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Sulfonated Poly(styrene)s-PBIOO® Blend Membranes: Thermo-Oxidative Stability and Conductivity

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ABSTRACT: Low-cost polymers poly(styrene) and poly(α-methylstyrene) have been sulfonated followed by blending with PBIOO® (30 wt % sulfonated ionomer, 70 wt % PBIOO). At this polymer ratio the sulfonated ionomer served as the macromolecular acidic cross-linker which led to enhancement of the PBIOO stability. Both membrane types were treated with Fenton's Reagent to investigate their resistance to oxidation and radical attack. Indeed, the blend membranes showed enhanced stability in oxidative conditions compared to the pure PBIOO membranes. Furthermore, the sulfonated poly(α-methylstyrene)-PBIOO blend membrane showed less weight loss during and after Fenton's Test than the corresponding poly(styrene sulfonic acid)-PBIOO membrane. Assuming all the characteristics of the blend membrane before and after the Fenton's Test, we concluded for a partial degradation of both sulfonated poly(styrene)s, whereas they remain in the blend membrane matrix due to the acid-base crosslinking. Thus, since the sulfonated poly((α-methyl)styrene)-PBIOO blend membranes conserved their integrity even after Fenton's Test they can be regarded as potential low-cost high-T fuel cell membranes. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2013**, *000*, 39860.

INTRODUCTION

H_3PO_4-doped polybenzimidazole (PBI) membranes can be used as proton conductors in fuel cells in the temperature range between 100 and 200°C, as shown by Wainright et al.[1] Main issues of these membranes are (i) the potential danger of leaching-out of phosphoric acid when the fuel temperature falls below 100°C due to condensation of water produced in the fuel cell reaction; (ii) their long-term stability in fuel cell operation. If the operation temperature of this fuel cell membrane type is well above 100°C, long-term stabilities of more than 6,000 h have been reported.[2] Accelerated fuel cell degradation tests such as Fenton's Test have uncovered unsatisfying radical degradation stabilities of this membrane type.[3] Efforts to improve the resistance to radical degradation and reducing the leaching-out of the dopant have been reported in the literature: (a) ionic cross-linking of the PBI by blending with a sulfonated ionomer;[3,4] (b) covalent cross-linking of the PBI;[5] (c) doping of the PBI with inorganic nanoparticles such as α-ZrP;[6] (d) preparation of meso-porous PBI membranes[7] and (e) substitution of PBI by other basic polymers such as pyridine building block-containing poly(arylene)s.[8] In recent contributions we have shown that PBI Celazol® membranes blended with a partially fluorinated arylene main-chain ionomer prepared by polycondensation of

decafluorobiphenyl with bisphenol AF comprise improved oxidative resistance, compared with pure PBI Celazol.[3,9] Moreover, this membrane type is not soluble in hot H_3PO_4, in contrast to PBI Celazol—obviously the ionic cross-links present in the blend membrane prevent dissolution. In another article, we have shown that the combination of the abovementioned sulfonated, partially fluorinated ionomer with electron-deficient polybenzimidazoles such as F_6-PBI and SO_2-PBI leads to further improvement of the stability of the blend membrane in oxidative environment.[10] Fuel cell tests of a SO_2-PBI-sulfonated ionomer blend membrane indicated good performance in the operating temperature range between 125 and 200°C.[10] The disadvantages of these blend membranes are the high synthetic effort for the preparation of both electron-deficient PBIs and partially fluorinated arylene main chain ionomers and the monomer costs being too high for commercialization. In order to reduce the costs, a commercial Fumion PBIOO® (FumaTech) and sulfonated poly(styrene) (PSSA) and poly(α-methylstyrene) (PαMSSA) have been selected as low cost polymers. However, poly(styrene) is nonresistant to radical attack (e. g. ·OH or ·OOH radicals which are always present in membrane fuel cells) due to cleavage of the tertiary C-H bond and therefore prone to fast membrane degradation.[11] The matter of choice for low cost

polymers which do not contain α-C-H bonds is poly(α-methyl-styrene). However, the monomer (α-methylstyrene) comprises a low ceiling temperature of 61.5°C in bulk[12] (e. g. the temperature at which $\Delta G_{polym} = 0 \rightarrow \Delta H_{polym} = T\Delta S_{polym}$) which renders the access to high molecular weight poly(α-methylstyrene). Nevertheless, poly(α-methylstyrene) has been obtained by a radical polymerization under high pressure at temperatures higher than its ceiling temperature.[13] Alternatively, polymers containing α-methylstyrene units have been prepared by copolymerization of α-methylstyrene with other monomers such a methacrylonitrile.[14] Gubler and Scherer have recently succeeded in grafting alternating copolymers of α-methylstyrene and methacrylonitrile onto fluorinated ethylene propylene (FEP) foils irradiated with a ^{60}Co γ-source.[15] After sulfonation of the poly(α-methylstyrene-alt-methacrylonitrile) grafted copolymer side chains the membranes were tested in a PEM fuel cell and showed higher stability than graft polymers from FEP and PSSA. In an earlier study Assink et al. investigated the oxidation stability of styrene and α-methylstyrene grafted onto poly(tetrafluoroethylene) (PTFE), followed by sulfonation of the phenyl rings. The grafted films were investigated in terms of oxidative stability by immersion in $K_3Fe(CN)_6$/5N NaOH solutions, followed by cycling test in a zinc/ferricyanide cell. It has been clearly shown that the α-methylstyrene-grafted membrane possessed under these conditions much higher oxidation stability than the styrene-grafted film.[16]

In this contribution we report on preparation and characterization of base-excess (70 wt % PBIOO®, 30 wt % sulfonated ionomer) acid-base blend membranes from PBIOO® and self-prepared PSSA and PαMSSA. The aim of this study was to find out whether the thermo-oxidative resistance of PαMSSA-PBIOO® is better than of PSSA-PBIOO blend membranes, due to the lack of radical sensitive C-H bonds in PαMSSA. Thus, Fenton's Test-aged membranes analyzed by elemental analysis and scanning electron microscopy—energy dispersive X-ray spectroscopy (SEM-EDX) were compared with the nonaged membranes. Moreover, the H_3PO_4 doping of the blend membranes was investigated in terms of doping properties and compared with the pure PBIOO membranes at the same doping conditions. The proton conductivity of the H_3PO_4-doped membranes was investigated in dependence of temperature and in dependence of humidification.

EXPERIMENTAL

Sulfonation of Poly(styrene) (PS) and Poly(α-methylstyrene) (PαMS)

The sulfonation of both PS and PαMS was done according a procedure described elsewhere.[17]

Blend Membrane Preparation

Separately, PSSA/PαMSSA in H^+-form were dissolved in DMAc to give a 10% solution. After that, n-propylamine was added to neutralize the SO_3H groups. Then poly-[(1-(4,4'-diphenylether)-5-oxybenzimidazole)-benzimidazole (PBIOO®) a 10% solution in DMAc was prepared and added to the PSSA/PαMSSA solutions. The final ratio of P(αM)SSA/PBIOO® was adjusted to 30/70 wt %. The solutions were poured into petri dishes and

dried at $T = 130$°C, 20 mbar for 2 h. After that, deionized water was poured on top of the polymer films to detach the so-formed membranes from the glass surface. Finally, the membranes were immersed in 10% HCl at 90°C for 48 h to induce the formation of the ionic cross-linking in the membrane followed by rinsing in water at 60°C for 48 h to remove low molecular acid residuals from the membrane matrix.

Characterization of Polymers and Blend Membranes

Ion-Exchange Capacity (IEC). PSSA and PαMSSA, both in acid form, were conditioned in an excess of 0.1N NaOH (RT, 24 h). After that, the solution was back-titrated against phenolphthalein with 0.1N HCl to determine the consumption of NaOH, and thus the IEC.

Thermal Stability. Thermal stability of the membranes was determined by thermogravimetry (TGA, Netzsch, model STA 449C) with a heating rate of 20°C/min under an atmosphere enriched with oxygen (65–70% O_2, 35–30% N_2). The decomposition gases were further analyzed in a FT-IR spectrometer (Nicolet Nexus FT-IR spectrometer) coupled to TGA in order to identify the degradation co-products of the membranes. The splitting-off temperature of the sulfonic acid group ($T_{SO_3H}^{onset}$) was determined by using the IR-active asymmetric stretching vibration of the S=O group at 1410 to 1302 cm^{-1}. The TGA-FTIR coupling experiment is described in a previous article.[18]

Elemental Analysis of the Blend Membranes. Elemental analyses (%S, %N) were accomplished by combustion of the membranes in an automated elemental analyzer at the Institute of Organic Chemistry of the University of Stuttgart.

Fenton's Test Experiments. A Fenton's Solution of 3 wt % H_2O_2 containing 4 ppm Fe^{2+} was used. Fe^{2+} was added as $(NH_4)_2Fe(SO_4)_2\cdot6H_2O$ in order to accelerate the hydroxyl radical production. Membrane samples were immersed in the Fenton's Solution at 68°C. After a certain period of time, the membrane samples were removed from the oxidizing solution, washed with water, dried at 120°C for 2 h and weighed. For successive measurements, fresh Fenton's Solution was prepared and preheated every 24 h, in which the dried membrane samples were immersed continuously.

Molecular Weight Determination via GPC (SEC). The molecular weight distribution of the blend membranes was measured before and after the Fenton's Test degradation by gel permeation chromatography (GPC)/size exclusion chromatography (SEC), carried out with an Agilent Technologies GPC system (Series 1200) using a light scattering detector (static light scattering detector SLD7000) combined with a viscosimetry detector (PSS ETA-2010) and a refractive index detector (Shodex RI71 for the concentration signal). The M_w of the polymers were obtained directly from the light scattering detector signal. The PSS WinGPC software uses a mathematical procedure, based on the work of Radke et al.,[19] to calculate the M_n from M_w. For the GPC analysis, 2 wt % solutions of the polymers and membranes in DMAc were prepared. For suppression of intra- and intermolecular polymer interactions and interactions of the macromolecules with the column material, 5 g/L LiBr was added to the polymer solutions before measurement. Toluene was added to

the solutions in order to correct any reversible changes in the column system. The molar mass distribution was measured with a flow rate of 1 mL/min at 50°C. For analysis of the received data we used the universal calibration as described by Benoit et al.[20,21] Due to the fact that the base-acid blend membranes were ionically cross-linked, they could not simply be dissolved after they were removed from the Fenton's Test. The ionic cross-linking sites in the membranes had to be broken before their dissolution in DMAc was possible. For doing so, the membranes from Fenton's Test solution were washed carefully with desalinated water to remove residuals of H_2O_2 and Fe salts. The membranes were then subjected to a $1N$ NaOH solution to break the acid-base interactions at 90°C. Thereafter, the membrane pieces were again washed with desalinated water to remove NaOH residuals from the membrane, followed by drying at 90°C for 24 h.

Scanning Electron Microscopy (SEM) of the Membranes. Onto the membrane surfaces ultra-thin Au or C layers were placed via vacuum deposition to make them electrically conductive. Consecutively, the membranes were investigated in the scanning electron microscope. In addition to the scanning electron micrographs, also EDX analyses of the membranes (surface and cross-section) were performed.

H_3PO_4 Doping Experiments. Initially, the membranes were doped in 85% H_3PO_4 at a temperature of 130°C for 15 and 30 min, respectively. After doping the weight increase of the membranes was determined. From the weight increase, the amount of H_3PO_4 molecules per PBIOO imidazole group was calculated.

For a better control on the doping level, further doping experiments were performed: the membranes were slowly doped by gradually increasing the temperature and the doping time. All the membranes were introduced into 85% H_3PO_4, removing membrane samples after conditioning at certain conditions. Initially, the blends were doped in 85% H_3PO_4 at RT for 20 h followed by $T = 80°C$ for 1 h and 2 h and $T = 100°C$ for 1 h and 2 h (see doping level as function of doping conditions in Figure 1).

Determination of the H^+ Conductivity of the Blend Membranes Doped with H_3PO_4. Through-plane conductivity measurements were carried out in a Membrane Test System (MTS 740) from Scribner Associates Inc. The sample chamber is equipped with both temperature and humidity sensors which allowed accurate recording of both temperature and relative humidity at the near proximity to the sample. Detailed description and the technical data for the setup are given elsewhere.[22]
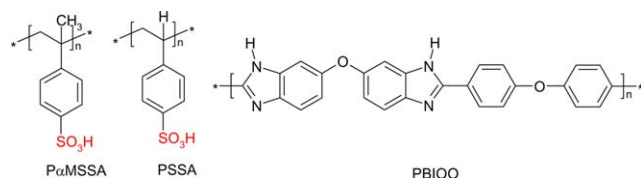

Figure 1. Polymers for the blend membranes investigated in this study. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The membrane samples 3 × 1 cm were compressed between gas diffusion layers (GDE) (E-TEK ELAT GDE 140-HT) and attached to the platinum electrodes with conductive carbon paint. Porous GDLs were used to facilitate gas-phase diffusion of water vapor to and from the membrane. The sample compressive loading was kept at 1.4 MPa for sufficiently good contact between the electrodes, GDEs and the membrane sample. Pretest showed that the membrane is equilibrated at given conditions in 10 min. Therefore after initial equilibration, the membrane samples were conditioned 15 min at each set of condition before run electrochemical impedance spectrometry (EIS) (Impedance Analyzer 1260, Solartron Analytical). A typical procedure for $T = 120°C$ and RH = 10 to 70% consists of preconditioning the sample at RH 70% for 30 min, followed by decreasing the RH with steps of 10%, conditioning for 15 min follow by five EIS measurements at each step. The specific conductivity was obtained from $\sigma = l/(A \times R)$, where l is the membrane thickness, A the overlapping area of the electrodes, and R the resistance derived from the high-frequency intercept of the complex impedance with the real axis.

RESULTS AND DISCUSSION

Sulfonation and Polymer Blends Preparation

PSSA and PαMSSA were obtained via sulfonation of PS and PαMS with fuming sulphuric acid by a well-known procedure.[17] In this particular case, strong molecular weight degradation took place when applying the original procedure to PS and PαMS when the reaction temperature was kept at 40°C (see Table I). The molecular weight degradation was much stronger in the case of sulfonation of PαMS, which might be attributed to its low ceiling temperature. The degradation of PαMS could be markedly reduced by reducing the reaction temperature down to 0°C. Despite the molecular weight loss, the ion-exchange capacities of both sulfonated polymers remained nearly the same ($IEC_{PαMSSA} = 4.5$ meq g^{-1}, $IEC_{PSSA} = 4.8$ meq g^{-1}). This, together with the equal degree of sulfonation for both PSSA and PαMSSA, being 82%, stands for the identical reactivity of both polymers under sulfonation conditions applied in this study. The high degree of sulfonation makes the polymers water soluble and therefore, they showed poor film forming properties.

In order to prepare polymer films, PSSA and PαMSSA were blended with the polybenzimidazole PBIOO. Stabilization of the blend polymer films occurs by the transfer of protons from the acid to the base functions of the polymers. The resulting ion-pairs along the polymer chains are holding the polymer scaffolds tightly together, leading to enhanced stability of the whole polymer membrane matrix. In this study base-excess blend membranes were prepared by blending PSSA and PαMSSA with PBIOO in the ratio of 30/70 wt % respectively. Since PSSA/PαMSSA has a content of only 30 wt % of the blend membrane, its functional groups (sulfonic acids) are completely protonating the basic PBIOO and are therefore solely acting as ionic cross-linker. Therefore, there are remaining unprotonated imidazole functions of PBIOO in the blend membrane which can be doped with phosphoric acid. By the attachment of H_3PO_4 molecules to the basic imidazole sites, the phosphoric acid is partially immobilized in the doped blend membrane. The ratio

Table I. M_w, M_n, and PDI Values of the Poly(styrene)s and the Respective Sulfonated Constituents, Determined via GPC (SEC)

Polymer	IEC [meq/g]/DS [SO₃H/RU]	M_n [Da]	M_w [Da]	PDI
Poly(α-methylstyrene) (Aldrich)	–	69,700[a]	103,600[a]	1.48
sJK1b(PαMSSA)	4.46/0.82	12,650[a]	31,900[a]	2.5
Polystyrene (Aldrich)	–	194,440[a]	362,000[a]	1.86
sJK2a (PSSA)	4.84/0.82	63,000[b]	86,000[b]	1.35

[a] Viscosity detector.
[b] Light scattering detector.

between the acidic and the basic polymer of is optimized to 30/70 wt % to provide simultaneously high mechanical stability and sufficient basic functionalities available for efficient doping with phosphoric acid.

Thermal Stability
In Figure 2, the TGA traces of both (a) PαMSSA and blend membrane PαMSSA-PBIOO as well as (b) PSSA and PSSA-PBIOO blend membrane are presented. The TGA of pure PBIOO is given for comparison. It is clearly seen that the thermal stability of the blend membranes is significantly higher than that of the sulfonated poly(styrene)s and the PBIOO. The reason for the higher thermal stability of the blend membranes, compared with the pure polymers, are the ionic cross-linking sites between the basic and acidic polymers, as shown in many of our studies in the past (e. g. see the review[23].

Furthermore the resistance of the blends to oxidation and radical attack was examined by Fenton's Test (FT). In Table II, the

Figure 2. TGA traces of (a) sulfonated poly(α-methylstyrene) (PαMSSA), PBIOO®, and the blend membrane 1684 (70 wt % PBIOO®, 30 wt % PαMSSA); (b) sulfonated poly(styrene) (PSSA), PBIOO®, and the blend membrane 1585 (70 wt % PBIOO®, 30 wt % PSSA) before Fenton's Test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

onset of splitting-off temperatures $T_{SO_3H}^{onset}$ of the sulfonated poly(styrene)s and the corresponding blend membranes before and during FT are presented. Comparing the $T_{SO_3H}^{onset}$ values of the sulfonated poly(styrene)s with those of the blend membranes, a strong increase of thermal stability can be seen both for the PαMSSA-PBIOO and PSSA-PBIOO blend membranes. The thermal stabilities of the PαMSSA blend membranes were slightly better than the thermal stabilities of the PSSA blend membranes. On the other hand, the $T_{SO_3H}^{onset}$ value of the PαMSSA is about 21°C lower than that of the PSSA. This could be due to the markedly lower molecular weight of PαMSSA, compared with PSSA. Generally, the $T_{SO_3H}^{onset}$ values of the sulfonated poly(-styrene)s-PBIOO blend membranes are much lower than those of sulfonated arylene-PBI blend membranes, which is due to the much better thermal stability of sulfonated arylene main-chain polymers ($T_{SO_3H}^{onset}$ of sulfonated poly(arylene)-PBI blends synthesized in our group, lying between 406 and 435°C,[24], compared with the sulfonated poly(styrene)s. Interestingly enough, at both blend membranes the $T_{SO_3H}^{onset}$ values remain nearly constant over the whole FT treatment time which is a strong indication for preservation of the macromolecular blend membrane structure through the ionic cross-linking network inside the membrane despite the radical attack to the macromolecules.

Results of Fenton's Test Degradation
Membrane Weight Loss During Fenton's Test (FT). In Figure 3, the membrane weight loss values of the PαMSSA-PBIOO and the PSSA-PBIOO blend membranes in dependence of FT treatment time are presented together with the weight loss of the
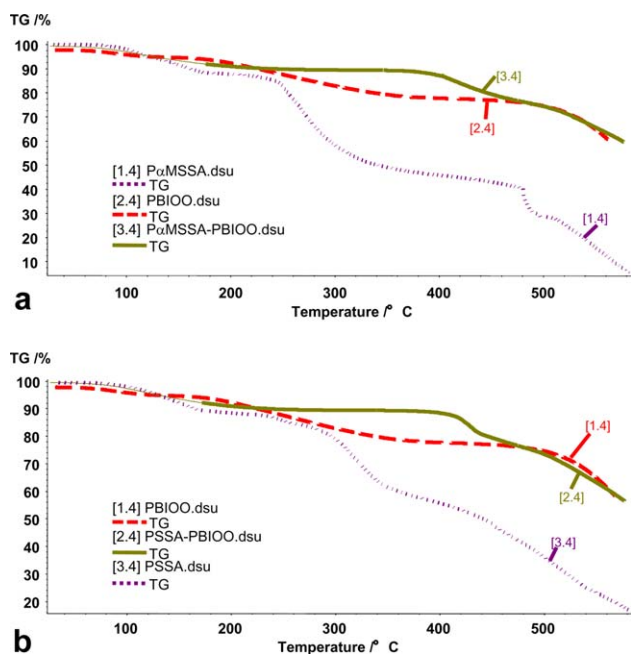
Table II. Onset-of SO₃H-Splitting-off Temperatures ($T_{SO_3H}^{onset}$) in °C of the Sulfonated Poly(styrene)s and the Referring Blend Membranes and S and N Content of the Blend Membranes before and during Fenton's Test

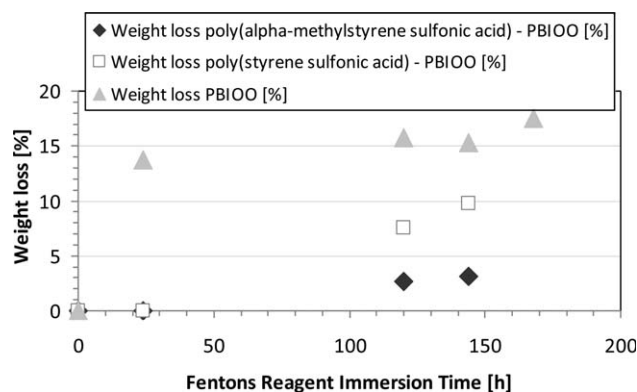| Polymer/membrane	$T_{SO_3H}^{onset}$ [°C]	S content [%]	N content [%]
sJK1b (PαMSSA)	192	NA	NA
sJK2a (PSSA)	213	NA	NA
1684_0 h	379	5.6	7.93
1684_24 h	372	–	8.1
1684_120 h	372	4.98	8.1
1684_144 h	370	4.57	8.08
1685_0 h	363	5.02	8.01
1685_24 h	365	4.84	8.23
1685_120 h	356	5.3	8.24
1685_144 h	357	5.06	8.22

Figure 3. Membrane weight loss during Fenton's Test.

pure PBIOO membrane for comparison. It is clearly seen that (1) the weight loss of the pure PBIOO is markedly higher than the weight loss of the blend membranes which is obviously caused by the ionic cross-linking of the blend membranes, and (2) the weight loss of the PαMSSA-PBIOO blend membrane is markedly lower than that of the PSSA-PBIOO membrane which is a strong indication for better oxidative stability of the PαMSSA, compared with PSSA. This is most probably due to the absence of tertiary C-H bonds in PαMSSA which are primarily susceptible to radical attack as already pointed out.[11,16]

It is interesting, too, that the weight loss of the PBIOO blend membranes starts later (only after 24 h) than that of the pure PBIOO. This time lag of the degradation is obviously caused by the ionic cross-linking of the blend membranes which retain the already partially degraded PBIOO macromolecules in the membrane matrix.

Change of Elemental Composition of the Membranes During FT. An important question is which of the blend components degrades faster. Therefore, elemental analyses were performed from the FT membrane samples before, and after different durations of FT. The %S and %N values are referring the content of the sulfonated poly(styrene) and the PBIOO, respectively (Table II). In case of PαMSSA-PBIOO, a slight decrease in S content of the membranes is found which is due to splitting-off of a part of the SO_3H groups from the PαMSSA during FT. The N content of the membranes remains in the same range which denotes constant degradation of the PBIOO macromolecules during FT. For PSSA-PBIOO, the S content remains constant within experimental error which might be an indication for degradation (depolymerization) of the PSSA macromolecules coupled with a constant degradation of the PBIOO chains during FT. Assuming the results of the weight losses, it is likely that the PSSA mainly depolymerises via radical attack to the tertiary C-H bond, while the degradation of the PαMSSA chains involves both partial desulfonation and depolymerization of the PαMSSA main chain.

Molecular Weight Distribution Determination. Before, during and after the FT the membrane samples were investigated by GPC (SEC) to monitor the effect of radical attack degradation onto molecular weight distribution (MWD) of the blend membranes and the pure PBIOO. Unfortunately, it is impossible to

separate the blend mixture into the blend components by SEC (Figure 4). An explanation for this behavior is in the strong ionic interactions between the blend components. On top of this, van der Waals, dipole-dipole and electrostatic interactions, as well as hydrogen bridges cannot be excluded.[25] Such stabilization of blend polymer membrane was already established for similar sulfonated ionomer-PBI blends.[10] In general, a success in separation of the components of a polymer blend has been obtained by coupling of the two chromatography techniques SEC (separation via different sizes of the macromolecules) and HPLC (separation via affinity differences of the macromolecules towards the column material).[26]

Molecular weight diagram (MWD) of the pure PBIOO membrane before and after FT is presented in Figure 4(c). One can clearly see that only slight and steady molecular weight degradation takes place during FT which is indicated by a shift of the molecular weight towards lower values. Figure 4(d) shows the MWD of the PαMSSA-PBIOO membrane, and Figure 4(e) the MWD of the PSSA-PBIOO membrane, during and after FT. In contrast to pure PBIOO, the molecular weights of the two blend membranes first shift to lower values up to 120 h of FT treatment, while after 144 h of immersion in FT the nondissolved membrane samples again show a virtual molecular weight increase which can be explained in the following way: during immersion in Fenton's Reagent, the degraded macromolecular chains are dissolving into Fenton's Solution which leads to a higher mean molecular weight of the remaining portion of non-dissolved membrane constituents.

It is interesting to mention that after 24 h of FT treatment the membranes were not soluble in DMAC anymore. Reason for the insolubility was possibly temporary cross-linking of the blend membrane by recombination of radical sites formed in the membranes during FT. By further FT treatment (120 and 144 h) the chain scission continues (including chain scission of the cross-links) so that the membrane becomes soluble again.

The molecular weight increase (disappearance of the lower molecular weight fraction at PαMSSA-PBIOO) at the membrane samples after 144 h of Fenton's treatment can be explained again with the accelerated degradation of lower molecular weight constituents of the blends and, after degradation, the dissolution of the macromolecule fragments in Fenton's Reagent solution so that they no longer can be captured by the SEC. The SEC results of the blend membranes clearly show that the membrane degradation by FT, where the radical concentration is much higher than in real fuel cell operation,[27,28] is not severe in the case of the investigated membrane types here. This statement is supported by the fact that the membranes do not lose their mechanical integrity after FT.

SEM Characterization of the Blend Membranes Before and During FT. In Figure 5, scanning electron micrographs (SEM) of the pure PBIOO before [Figure 5(a)] and after 120 h of FT [Figure 5(b)] are presented. It can be seen in (b) that after 120 h of treatment only a few holes have been formed on the membrane surface. The surface of the PαMSSA-PBIOO membrane shows a slightly higher roughness (hole defects) than the pure PBIOO membrane [Figure 5(d)], which can be explained with a
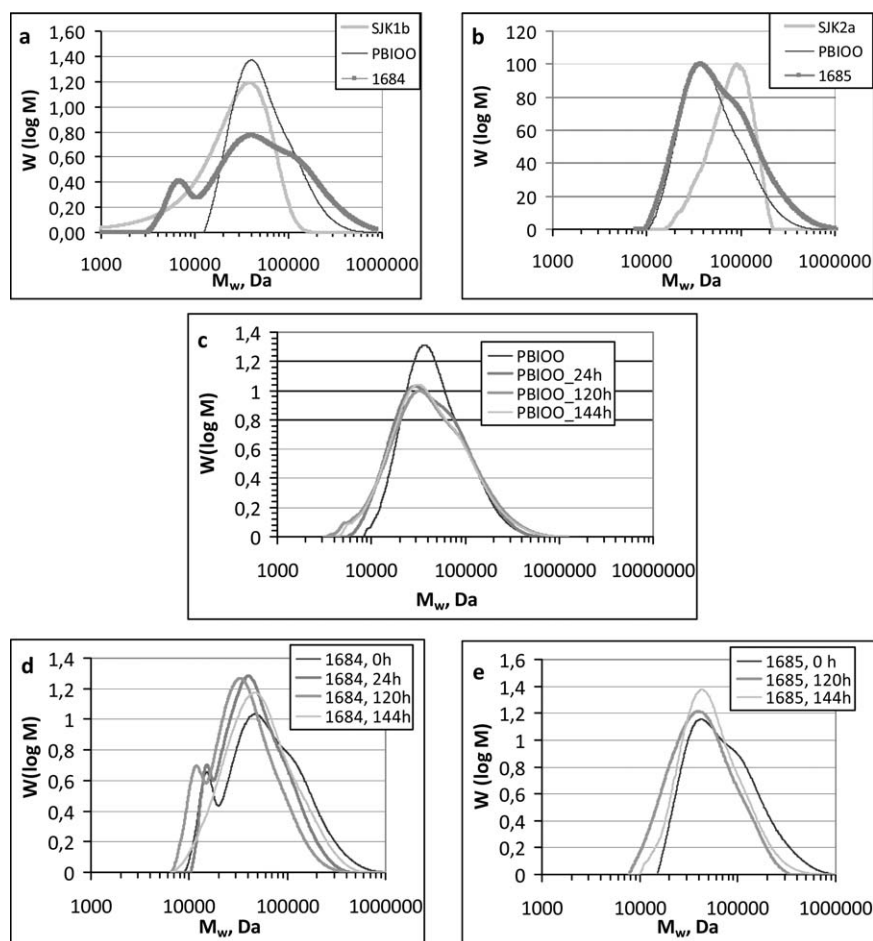
Figure 4. Molecular weight distribution diagrams (MWD) of (a) PBIOO, PαMSSA and PαMSSA-PBIOO before Fenton's Test (FT); (b) PBIOO®, PSSA, and PSSA-PBIOO before FT; (c) PBIOO before and after 24 h, 120 h, 144 h of FT; (d) undissolved residuals of PαMSSA-PBIOO before and after 24 h, 120 h, and 144 h of FT; (e) undissolved residuals of PSSA-PBIOO before and after 24 h, 120 h, and 144 h of FT.

lower chemical stability of the PαMSSA (containing aliphatic C-H bonds), compared with PBIOO (containing only aromatic C-H bonds). If, however, the surface of the PαMSSA-PBIOO membrane is compared with the one of the PSSA-PBIOO membrane after 120 h of FT [Figure 5(f)], the PSSA-PBIOO membrane is apparently much more affected by the radicals present in FT than the PαMSSA-PBIOO. In the case of PSSA-PBIOO dissolution of the degraded membrane fragments lead to the observed high roughness of the membrane surface. In Figure 5(g–i) the surfaces of PαMSSA-PBIOO, PSSA-PBIOO, and PBIOO after 144 h of FT treatment, are shown for comparison. The stronger weight loss of PSSA-PBIOO membrane sample under FT and can again be explained with the higher susceptibility to radical degradation due to its tertiary C-H bonds, which are not present in the case of PαMSSA. In addition, SEM of the cross-sections of the membranes has been performed and accomplished by EDX analysis of the space resolved N (representing the blend component PBIOO®) and S (representing the blend component PSSA and PαMSSA, respectively). This test aimed to see if there is uneven radical degradation of the membrane components, comparing the membrane surface and the membrane interior, since one would expect that under FT the more instable blend membrane component is preferentially

degrading to low-molecular compounds which are washed out from the membrane matrix during Fenton's Test. In Figure 6, SEM micrographs of the cross-section of the blend membrane 1684 (PBIOO/PαMSSA) including the space-resolved N and S content over the membrane thickness, respectively are shown before FT (a), and after 144 h of Fenton's Test (b). Following observations are made: (1) before FT, the N content is changing over the cross-section of the membrane. This finding can be explained with solvent residuals in the membrane due to insufficient evaporation during membrane formation process since the N-containing solvent DMAc was used for membrane preparation whose residual concentration in the cast membrane changes from the surface facing the casting support (highest concentration) to the surface facing the air (lowest concentration). After FT, the N imparity over the membrane cross-section has disappeared which is due to complete transfer of the solvent residual into Fenton's Solution (2). The S content of the membrane over the cross-section is roughly constant before and after FT which, interestingly enough, indicates an equicontinuous degradation of both blend components during FT which is contrary to the initially mentioned expectations that the sulfonated poly(styrene)s degrade faster than PBIOO. This finding might be due to the fact that the blends show a homogeneous
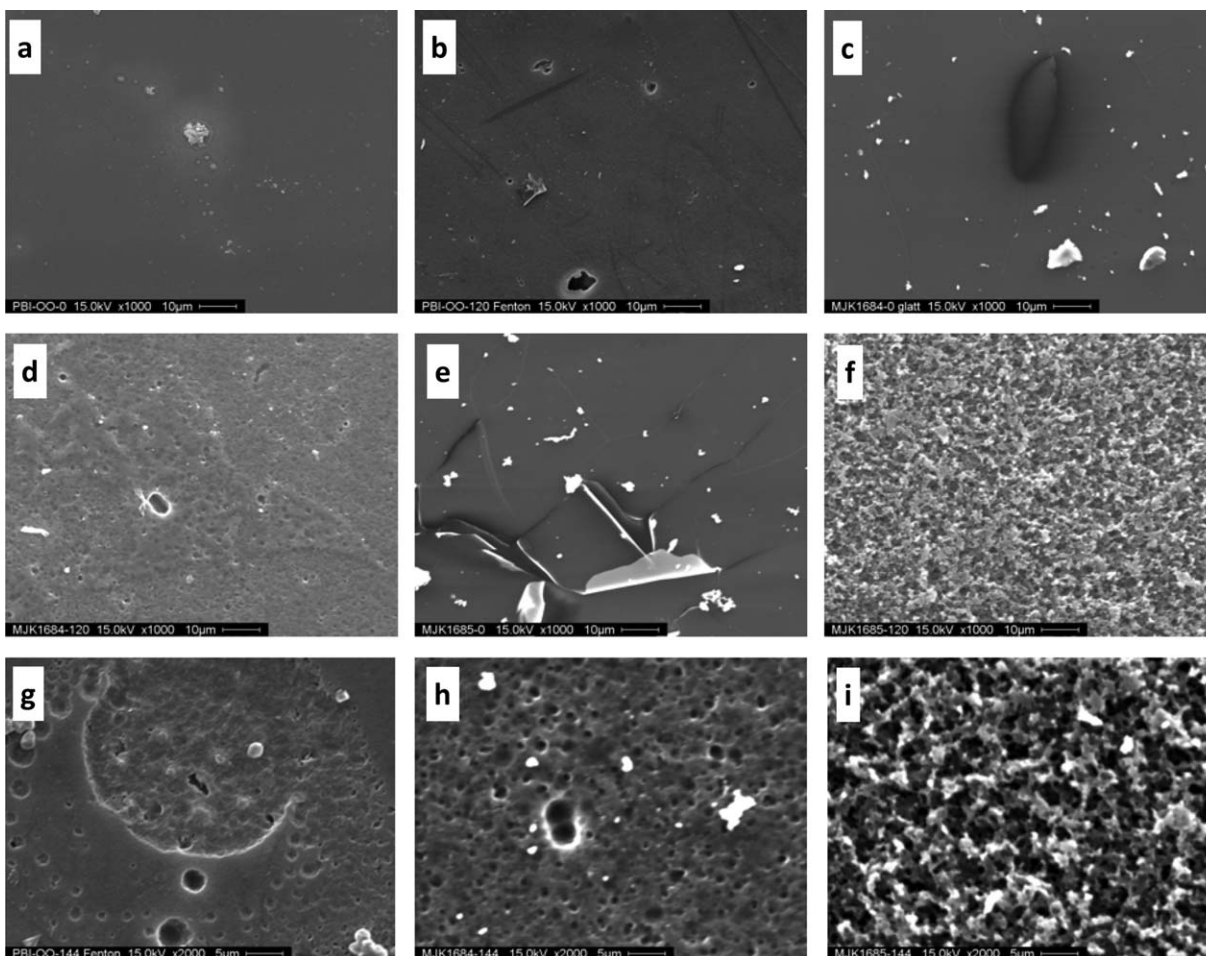
Figure 5. SEM of (a) PBIOO before FT; (b) after 120 h of FT; (c) PαMSSA-PBIOO before FT; (d) PαMSSA-PBIOO after 120 h of FT; (e) PSSA-PBIOO before FT; PSSA-PBIOO after 120 h of FT, each magnification ×1000; (g) PBIOO after 144 h of FT, magnification ×2000; (h) PαMSSA-PBIOO after 144 h of FT, magnification ×2000; (i) PSSA-PBIOO after 144 h of FT, magnification ×2000.

morphology leading to the simultaneous access of the radicals on both PαMSSA and PSSA and PBIOO macromolecules. In Figure 7, SEM micrographs of the cross-section of the blend membrane PSSA-PBIOO including the space-resolved N and S content over the cross-section of the membrane, are presented before FT (a), and after 144 h of FT (b). In contrast to the PαMSSA-PBIOO membrane, in the PSSA-PBIOO membrane the N and S distribution over the cross-section is constant both before and after 144h of FT. Obviously in the PSSA-PBIOO membrane no solvent residuals have been present before Fenton's Test. Moreover the S content of this membrane before and after FT remains roughly constant, indicating an equicontinuous degradation of both blend components, which is the case for the PαMSSA-PBIOO membrane, too. This postulated equicontinuous degradation of both blend components is also supported by the elemental analysis data, as shown before (see Table II). From the EDX results also the atom% N and S content and the atomic relation N/S of the membranes before and after 144 h of FT were extracted. The results are displayed in Table III. One can see for the PαMSSA-PBIOO membrane that the N/S ratio changes, which can be explained with the extraction of solvent residuals during FT, as mentioned before. For the

PSSA-PBIOO membrane, the N/S relation remains constant before and after FT, which indicates equicontinuous degradation of the two blend components PBIOO and PSSA by FT. Obviously the degradation of the more radical-sensitive blend component PSSA triggers also the decomposition of the PBIOO blend component by a high radical concentration onto the PSSA macromolecules because of the sensitive tertiary C-H bond. This is an explanation for the higher weight loss of the PSSA-PBIOO blends, compared with the PαMSSA-PBIOO blends.

H_3PO_4 Doping of PBIOO and of the PBIOO Blend Membranes. In Table IV, the results of H_3PO_4 doping at 130°C of PBIOO and of the blend membranes are presented. From the data the PBIOO membrane stabilization effect brought about by the ionical cross-linking with the sulfonated poly(styrene)s can be easily seen since the pure PBIOO membranes dissolve under the doping conditions applied. In other contributions dealing with polybenzimidazole/H_3PO_4 high-temperature membranes this ionical cross-linking stabilization effect was also proven when using other sulfonated ionomer membranes.[3,4,9,10]

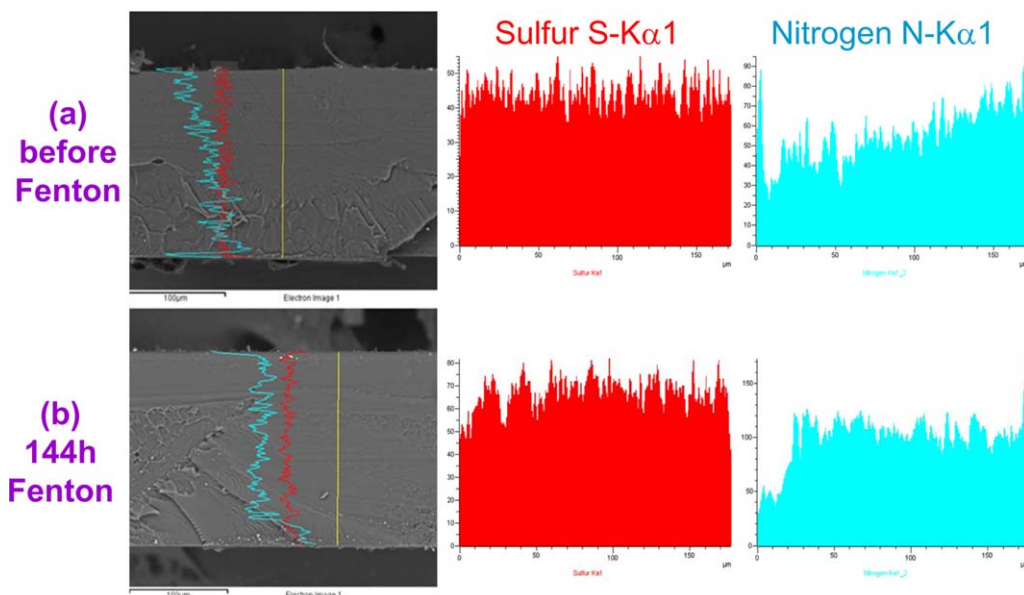In order to achieve better control over the doping process, a stepwise increase of the temperature was applied to the

Figure 6. SEM of the cross-section of the blend membrane PαMSSA-PBIOO including the space-resolved N and S content, (a) before and (b) after 144 h of FT determined by EDX analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

membranes immersed in 85% H_3PO_4 (Figure 8). Increase of the doping level with both the time and temperature is apparent for both the blends. The doping level in the case of PαMSSA-PBIOO, however, increased faster than in the case of PSSA-PBIOO. This might be attributed to the difference in the structure of PαMSSA, where the methyl group may create larger free volumes around the polymer chain and thus more space for the phosphoric acid. Nevertheless, both blend membranes were doped to almost equal doping level (300%) to compare their proton conductivities.

Proton Conductivity of the Blend Membranes. Conductivity as function of relative humidity (RH) at $T = 120°C$ was

measured for both PαMSSA-PBIOO and PSSA-PBIOO doped with phosphoric acid (300 wt %) [Figure 9(a)]. Beside the little higher conductivity of PαMSSA-PBIOO than PSSA-PBIOO, which can be due to the local structure of the membrane (see Discussion in the former section), both systems showed high conductivity and weak dependence to RH. For both the blends the conductivity in the range of 15 to 60% RH increases by less than factor of 2. This independence of the conductivity from RH is typical for phosphoric acid doped systems and based on the ability of the phosphoric acid to conduct protons at lower water content. Nevertheless, in the whole RH interval the conductivity followed a linear increase with the increase of the RH. Additionally, no hysteresis was observed by running impedance
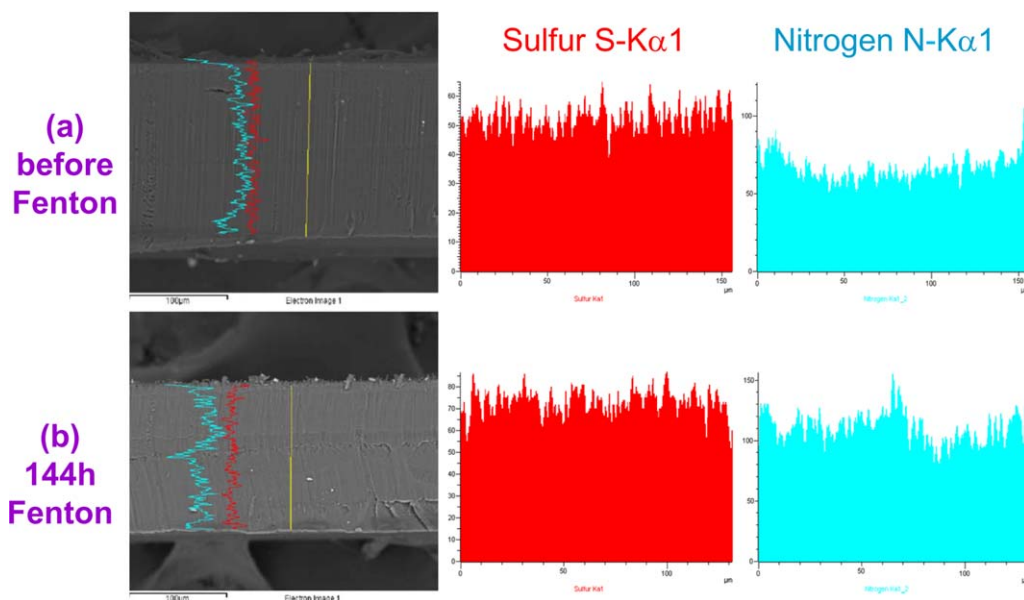

Figure 7. SEM of the cross-section of the blend membrane PSSA-PBIOO including the space-resolved N and S content, (a) before and (b) after 144 h of FT determined by EDX analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Atom%N and Atom%S and Relation N/S of the Blend Membranes from EDX Analysis

Membrane	N content (normalized) (at%)	S content, (normalized) (at%)	N/S
1684, 0 h	7804	2196	3,553,734
1684, 144 h	7529	2471	3,046,945
1685, 0 h	7782	2218	3,508,566
1685, 144 h	7776	2224	3,496,403

measurements forwards and backwards the RH. This is a sign for absence of irreversible membrane microstructure rearrangement processes at this temperature ($T = 120°C$).
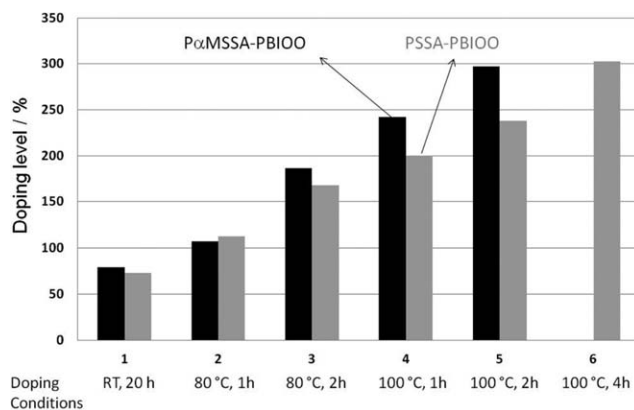
Conductivity as function of temperature at constant RH (26%) is given for both the systems in Figure 9(b). Similarly to the previous measurement the conductivity of both PαMSSA-PBIOO and PSSA-PBIOO are nearly the same with a small overweight of PαMSSA-PBIOO. Contrary to the first measurements in this case the conductivity did not follow any linear behavior, rather remained constant up to $T = 120°C$. Above this temperature ($T = 120–150°C$) the conductivity increased linearly with the temperature. This unusual behavior represents the existence of other factors that dominate over the temperature (overcompensating the impact of the temperature on conductivity) at $T < 120°C$.

CONCLUSIONS

PBIOO and of PBIOO-excess blend membranes with sulfonated poly(α-methylstyrene) (PαMSSA) and sulfonated poly(styrene) (PSSA), were prepared and treated with Fenton's Reagent (FR). The major hypothesis of the work was to experimentally prove the better radical resistance of blend membranes containing PαMSSA than PSSA due to the absence of tertiary C-H bonds in PαMSSA. The membranes were characterized before, during and after Fenton's Test (FT), which yielded following results:the thermal stability of the blend membranes was significantly better than the thermal stability of pure PBIOO, which is due to the ionical cross-linking in the blend membrane. It remained constant after FT which proves the morphological and chemical integrity of the blend membranes under these harsh conditions. The onset of splitting-off temperatures $T_{SO_3H}^{onset}$ of the blend membranes were much higher than that of the pure sulfonated

Table IV. H$_3$PO$_4$ Doping Results of the Membranes

Membrane	Doping time (min)	Weight increase (%)	H$_3$PO$_4$ per PBIOO RU
PBIOO	15	Dissolved	–
	30	Dissolved	–
1684 (PBIOO-PαMSSA)	15	68	3.5
	30	291	15
1685 (PBIOO-PSSA)	15	71	3.7
	30	227	11.7

Figure 8. Doping of PαMSSA-PBIOO and PSSA-PBIOO blend membranes with phosphoric acid at conditions given beside the x-axes.

poly(styrene)s which is due to the stabilization of the sulfonate groups by the ionic cross-linking. The fact that both the TGA traces and $T_{SO_3H}^{onset}$ remain constant during FT indicates that the phenyl rings of the sulfonated poly(styrene)s remain unaffected by the oxidative treatment, and radical attack obviously takes place mainly at the aliphatic-main chain of the poly(styrene)s. In TGA, (1) the blend membranes lost much less weight than the pure PBIOO membrane which is due to membrane stabilization
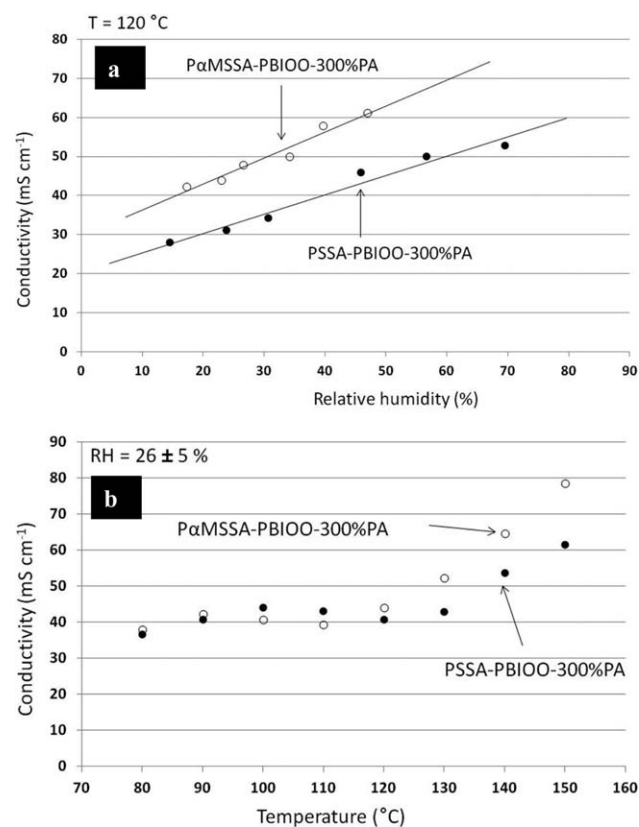
Figure 9. (a) Conductivity as function of relative humidity for PαMSSA-PBIOO and PSSA-PBIOO blend membranes both doped with phosphoric acid (300%); (b) conductivity as function of temperature for PαMSSA-PBIOO and PSSA-PBIOO blend membranes both doped with phosphoric acid (300%).

by the ionical cross-linking; (2) the weight loss of the PαMSSA blend membranes was lower than that of the PSSA-containing blend membranes, proving the higher radical resistance of the PαMSSA. No significant change in %S and %N of the blend membranes was observed which accounts for steady and moderate FT degradation of both PBIOO and PαMSSA/PSSA. By GPC analysis it was found that only moderate shift of MW curves to lower molecular weight values took places during FT which reflects the good stability of both PBIOO and PBIOO blend membranes under these conditions. SEM micrographs of the surface of the (blend) membranes indicate that the PSSA-containing blend membranes were much stronger attacked by FT than the PαMSSA-containing blend membranes, again reflecting the higher oxidative stability of the PαMSSA blend component and consequently a better oxidative stability of the PαMSSA-PBIOO blend membrane. H_3PO_4 doping experiments clearly showed the stabilization of the membranes by ionical cross-linking with sulfonated poly(styrene)s since the pure PBIOO membranes dissolved under the same doping conditions. The conductivities of H_3PO_4-doped PαMSSA-PBIOO and PSSA-PBIOO were measured at 120°C, varying the relative humidity (RH) and vice versa RH = 26% varying $T = 80$ to150°C. The proton conductivities of both doped blend membranes were similar with a slight superiority of PαMSSA-PBIOO which may be due to the structure of PαMSSA containing the bulky methyl group, creating higher free volume. These free volumes led to higher doping degree for PαMSSA-PBIOO than PSSA-PBIOO at 100°C, 2 h and higher diffusion rates of the phosphoric acid at similar doping degree.

Concluding the obtained results, it is obvious that PαMSSA-PBIOO blend membranes show a better property profile than PSSA-PBIOO blend membranes or even PBIOO for the potential application in high-temperature H_3PO_4-doped PEM fuel cell membranes.

In future, following work is planned: The H_3PO_4 doping experiments of the blend membranes will be continued to find out the optimal doping degree, the doped membranes will be characterized in terms of proton conductivity under different humidification, thermal stability, and oxidative stability, and the fuel cell performance of the doped PBIOO®-PαMSSA blend membranes will be investigated.

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