in cross-linking reaction.

3.2.2. FT-IR characterization

The FT-IR spectra of unmodified PEEK and PEEK- SO_2Cl , PEEK- SO_2Li and of one of the cross-linked membranes are shown in Fig. 5.

The band of group $-\text{SO}_3\text{H}$ from sPEEK can be seen at 1083 cm^{-1} (SO_3 symmetrical stretching). The typical band of $-\text{SO}_2\text{Cl}$ is at the $1385\text{--}1360\text{ cm}^{-1}$ (SO_2 asymmetric vibration [11]). Like at the sulfonated PSU, the S=O symmetrical stretching of the sulfinate group can be seen in the range between 960 and 980 cm^{-1} [9]. For sulfonated-sulfochlorinated PEEK, the typical band is found at 970 cm^{-1} (polymer PS-2). No sulfinate band was found after cross-linking in the corresponding membrane (MPS-2), which indicates the complete alkylation of the sulfinate group and therefore complete cross-linking. In Fig. 6, the IR spectra of

Table 2
Sulfinate group content of the different prepared polymers, and IEC of the corresponding covalently cross-linked membranes

Sulfonated polymer (No.)	SO_2Li content (groups/repeat unit)	SO_2Cl content (groups/repeat unit)	Cross-linked membrane (no.)	IEC of membrane calculated (experimental) ($\text{meq}_{\text{SO}_3\text{H}}\text{ g}^{-1}$)
PS-2	0.58	0.4	MPS-2	1.0 (1.01)
PS-3	0.51	0.47	MPS-3	1.26 (1.26)
PS-4	0.304	0.676	MPS-4	1.82 (1.51)
PS-5	0.218	0.764	MPS-5	2.07 (2.0)

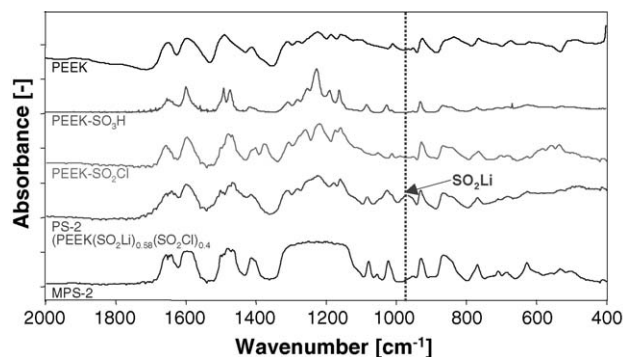


Fig. 5. FT-IR spectra of unmodified PEEK, one-fold sulfonated PEEK (sPEEK), one-fold sulfochlorinated PEEK (PEEK-SO₂Cl) and partially reduced PEEK-SO₂Cl (PEEK-SO₂Li, PS-2) and one of the cross-linked membranes (membrane, MPS-2).

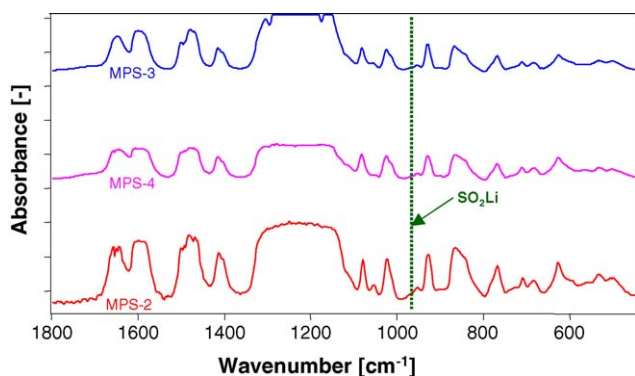


Fig. 6. FT-IR spectra of three of the cross-linked membranes MPS-2, MPS-3, and MPS-4.

three of the cross-linked membranes are shown, indicating absence of residual sulfinic groups.

3.2.3. Thermal stability

The thermal stabilities of the PEEK polymers and membranes were determined by TGA and TGA-FT-IR coupling

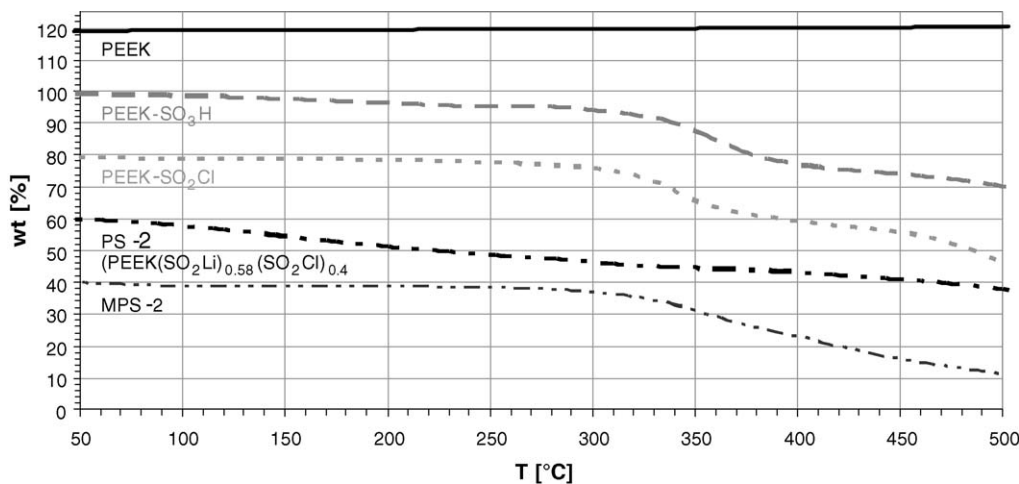


Fig. 7. Thermal gravimetric analysis (TGA) of unmodified PEEK, sulfonated PEEK (sPEEK), one-fold sulfochlorinated (PEEK-SO₂Cl) and sulfonated-sulfochlorinated PEEK (PS-2).

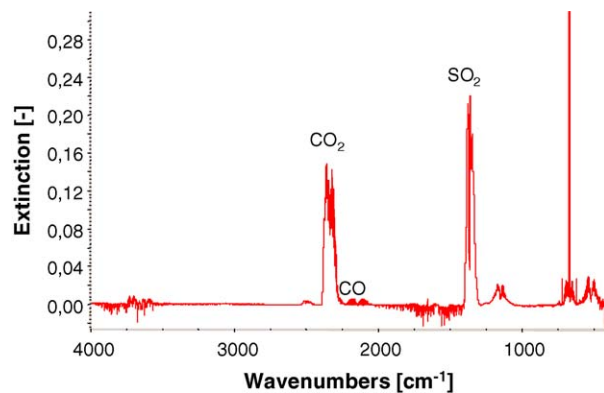


Fig. 8. FT-IR spectrum of the TGA decomposition gases at $T=350^{\circ}\text{C}$.

measurements. In Fig. 7, the TGA traces of the polymers PEEK, sPEEK (PEEKSO₃H), PEEKSO₂Cl, and PS-2 are presented.

The unmodified PEEK is very stable and a start of some degradation was observed only at high temperatures of about 580 °C due to the main chain decomposition. The major pyrolysis products are CO, phenol, and CO₂ as determined from TGA-FT-IR coupling experiments [14].

There are two steps of TGA weight loss for sPEEK. From the analysis of the TGA-FT-IR coupling data it can be determined that the splitting-off of the sulfonate group starts at $T=280^{\circ}\text{C}$, which is indicated by appearance of the SO₂ band in the FT-IR spectrum between 1288 and 1410 cm^{-1} [15]. Therefore, the first step from 280 to 480 °C is the splitting-off of the sulfonate group, the experimental weight loss is about 20% which is in good agreement with the theoretical 0.98 sulfonate group weight loss value (22.0 wt.%) by thermal splitting-off. In Fig. 8, the FT-IR-spectrum of the TGA decomposition gases of sPEEK at $T=350^{\circ}\text{C}$ is shown. The SO₂ band shows up clearly. However, also some backbone degradation is already taking place at $T=350^{\circ}\text{C}$, as is indicated by the occurring CO and CO₂ bands.

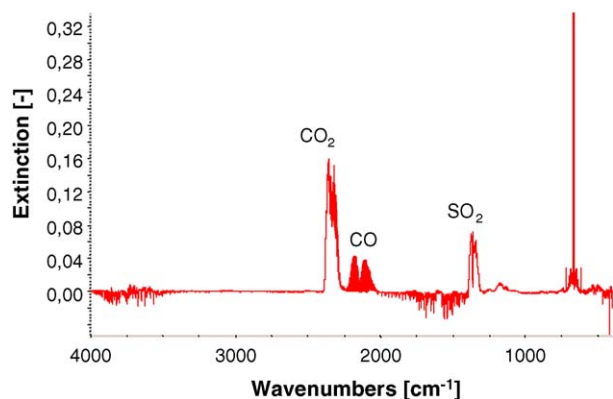


Fig. 9. FT-IR-spectrum of the TGA decomposition gases of sPEEK at $T=426.8\text{ }^{\circ}\text{C}$.

The second step is the PEEK backbone degradation beginning at about $320\text{ }^{\circ}\text{C}$, which is indicated by appearance of CO ($2032\text{--}2240\text{ cm}^{-1}$) double band and CO_2 band ($2240\text{--}2400\text{ cm}^{-1}$). In contrast to unmodified PEEK, the thermal cracking product phenol ($3150\text{--}2970\text{ cm}^{-1}$) could not be observed in the thermal cracking gases of sPEEK. Obviously the thermal stability of the PEEK backbone decreases markedly when it is chemically modified. Fig. 9 shows the FT-IR-spectrum of the TGA decomposition gases of sPEEK at $T=427\text{ }^{\circ}\text{C}$, mainly consisting of CO and CO_2 .

The PEEK- SO_2Cl sulfochloride group is split off beginning at about $240\text{--}450\text{ }^{\circ}\text{C}$. The weight loss is about 23% which is in good agreement with the theoretical 0.98 sulfochloride group/repeat unit weight value (22.0%). The sulfinate group of the polymer is decomposed from 50 to $320\text{ }^{\circ}\text{C}$ in a partially reduced PEEK (PS-2). The 15% weight loss is higher than the theoretical SO_2Li group weight (about 11.1%) of 0.58 groups/repeat unit. This means that up to $320\text{ }^{\circ}\text{C}$ also the splitting-off of the residual SO_2Cl groups has started. From 280 to $480\text{ }^{\circ}\text{C}$ is due to $-\text{SO}_2\text{Cl}$ splitting-off, the weight loss is about 10% which is in good agreement compared with the theoretical value 8.96% for 0.42 group $-\text{SO}_2\text{Cl}$ /repeat unit. From about $500\text{ }^{\circ}\text{C}$, the accelerated degradation of the polymer backbone takes place. In Fig. 10, the TGA traces of the membranes MPS-2, -3, -4, -5 are shown together with the TGA trace of a blend

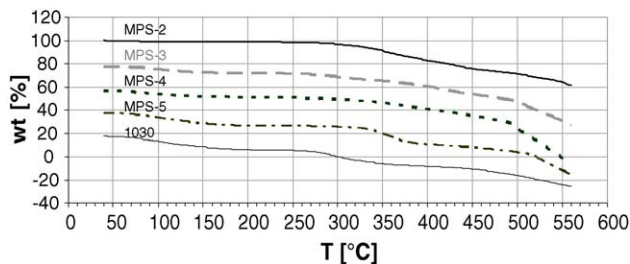


Fig. 10. TGA traces of the membranes MPS-2, -3, -4, -5 and the TGA trace of the blend membrane 1030.

membrane denoted as “1030”, which is composed of sPEEK ($\text{IEC}=2.7\text{ meq g}^{-1}$) and PSU- SO_2Li (1 group/repeat unit), which was cross-linked with 1,4-diiodobutane and showed comparable IEC and H^+ -conductivity as the MPS-three membrane (description of the synthesis, composition and properties of 1030 membrane see [16,17]). Fig. 10 shows clearly that the cross-linked PEEK ionomer membranes have a better thermal stability than the blend membrane 1030. An in-depth analysis of the thermal stability of the two membranes MPS-3 and 1030 via TGA-FT-IR coupling indicates that the start temperature of the SO_3H group splitting-off is $241\text{ }^{\circ}\text{C}$ in the MPS-3 membrane, and $228\text{ }^{\circ}\text{C}$ in the 1030 membrane.

For the membrane MPS-3 both the sulfonate group ($-\text{SO}_3\text{H}$) decomposition and cross-linking bonds ($-\text{SO}_2-\text{CH}_2-$) degradation takes place from 240 to about $450\text{ }^{\circ}\text{C}$ which corresponds to about 24.06% weight loss. This is also in good agreement with the theoretical weight percentage of both sulfonate and (cross-linked) sulfinate groups of 24.2%. At $450\text{ }^{\circ}\text{C}$ to higher temperatures, the thermal degradation of the polymer backbone starts.

3.2.4. Water uptake of the membranes in dependence on the IEC and temperature

The swelling as a function of IEC at ambient temperature is shown in Fig. 11. The swelling is lower than 40% for low IEC at ambient temperature ($25\text{ }^{\circ}\text{C}$) and shows a slight increase to about 1.5 meq g^{-1} . For higher IECs it strongly increases (MPS-5). At 2.0 meq g^{-1} , the swelling is more than 170% at ambient temperature. Of course, this large swelling decreases the mechanical stability of the membrane.

The dependence of the water uptake behaviour on the temperature was also studied, see Fig. 12. At lower ion-exchange capacities ($\text{IEC}<1.26$), the swelling only slightly increases with temperature. This is advantageous for the application in fuel cells. When the membrane IEC is 2.0 meq g^{-1} (MPS-5), the swelling sharply increases to a high level at about $40\text{ }^{\circ}\text{C}$. The high swelling degree remains constant at high temperatures. Interestingly, the swelling value of the blend mem-

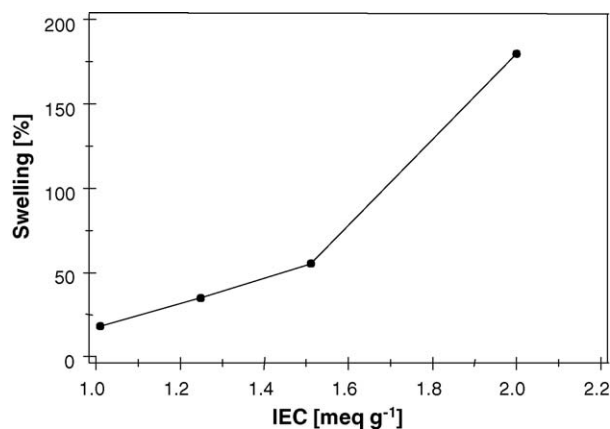


Fig. 11. The swelling (water uptake) at ambient temperature as a function of IEC of the cross-linked MPS membranes.

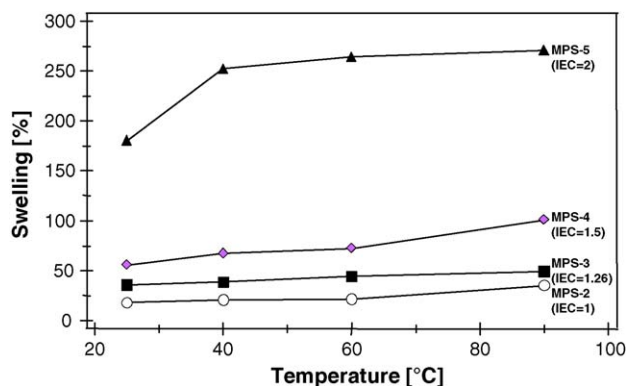


Fig. 12. Water uptake as a function of the temperature for the MPS membranes: MPS-2 (IEC = 1.01), MPS-3 (IEC = 1.26), MPS-4 (IEC = 1.51), and MPS-5 (IEC = 2 meq g⁻¹).

branes (not shown here) is higher at the same temperature although the IEC is lower. In particular, the blend membrane 1030 which has an IEC of 1.15 meq g⁻¹ at 90 °C exhibits a swelling of 57.5%, which is higher than the swelling value of the membrane MPS-3 with 50% swelling at the same temperature (MPS-3 has an IEC of 1.26 meq g⁻¹). This finding indicates that it is advantageous to prepare membranes in which all of the macromolecular chains are integrated in the covalent network, as it is the case at the MPS membranes. In the blend membrane 1030, the sulfonated blend component is only entangled in the network formed of PSU-sulfinate and 1,4-diiodobutane, which leads to higher swelling of the membrane at elevated T and can even lead to partial bleeding-out of the sulfonated macromolecules at $T > 100$ °C.

3.2.5. Dependence of membrane resistance on IEC

The special H⁺ resistance ($R_{sp}^{H^+}$ (Ω cm)) of the membranes in dependence on the IEC is shown in Fig. 13. The R_{sp} decreases as the IEC increases. Interestingly, the membrane MPS-3 shows a specific resistance being in the same range as the $R_{sp}^{H^+}$ of the Nafion 117 membrane (10 Ω cm). The $R_{sp}^{H^+}$ value of the 1030 blend membrane (IEC = 1.15 meq g⁻¹) is 9.4 Ω cm, being in the same range as at the MPS membranes having comparable IEC.

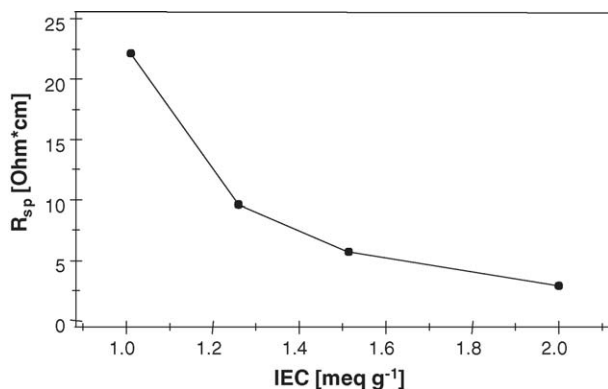


Fig. 13. $R_{sp}^{H^+}$ of the MPS membranes as a function of the IEC.

3.2.6. Cross-linking degree of the MPS membranes

The starting polymer which was subjected to partial reduction is water-soluble (the sulfonated PEEK having an IEC of 2.7 meq g⁻¹). The membranes which have been prepared from the different partially reduced sulfonated-sulfonated PEEKs are all water-insoluble which is a strong indication for complete cross-linking. In order to investigate whether the membranes contain nevertheless soluble components, the membranes were first weighed in dry state, then immersed in 90 °C hot *N,N*-dimethylacetamide (DMAc) for 3 days, and finally washed with methanol and dried to constant weight. If the membranes still would contain soluble components these would be extracted by the hot DMAc which is an excellent solvent for polymers of the investigated type. It was found that none of the membranes suffered weight loss which led us to the conclusion that the covalent network was formed completely, confirming the IR results of the membranes (Figs. 5 and 6). In the spectra, no residual sulfinate bands could be found.

3.2.7. Application of sulfonated PEEK in DMFC

The partially sulfonated PEEK (PEEK-31/PS-2, with 0.58 group -SO₂Li and 0.42 group SO₂Cl) membranes which were cross-linked with diiodobutane to form a proton exchange membrane with 1.01 meq g⁻¹ IEC (MPS-2) were tested in a 25 cm² single cell DMFC. Unsupported catalysts from Johnson Matthey were used with high noble-metal loadings in order to first test the function of the novel membranes without too much interference from the electrodes. The anode contained about 5.3 mg cm⁻² Pt-Ru black whereas in the cathode about 6.5 mg cm⁻² Pt black was used. For 1 M methanol solution and air condition, the measured $U-I$ curves for different temperatures and different air flows are shown in Fig. 14. The open circuit voltage in the range of 765–790 mV is similar for all conditions. This is interesting as the concurrently measured methanol cross-over rate increases with higher temperature and higher air or methanol flow rates. One would expect that the varying methanol con-

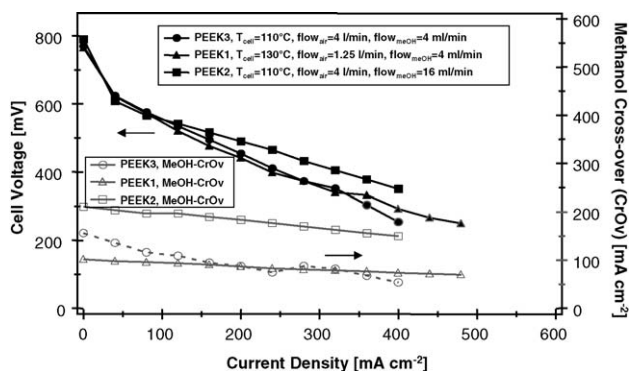


Fig. 14. Polarization curve of the cross-linked partial sulfonated PEEK membrane in a DMFC test, 25 cm², anode: PtRu/C 5.3 mg cm⁻², cathode: Pt/C 6.5 mg cm⁻², 1 mol methanol solution, pressure anode: 1.5 bar (abs), cathode 3 bar (abs), humidification temperature: 80 °C, other conditions as indicated in the figure.

centrations at the cathode would lead to a significant mixed potential formation and thereby affect the open cell voltage. The absence of a pronounced influence on the open cell voltage indicates that the high air flow rates used can compensate the detrimental effect of the presence of methanol at the cathode. The U – I curves for all conditions are similar up to about 100 mg cm^{-2} . From 100 to 400 mg cm^{-2} large differences between the different testing conditions are observed and the best performance is observed at 110°C with the highest flow rates at the anode (16 mL min^{-1}) and cathode (4 L min^{-1}). This is also the operation condition exhibiting the highest methanol cross-over rates. It is often observed with numerous different membrane materials that high methanol cross-over rates do not necessarily mean low performance [10,15]. The partially sulfinated PEEK membranes show stable operation in the DMFC, however, the performances achieved are not as high as with other polyarylene membranes or Nafion105 [10,15]. This may be due to lower proton conductivity of these systems. It should be pointed out here that the area resistance of the membrane used in the DMFC testing is considerably higher compared to Nafion 105 (about 0.18 – $0.23 \Omega \text{ cm}^2$ for the PEEK membrane versus $0.12 \Omega \text{ cm}^2$ for Nafion 105). As a conclusion, the membranes show promising DMFC performance but need to be optimized. We expect improved performance after further development as was observed for other membrane systems [15].

4. Conclusions

A promising new route for covalently cross-linked PEEK membranes was developed via synthesis of PEEK polymers with both sulfinic and sulfonate groups onto the same backbone. The new cross-linked membranes are thermally stable, show low resistance and reduced water uptake which only moderately increases with temperature. A good H^+ -conductivity is measured although the membranes show reduced swelling. The investigation of one of the membranes

in a DMFC shows stable performance under air condition and elevated temperatures of up to 130°C . Further optimization in the DMFC application is however needed. In ongoing research, the transferability of Na_2SO_3 sulfochloride reduction process to other poly(etherketone sulfochloride)s will be investigated.

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