Blended and Cross-Linked Ionomer Membranes for Application in Membrane Fuel Cells[×]

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Abstract

Differently cross-linked blend membranes were prepared from commercial arylene main-chain polymers of the poly(etherketone) and poly(ethersulfone) classes, modified with sulfonate groups, sulfinate cross-linking groups, and basic N-groups.

The following membrane types have been prepared: (i) Van-der Waals/dipole-dipole blends by mixing a polysulfonate with unmodified PSU. This membrane type showed a heterogeneous morphology, leading to extreme swelling and even dissolution of the sulfonated component at elevated temperatures. (ii) Hydrogen bridge blends by mixing a polysulfonate with a polyamide or a polyetherimide. This membrane type showed a partially heterogeneous morphology, also leading to extreme swelling/dissolution of the sulfonated blend component at elevated temperatures. (iii) Acid-base blends by mixing a polysulfonate with a polymeric N-base (in-house developed/commercial). A wide range of properties could be achieved with this membrane type by variation of the different parameters. Membranes showing excellent stability and good fuel cell performance up to 100 °C (PEFC) and 130 °C (DMFC) were obtained. (iv) Covalently cross-linked (blend) membranes by either mixing a polysulfonate with a polysulfinate or by preparing a polysulfinatesulfonate, followed by reaction of the sulfinate groups in solution with a dihalogeno compound under S-alkylation. The membranes prepared showed effective suppression of swelling without a loss in the H^+-conductivity. The membranes showed good PEFC (up to 100 °C) and DMFC (up to 130 °C) performance. (v) Covalent-ionically cross-linked blend membranes by mixing polysulfonates with polysulfinates and polybases or by mixing a polysulfonate with a polymer carrying both sulfinate and basic N-groups. The covalent-ionically cross-linked membranes were tested in a DMFC up to 110 °C and demonstrated good performance. (vi) Differently cross-linked organic-inorganic blend composite membranes *via* various procedures. The best results were obtained with blend membranes having a layered zirconium phosphate "ZrP" phase: they were transparent, and showed good H^+-conductivity and stability. The application of one of these composite membranes in a PEFC yielded good performance up to T = 115 °C.

Keywords: Acid Base, Blend, Cross-Linking, DMFC, PEFC, Sulfinate ζ-Alkylation, Swelling

1 Introduction: State of the Art in Fuel Cell Membrane Development

Fuel cell research and development is one of the key topics in material science and engineering, because fuel cells could help to solve the problems connected with the consumption of the global energy carrier reserves, and with environmental problems connected with the use of fossil fuels in transport systems and in energy production. Fuel cells are an obvious building block in the development of environmentally friendly economies, since they can be used for energy supply in transport applications (cars, buses, trucks, train engines) as well as in stationary applications (decentralized power stations, home energy supply), and in mobile applications (laptop computers, cellular phones, handhelds, etc.). For the above-mentioned reasons, fuel cell component research and development efforts have increased considerably during the last decade.

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The membrane systems developed can be roughly separated into the following material classes (see [1]):

- perfluorinated ionomer membranes of the Nafion®, Flemion, Dow Membrane type;
- partially fluorinated ionomer membranes. Among this material class is the BAM3G membrane type composed of sulfonated or phosphonated poly(α,β,β-trifluorostyrene) and its copolymers [2–4] and the different types of grafted membranes based on partially fluorinated polymer foils, as developed by Scherer [5], Sundholm [6], and others;
- nonfluorinated ionomer membranes. Numerous different types of nonfluorinated ionomer membranes, among them ionomer membranes based on styrene polymers and copolymers containing polystyrene units [7], different sorts of arylene main-chain polymers, poly(phenylene) [8], poly(ethersulfone) [9–11], poly(etherketone) [12–15], poly(phenylene oxide) [16, 17], and poly(phenylene sulfide) [18], and membranes based on an inorganic backbone like poly(phosphazene)s [19, 20], poly(siloxane)s [21], have been developed over the years;
- composite membranes: The composite materials can be roughly subdivided into the following material types:
  - ionomers filling the pores of a porous support material (fleeces, nonwovens, textiles, porous teflon foils of the GoreTex® type ("GoreSelect®" [22, 23]);
  - high-molecular/low-molecular composites like blends of poly(benzimidazoles) with phosphoric acid as the proton-conducting component or phosphoric acid blended into other organopolymers [24–27], or blends of a sulfonated polymer with amphoterics like imidazoles or pyrazoles or imidazole-containing oligomers or polymers alone [28, 29], or blends of sulfonated polymers with heteropolyacids [30–32];
  - organic/inorganic micro- or nanocomposites like an (proton-conducting) organopolymer filled with an inorganic oxide (SiO_2 [33–35], TiO_2, ZrO_2 [36]), hydroxide, or salt (layered zirconium phosphates or zirconium sulfophenylphosphonates [37, 38], where the inorganic or inorganic-organic component is also capable of contributing to proton transport, etc.)
  - blend membranes from different organopolymers, particularly where interactions exist between the proton-conducting component and the other polymer(s).

The shortcomings of the present membrane types with respect of their application in fuel cells are given below:

- Application in H_2 membrane fuel cells (H_2-PEFC):

The commercial perfluorinated ionomer membranes like Nafion® are expensive (500–800 US$ m^{-2}). Moreover, at $T > 100$ °C the membranes show a significant amount of drying-out, leading to a conductivity drop of several orders of magnitude [39, 40]. One general problem especially of nonfluorinated ionomer materials is that they show a high water uptake when they have a proton conductivity sufficient for fuel cell operation.

- Application in direct methanol fuel cells (DMFC):

The Nafion® type membranes are expensive, hindering their broad application. The perfluorinated membranes also show a high methanol permeability [41, 42], leading to poisoning of the cathode catalyst and therefore to large reduction in power density. Some ionomer membrane types are instable in methanol solutions, leading in extreme cases (particularly high temperature) to dissolution of the polymer.

From these shortcomings, the tasks for the designation of improved fuel cell membranes, compared to the state of the art, can be defined. The property profile of improved ionomer fuel cell membranes includes high H^+-conductivity, low water/methanol uptake, low methanol (and other liquid fuel) permeability, fuel cell-applicability at $T > 100$ °C, because the higher the fuel cell operation temperature is, the higher is the fuel utilization, and applicability in other (electro) membrane processes as well. Last but not least, the membranes should have a low price.

In the following section we will describe in detail our scientific-technological approach(es) for development of novel ionomer membranes fulfilling the abovementioned property profile.

2 Review of the Membrane Development

The above mentioned property profile of ionomer membranes for use in fuel cells had led to the development of the approaches listed in Table 1.

Table 1 Approaches for polymer and membrane development for fuel cells.

Requirements	Approaches
High H^+-conductivity	Use of sulfonated polymers as the proton-conductive component in the fuel cell membranes at $T < 100$ °C
Low water/methanol uptake	Use of nonfluorinated ionomers
Physical and/or chemical cross-linking of the fuel cell membranes	Low methanol (and other liquid fuel) permeability
Use of nonfluorinated ionomers	Physical and/or chemical cross-linking of the fuel cell membranes
Fuel cell-applicability also at T > 100 °C	Development of organic-inorganic composite membranes, based onto our cross-linked ionomer membrane systems, where the inorganic membrane component serves as water storage, or even contributes to H^+-conduction
Low price	Use of commercially available polymers for chemical modification and membrane formation, which avoids expensive development of novel polymers

The water uptake of ionomer membranes can be reduced by introduction of specific interactions (Figure 1) between the macromolecular chains. In polymers, different types of interactions are always present together, e.g. van der Waals interactions between the macromolecules are present in every polymer, and electrostatic interactions are always connected with hydrogen bridge and dipole-dipole interactions. In any case, introduction of chemical bonds between the macromolecules has the strongest impact on the polymer structure, because covalent cross-links are "fixing" the polymer morphology, while physical interactions between the macromole-

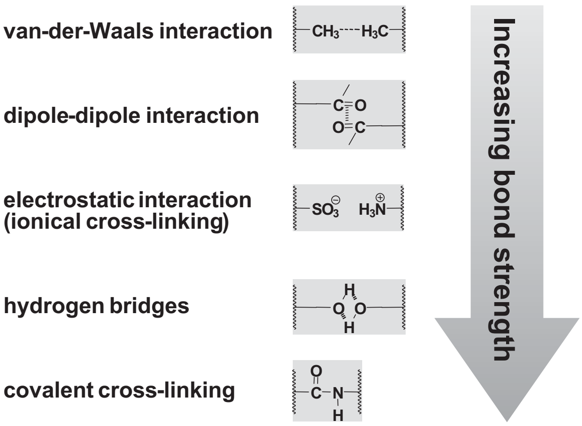


Fig. 1 Specific interactions between macromolecules.

cules can be detached, e.g. hydrogen bridges can be dissociated by temperature increase.

2.1 *Interaction-Blend Membrane Types*

Ionomer membrane types have been developed which show the different types of interaction forces between the blend components. In Table 2, an overview is given of the different ionomer membrane types developed. In the following, the developed (blend) membrane types will be described in more detail.

Table 2 Overview over the different ionomer membrane types developed.

Interaction type	Ionomer systems	Remarks
Van der Waals / dipole-dipole interaction	Blends from sulfonated PSU and unmodified PSU	Inhomogeneous morphology, unacceptably high swelling
H-bridges	Blends from sulfonated PEEK and PEI Ultem® or PA Trogamid P®	Partially inhomogeneous morphology, unacceptably high swelling
Electrostatic interaction (ionic cross-linking) / hydrogen bridges	Blends of sulfonated poly(etherketone)s/sulfonated poly(ethersulfone)s and basic polymers (commercial and self-developed)	In most cases homogeneous morphology, partial high swelling at elevated *T*
Covalent cross-linking	Blends from sulfonated arylene main-chain polymers and polysulfinates, polyarylenesulfonate-sulfinates, cross-linked with dihalogeno compounds	Homogeneous morphology, swelling effectively reduced

2.1.1 *Van der Waals/Dipole-Dipole Interaction Blends*

The basic idea for this membrane type was to "reinforce" the sulfonated ionomer membrane with unmodified polymer, due to the fact that polymers lose much of their mechanical strength by sulfonation or other modification reactions. As basic polymer, we selected the commercial PSU Udel®, because this polymer is relatively cheap, shows good chemical and mechanical stability and can be easily sulfonated by different methods. The first mixture trials of unmodified and sulfonated PSU showed that the mixing of the unmodified and of the sulfonated PSU in a dipolar-aprotic solvent (N-methylpyrrolidinone NMP, N,N-dimethylacetamide DMAc or dimethylsulfoxide DMSO) led to inhomogeneous solutions and, after solvent evaporation, to inhomogeneous blend membranes which showed very bad mechanical stability. We concluded that the sulfonic acid group is responsible for the incompatibility of the polymers, due to its hydrophilicity and ionogenity. Moreover, the van der Waals and dipole-dipole forces between the two polymers are obviously too weak to lead to blend component compatibility. Therefore, in a second approach the unmodified PSU was mixed with a nonionic precursor of the polymeric sulfonic acid to improve compatibility of the polymers forming the blend. For this purpose, we transformed the PSU-SO_3H into PSU-SO_2Cl, PSU-SO_2OCH_3, and PSU-$SO_2NHC_3H_7$ [43]. However, the blend membranes of unmodified PSU with these modified sulfopolymers had unsatisfying properties. The PSU/PSU-SO_2Cl and PSU/PSU-SO_2OCH_3 blend membranes still had, after hydrolysis of the nonionic sulfogroups to SO_3H, an inhomogeneous morphology (although the solutions of PSU with PSU-SO_2Cl and PSU-SO_2OCH_3 in tetrahydrofuran (THF) were homogeneous), leading to high membrane swelling in water and therefore to mechanical instability. Moreover, considerable leaching-out of the PSU-SO_3H was observed, due to insufficient entanglement of PSU and PSU-SO_3H because of polymer incompatibility. In the PSU/PSU-$SO_2NHC_3H_7$ blend membranes, the $SO_2NHC_3H_7$ groups could not be hydrolyzed into SO_3H groups. For the above-mentioned reasons, this van der Waals/dipole-dipole interaction blend membrane approach was not considered further by us.

2.1.2 *Hydrogen-Bridge-Interaction Blend Membranes*

Many polymers which are capable of forming hydrogen bridges and show good chemical and mechanical stabilities, are commercially available. Therefore we concluded that blending a sulfonated ionomer with a hydrogen-bridge-forming polymer should be a cost-effective way for the reduction of swelling of the sulfonated ionomer. Therefore, blend membranes were prepared from sulfonated poly(etheretherketone) sPEEK , the polyamide PA Trogamid P® (producer: Hüls) and the poly(etherimide) PEI Ultem® [44]. The resulting membranes showed good proton conductivities. The hydrogen bridge interaction between the PEEK-SO_3H polymer and the PA or PEI polymer in the blend membrane was indicated by an increase in the glass transition temperature (T_g) of the blend by 5–15 K, compared to pure PEEK-SO_3H. However, the swelling value of the hydrogen-bonded blend membranes at elevated temperatures was very high, even leading in some cases to dissolution of the membrane at $T = 90$ °C. Moreover, some phase separation occurred in the blend membranes, and there are concerns that the PA amide bonds and the PEI imide bonds show insufficient hydrolysis stability in acidic environment, which is present during fuel cell operation.

Therefore, the work with these blend membrane types was stopped.

2.1.3 Ionically Cross-Linked Acid-Base Blends and Acid-Base Ionomer Membranes

Since membrane types 1 and 2 show unsatisfying properties, we searched for blend membrane types where the blend membrane components showed stronger interactions. We discovered acid-base blend membranes made by mixing polysulfonates and polybases which showed good mechanical and thermal stabilities, which were even better than the mechanical and thermal stability of the sulfonated polymers alone, and performed very well in fuel cells [45, 46]. The structure of acid-base blend membranes is depicted schematically in Figure 2. The interaction forces between the acidic and the basic blend component include electrostatic and hydrogen bridge interaction. The sulfonated poly(ethersulfones) and poly(etherketones) were combined with both commercially available basic polymers (e. g. polybenzimidazole Celazole® (producer: Celanese), poly(4-vinylpyridine), poly(ethylene imine)) and with self-developed basic polymers derived from poly(ethersulfones) [47] and from poly(etherketones), including polymers which carry both sulfonic and basic groups on the same backbone [48]. A wide variety of acid-base blend membranes with a broad property range was obtained. The most important characterization results of the ionically cross-linked ionomer membranes are discussed in the section "Membrane characterization and fuel cell results" Acid-base blend membranes have also been prepared from sulfonated polysulfone PSU Udel® and polybenzimidazole PBI Celazol, and the properties of this membrane have been compared with those of Nafion® [49]. They confirmed the previous finding [50, 51] that ionomer-PBI blends show a marked reduction in methanol permeability both *ex-situ* [50] and *in-situ* [51], compared to Nafion®. The synthesis and characterisation of acid-base blend membranes from sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) and polybenzimidazole PBI Celazole® [52, 53] has been reported recently. Interestingly, it was found that these membranes show good oxidative stability: after immersing the membrane samples for 72 h in 80 °C hot 3% H_2O_2 aqueous solution containing ferrous ions, no weight decrease of the membranes was observed. These results confirm thermogravimetric analysis results with acid-base blend membranes, which also indicated an excellent thermal stability of acid-base blends, particularly blend membranes with PBI [54]. Moreover, other groups have also started the investigation of acid-base ionomer blends with PBI as the base component, like blend membranes of sPEEK, PBI and PAN [55]. Hasiotis et al. report blends from sulfonated PSU, PBI, which were doped with phosphoric acid [56]. They found that the ternary blend membranes showed better H^+-conductivities and better mechanical stability than binary blends of PBI/H_3PO_4. The membranes were investigated in a PEFC up to T = 190 °C.

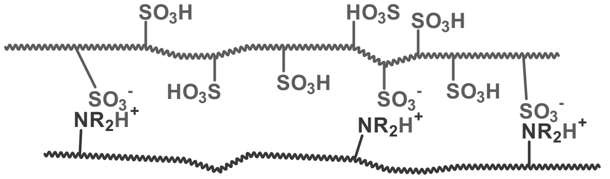


Fig. 2 Scheme of ionically cross-linked acid-base blend membranes.

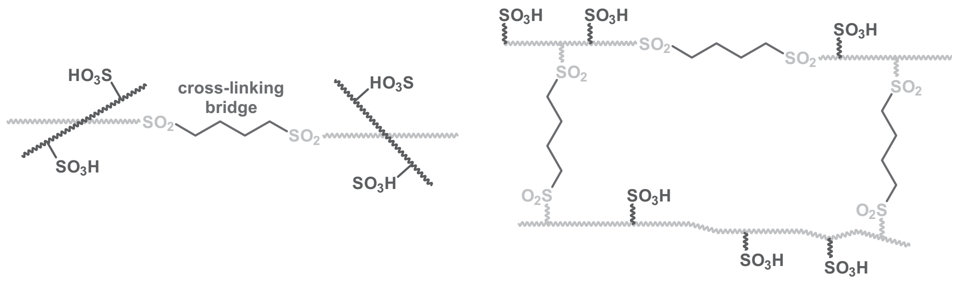
One disadvantage of the ionically cross-linked (blend) membranes from polysulfonates and polybases is that the hydrogen bridges and electrostatic interactions break in aqueous environment when the temperature is raised to $T > 70$–90 °C, leading to unacceptable swelling in water at $T > 70$–90 °C and therefore mechanical instability which could lead to destruction of the membrane in the fuel cell. To overcome this instability, covalently cross-linked (blend) membranes have also been developed.

2.1.4 Covalently Cross-Linked (Blend) Membranes

The need for an effective reduction of ionomer membrane swelling led us to search for covalent cross-linking procedures which show good chemical stability in the aqueous acidic environment which is present in the fuel cell. In the literature, only a limited number of covalently cross-linked ionomer membrane types is found, one approach being developed by Ledjeff et al., who covalently cross-linked a partially N-imidazolized sulfonated PES Victrex® ionomer with 4,4′-diaminodiphenylsulfone [57]. However, there are strong concerns whether the sulfonamide bonds are sufficiently stable in the strongly acidic environment of a fuel cell. In a very recent paper of Guiver et al. described a novel cross-linking procedure for sulfonated poly(etherketone), involving reaction of the sulfonic acid groups of polyetheretherketone with oligoalcohols such as ethylene glycol, glycerine and meso erythrite under condensation (ester formation) [58]. However, the stability of these covalently cross-linked membrane systems in acidic environment was not investigated. Some years ago, we have discovered a novel cross-linking process in which sulfinate groups SO_2Me (Me = Li, Na...) are involved. It consists of a nucleophilic substitution (S-alkylation) of the sulfinate group with di- or oligohalogenealkanes or –arylenes [59]:

$$\text{Polymer-SO}_2\text{Li} + \text{Hal-R-Hal} + \text{LiO}_2\text{S-Polymer} \rightarrow \text{Polymer-S(O)}_2\text{-R-S(O)}_2\text{-Polymer}$$

Preferred halogenoalkanes were α,ω-dibromo- or α,ω-diiodoalkanes Br(I)-$(CH_2)_x$-Br(I) with x = 3–12, preferred dihalogenoarylenes were bis(4-fluorophenyl)sulfone, bis-(3-nitro-4-fluorophenyl)sulfone, bis(4-fluorophenylphenyl)phosphinoxide, decafluorobenzophenone and decafluorobiphenyl. The cross-links created by S-alkylation are stable in aqueous environment, under both alkaline, neutral and acidic conditions, and in hot dipolar-aprotic solvents like NMP or DMAc. Moreover, the membranes showed good thermal stabilities. Two different membrane types (Figure 3) have been developed:



type (i) type (ii)

Fig. 3 Scheme of covalently cross-linked membranes; type (i): ionomer blend, type (ii): ionomer.

(i) cross-linked blend membranes by mixing sulfonated polymers with sulfinated polymers and the cross-linker in a dipolar-aprotic solvent (mostly NMP);
(ii) cross-linked blend membranes by mixing a polymer carrying both sulfonate and sulfinate groups onto the same backbone in NMP with the cross-linker.

The advantage of the membrane type (i) is that it can be prepared very easily: both polymers are dissolved in the same solvent, and the cross-linker is added. A further advantage of the type (i) ionomer blend membranes is that a very broad property range can be obtained by variation of mass relation of the sulfinated and the sulfonated blend component, by variation of the ion-exchange capacity of both blend components, by variation of the backbone type of the blend components, and by variation of the cross-linker (different chain length of the cross-linkers, use of aliphatic or aromatic cross-linkers, use of mixtures of cross-linkers, etc.). The disadvantage of this type is that the polysulfonate macromolecules can diffuse out of the blend membrane, because they are only entangled in the covalent network built up by the sulfinated polymer and the cross-linker. However, this problem can be minimized by increase of the cross-linking density of the network. The advantage of the membrane type (ii) is that all macromolecules are taking part in the network, and therefore no bleeding-out of the sulfonated component can take place. The disadvantage is that the effort involved in the preparation of mixed sulfonated/sulfinated polymers is higher than that for the preparation of 100% sulfonated or 100% sulfinated polymers. The preparation of the starting polymers for the cross-linked membranes is described in the section "Polymer modification for blend membranes"., and principal characterization results of a selection of the covalently cross-linked membranes are given in the section "Membrane Characterization and Fuel Cell Results".

2.1.5 *Covalent-Ionically Cross-Linked (Blend) Membranes*

Both ionically crosslinked membranes (splitting-off of the ionic bonds at *T* = 70–90 °C) and covalently cross-linked membranes (bleeding-out of sulfonated macromolecules from covalently cross-linked blend membranes, brittleness of dry membranes) show disadvantages. To overcome these disadvantages, we started the development of covalent-ionically cross-linked membranes [60]:

(i) blending of a polysulfonate with a polysulfinate and a polybase, under addition of a dihalogeno cross-linker, which is capable of reacting with both sulfinate groups and tertiary amino groups under alkylation and therefore cross-linking (Figure 4);

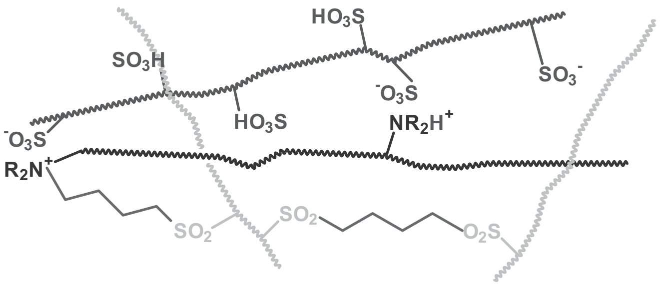


Fig. 4 Scheme of covalent-ionically cross-linked membranes.

(ii) blending of a polymer carrying both tertiary amino and sulfinate groups with a polysulfonate under addition of a dihalogeno cross-linker which alkylates both sulfinate and tertiary amino groups;
(iii) blending of a polymer carrying both sulfinate and sulfonate groups with a polybase under addition of a dihalogeno cross-linker.

We found that the disadvantage of the membrane type (i) is incompatibility between the polysulfinate and the polyamine, leading to phase-separated membranes which show unsatisfying mechanical stability and insufficient suppression of water uptake at elevated temperatures. Although not yet clear, it may be speculated that the incompatibility of sulfinate and base polymers is due to the repulsion of the base group lone electron pair and the sulfinate group lone electron pair. This disadvantage of type (i) can be avoided with membrane types (ii), where the incompatible functional groups are bound to the same backbone in statistical distribution, and with membrane type (iii) where the repulsion of the basic polymer with the sulfinate groups of the second polymer can be balanced by hydrogen bridges and/or dipole-dipole interaction of the base groups with the sulfonate groups of the second polymer. The membrane types (ii) and (iii) are transparent to visible light, indicating a homogeneous membrane morphology. One could also think of the preparation of a polymer carrying sulfonate groups as well as sulfinate groups and basic groups onto the same backbone, e.g. by reaction of a lithiated polymer with the three electrophilic SO_2 (for sulfinate groups), SO_2Cl_2 (for sulfochloride → sulfonic acid groups) and an aromatic carbonyl base (for basic groups). This polymer would inherently form a morphologically homogeneous membrane. However, such a polymer would be very expensive due to the need for careful dosage of the electrophile mixture, possible reaction between the different electrophiles, reaction at low temperatures and reaction in a protective atmosphere, so it would probably not be suitable for mass production.

2.1.6 *Composite Blend Membranes*

Due to the fact that pure organic sulfonated ionomer membranes progressively lose their H^+-conductivity when the temperature is raised above 100 °C if the fuel cell is not pressurised, due to drying out (evaporation of the water which is a "vehicle" for proton transport), we have started combining our differently cross-linked (blend) ionomer membranes with different inorganics, as schematically presented in Figure 5. We have prepared the following composite membrane types:

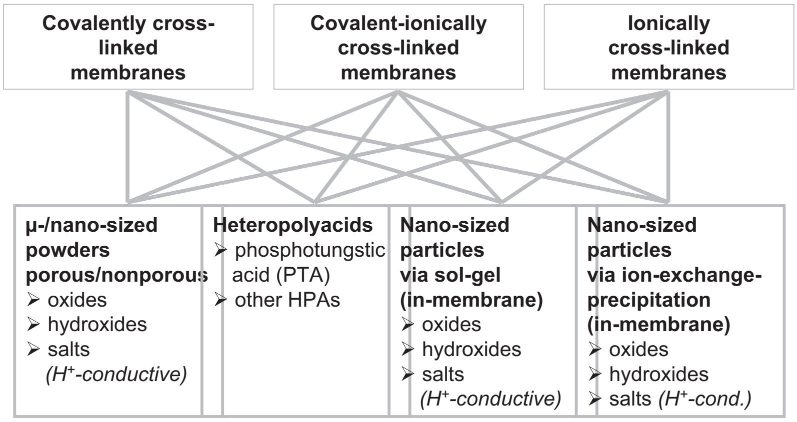


Fig. 5 ICVT strategies for ionomer composite membranes.

(i) Covalently or ionically cross-linked blend membranes, filled with μ-sized oxide (SiO_2, TiO_2) or layered zirconium phosphate "ZrP", introduced as a powder into the polymer solutions.
The problem of this membrane type is that inorganic oxide or salt powders tend toward agglomeration in the polymer solution and, after solvent evaporation in the membrane, reduces the active surface for water adsorption and possible proton transport dramatically. Therefore we applied literature-known procedures for formation of in-membrane nanoparticles to our membrane types (particularly Jones, Roziere, Bauer et al. performed pioneering work in this field [61–65]):

(ii) Covalently or ionically cross-linked blend membranes, filled with layered ZrP by ion-exchange-precipitation:
    (i) ion-exchange of the SO_3H form of the membranes in a $ZrOCl_2$ solution to yield the membranes in the $(SO_3)_2ZrO$-form
    (ii) immersion of the ion-exchanged membranes in H_3PO_4; during immersion, the H_3PO_4 diffuses into the membrane, and by reaction with the ZrO^{2+} ions, the layered ZrP is precipitated in the membrane matrix.

(iii) Ionically cross-linked blend membranes from sulfonated poly(etherketone)s, PBI and the heteropolyacid tungstenic phosphoric acid (TPA).

Heteropolyacids (HPA) are strong Broenstedt acids [66], and are interesting candidates for blending with ionomer membranes in order to increase their H^+ conductivities. However, HPAs are water-soluble which leads to concerns that they may diffuse out of the ionomer membranes with time, and different authors have reported that partial leaching-out of the HPAs from the membrane does indeed takes place [30]. A marked reduction of the leaching-out rate of the HPA molecules could be realized by synthesis of novel HPAs, as reported by Nunes et al [31]. Our motivation for this development of ionomer-HPA blend membranes was to answer the question whether the ionic cross-links in ionically cross-linked blend membranes and the resulting interactions between the HPA molecules and the ionomer blend membrane components (ionical cross-linking, H bridges, dipole-dipole interaction) could prevent leaching-out of the HPA.

2.2 Polymer Modification for Blend Membranes

2.2.1 *Synthesis of Sulfonated Polymers*

For the synthesis of sulfonated poly(etherketone)s the well-known procedures were applied which involve sulfonation in 96% sulfonic acid [12, 67] or in oleum [14, 68]. For the synthesis of sulfochlorinated poly(etherketone)s, the method described in [12] was used. PSU Udel® and PPSU Radel R® were sulfonated with n-butyllithium, as first described by Guiver [69]. The procedure involves reaction of the lithiated poly(ethersulfone) with SO_2, yielding PSU/PPSU-sulfinate, followed by oxidation with NaOCl to the PSU-sulfonate [11], or reaction of the lithiated poly(ethersulfone) with SO_2Cl_2, yielding PSU-SO_2Cl [70], followed by hydrolysis to the PSU/PPSU sulfonic acid.

2.2.2 *Synthesis of the Sulfinated Polymers*

For the synthesis of the PSU/PPSU-sulfinates, the above-mentioned reaction of lithiated polymers with SO_2 was used. For the synthesis of poly(ethersulfone)s carrying both sulfinate and sulfonate groups, we partially oxidized the PSU/PPSU-sulfinates with sub-portions of NaOCl [71]. Poly(etheretherketone sulfinate)s were prepared by reduction of poly(etheretherketone sulfochloride)s with aqueous Na_2SO_3 [72].

2.2.3 *Synthesis of Basic Polymers*

Amino groups were introduced into poly(ethersulfone)s by the following methods:

(i) Introduction of the NH_2 group *ortho* to the sulfone bridge of the poly(ethersulfone) was performed *via* a method developed by Guiver et al [73, 74]. The poly(ether sulfone amine) was then stepwise alkylated to the secondary and the tertiary polymeric amine by sequential addition of n-BuLi and CH_3I [43].

(ii) Introduction of the NH_2 group *ortho* to the ether bridge of poly(ethersulfone)s or *ortho* to the ether bridge of poly(etheretherketone) was done following [75, 76]. The poly(ethersulfone) primary amines were then alkylated to the secondary amines by deprotonation with LDA, followed by alkylation with CH_3I. The poly(ethersulfone) secondary amines were alkylated to the tertiary amines by reaction with KOH/CH_3I in DMSO. The poly(etheretherketone) primary amines were alkylated to the tertiary amines by reaction with KOH/CH_3I in one step.

(iii) Poly(ethersulfone)s were modified with tertiary amines by reaction of their lithiated form with basic aromatic aldehydes and ketones [47, 77, 78].

(iv) Poly(ethersulfone)s were modified with tertiary amines also by reaction of their lithiated species with basic aromatic carboxylic acid esters, as shown in [47].

Interestingly, the created keto bridges of the product polymers are not attacked by residual PSU-Li sites to cross-link the polymer [47, 77].

2.2.4 *Synthesis of Polymers Containing Both Basic and Sulfinate Groups*

Poly(ethersulfone)s carrying both sulfinate and basic groups were prepared starting with lithiated poly(ethersulfone) [60, 79, 80].

2.2.5 *Synthesis of Polymers Containing Both Basic and Sulfonate Groups*

Poly(etheretherketone) carrying both primary amino and sulfonate groups was prepared by nitration-reduction procedure [48].

2.3 *Membrane Characterization and Fuel Cell Results*

We review here the dependence of most important characterization and fuel cell application results of the different membrane types we have developed in our lab using different parameters.

2.3.1 *Ionically Cross-Linked Blend Membranes*

Dependence of the Membrane Properties on the Size of the Repeating Unit of Polybase

To ensure complete ionic cross-linking, the repeating units of the acidic and the basic blend component should be comparable in size and in density of functional groups. We compared the extent of formation of ionic cross-links using the same polymeric sulfonic acid (sulfonated PSU, ion-exchange capacity IEC = 1.6 meq g^{-1}), but the two polybases polybenzimidazole (PBI, base capacity 6,5 meq g^{-1}) and polyethylenimine (PEI, base capacity 23.2 meq g^{-1}) [81]. When the calculated (from the molar relation acid/base) and experimentally obtained *IEC*s of the two acid-base blend membranes were compared, the calculated and experimental *IECs* were similar for sPSU/PBI blends, while for the sPSU/PEI blends the experimental *IECs* were much higher than calculated. This allows the conclusion that, from a steric point of view, for the sPSU/PEI blends, it is not possible that every amino group finds its acidic counterpart due to the extreme difference in functional group densities of sPSU and PEI, respectively. Conversely, for the sPSU/PBI blends, the functional group densities are not as different as is the case for the sPSU/PEI blends, allowing that every acidic group finds its basic counterpart, taking into account the excess in acidic groups in the sPSU/PBI blends and the chain segment mobilities of the blend components.

Dependence of the Membrane Properties on the Base Strength of the Base

We investigated to which extent the strength of the polybase influences the percentage of formation of acid/base cross-links. The calculated and experimental ion-exchange capacities were compared to acid/base blends using the relatively strong polybases PBI (calculated p_k^a of its protonated form 5.6), poly(4-vinylpyridine) (P4VP, calculated p_k^a of its protonated form 6), and PSU-*ortho*-ether-diamine (POSAII, calculated p_k^a of its protonated form +4) with the *IEC*'s of acid/base blends using the very weak polybase PSU-*ortho*-sulfone-diamine (POSAI, calculated p_k^a of its protonated form –1.5). The results showed very clearly that for the PBI, P4VP- and POSAII-containing acid/base blends the calculated and experimental *IEC*'s were very close together [54, 81, 75], while for the POSAI acid-base blends the experimental *IEC*'s were much higher than the calculated ones [75, 81], assuming that at a p_k^a of the conjugated acids to the respective bases of < 0–2 the formation of acid-base bonds, or, in other words, the protonation of the base groups is incomplete. Therefore, for an effective suppression of swelling by ionic cross-links, the chosen base should be strong enough to ensure complete protonation when forming the acid/base blends. A very good polybase candidate on that score is PBI, due to its high base strength and excellent chemical stability [82].

Dependence of the Membrane Properties on the Ionical Cross-Linking Density

We have recently [68] compared the properties of membranes, composed of sulfonated poly(etherketoneetherketoneketone) sPEKEKK Ultrapek® and PBI, having the same *IEC* of 1.35 meq SO_3H g^{-1}, but different ionic cross-linking densities. The different cross-linking density was obtained by use of sulfonated sPEKEKKs with different *IECs* ranging from 2.5 to 4.1 meq SO_3H g^{-1}. As expected, the water uptake of the membranes decreased with increasing cross-linking density: the membrane having the lowest cross-linking density in this series had a swelling value of 260% at 90 °C, while at 90 °C the swelling degree of the membrane with the highest cross-linking density amounted to 90%. Interestingly, in the same membrane series, an increase in electrical resistance with increasing cross-linking density was observed (membrane with the lowest cross-linking density: $R_{sp}^{H+} = 5\ \Omega$ cm; membrane with the highest cross-linking density: $R_{sp}^{H+} = 11\ \Omega$ cm). An explanation for this finding could be that the ionic cross-links hinder the H^+ transport through the H^+-conducting channels of the membranes by repulsion forces [68]. The thermal stability of all membranes up to 240 °C from this series is comparable. In Figure 6, the TGA traces of the membranes with the highest and the lowest cross-linking density in this series are shown. When the PBI portion of the acid-base blend membranes, containing the same sulfonated polymer having the same *IEC*, is increased, a mass relation is reached where the amount of acidic groups balance the amount of basic groups, or, in other words, where no excess of free SO_3H groups is available. Consequently, such membranes are no longer H^+-conductive [54].

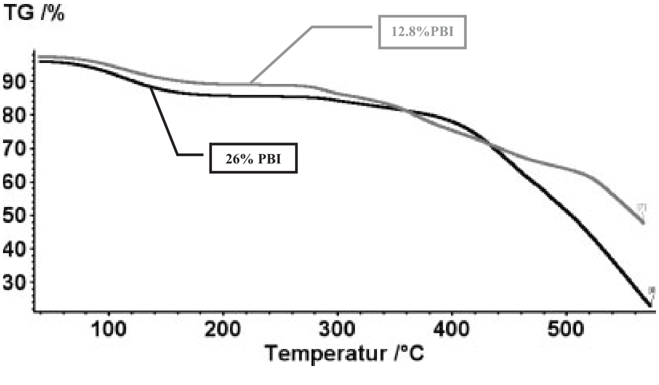


Fig. 6 TGA of sPEKEKK/PBI blend membranes with a PBI content of 12.8% and of 26%, respectively.

Dependence of the Membrane Properties from the Membrane Preparation Method

In case of very weak polybases, like POSAI, it was possible to mix the polybase with the polymeric sulfonic acid in the same (dipolar-aprotic) solvent without precipitation of a polyelectrolyte complex. This phenomenon is due to the very low extent of formation of ionic cross-links in such blends [54]. In the case of stronger bases like PBI or P4VP the polysulfonate solution must be mixed in salt form with the polybase to avoid polyelectrolyte complex precipitation. Two procedures have been applied:

(i) The polymeric sulfonic acid was dissolved in a dipolar-aprotic solvent, followed by neutralisation of the SO_3H groups with a base like n-propylamine or triethylamine. Then the polybase solution in a dipolar-aprotic solvent was added, followed by membrane casting and solvent evaporation. During solvent evaporation, a part of the ammonium sulfonate groups decomposed, leaving back the sulfonic acid group, which immediately reacted with a basic group in its environment. In other words, with this procedure a part of the ionic cross-links is created during membrane formation.

(ii) The polymeric metal sulfonate (cations: Li, Na) was dissolved in a dipolar-aprotic solvent, followed by polybase addition. Then the solvent was evaporated. The resulting membrane had to be treated with mineral acid to protonate the sulfonate groups and therefore to create the ionic cross-links.

The membranes prepared *via* methods (i) and (ii) showed different morphology: the (i) membranes showed a homogeneous morphology, while in the membranes (ii) a partially phase-separated morphology occurred in some cases, like reported in [79]: two membranes, composed of sulfonated PEK (*IEC* = 1.8 meq g^{-1}) and the two bases PBI and PSU-ortho-sulfone-C(OH)(4-diethylaminophenyl)$_2$ were prepared, the first prepared from sPEK in the SO_3H form, neutralized with n-propylamine (membrane "504H"), the second prepared from sPEK in the SO_3Li form (membrane "504Li"). The morphology of both membranes was determined with transmission electron microscopy (TEM). The TEMs of both membranes are shown in Figure 7. The 504H membrane showed a homogeneous morphology, while at 504Li some phase-separation could be observed. These findings can be explained as follows: in membrane 504H, during membrane formation a part of the ionic cross-links between the acidic and the basic polymers is formed, leading to compatibiltiy of the blend components. In membrane 504Li, only weak van-der-Waals and dipole-dipole interaction is present between the acidic and the basic blend components – the insufficient interactions between the blend components lead to partial incompatibility. The partial incompatibility also influences the membrane properties [79]: due to incomplete ionic cross-link formation

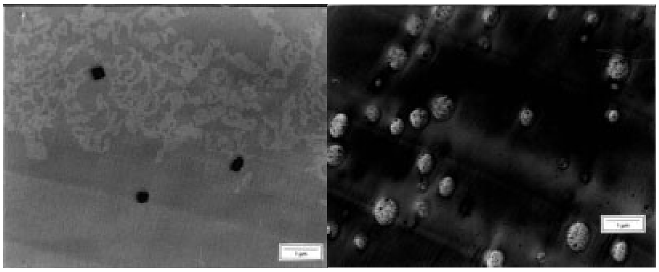

504H
504Li

Fig. 7 TEM of membrane 504H and 504Li, magnification 6,600X.

at the 504Li membrane, the *IEC* of the 504Li membrane has a value of 1.34 meq g^{-1} (calculated from acid/base molar relation, *IEC* = 1.11 meq g^{-1}), while the experimental *IEC* of 504H is 1.12 meq g^{-1}. Moreover, the swelling value of the 504Li membrane, particularly at higher temperatures in water, is higher than that of the 504H membrane: at 90 °C, the 504Li membrane shows a swelling value of 134%, while the swelling value of 504H at 90 °C amounts to 74%. In the DMFC experiment, the 504Li membrane shows slightly better performance than the 504H membrane which is due to their higher free SO_3H group concentration.

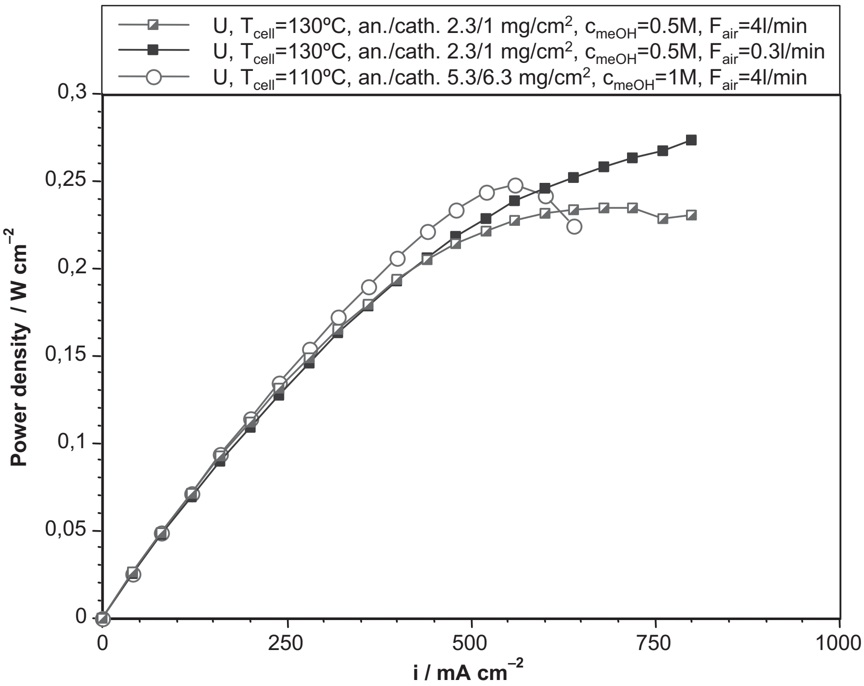


Fig. 8 Current density/power density curves of membrane 565 under different applied conditions.

Influence of the Addition of a Radical Scavenger

It is known that in membrane degradation processes in fuel cells, radicals are involved which are generated during fuel cell operation [83]. Therefore, it was investigated whether the addition of substances which are capable of acting as radical scavengers improved the chemical stability of the ionomer membranes. For this purpose, blend membranes from PEK-SO_3Li, PBI and the radical scavenger poly(N,N′-bis-(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-diamino-hexane-co-2,4-dichloro-6-morpholino-1,3,5-triazine were prepared [84]. The membranes were investigated *via* thermogravimetry in a 65% O_2 atmosphere to check their thermal stability. However, from TGA no positive effect of the radical scavenger onto the thermal stability could be detected – all the membranes sPEK/PBI/scavenger, sPEK/PBI, and sPEK/scavenger had nearly identical thermal stabilities. In all three membranes, the splitting-off of the sulfonic acid group, which is the first step of membrane decomposition, started at around 230 °C. The membrane decomposition process in the TGA was investigated by a TGA-FTIR coupling setup, which allows the FTIR-analysis of the TGA decomposition gases [84]. On the other hand, direct investigation of these membrane types in a fuel cell, placed in the resonator of an electron resonance spectrometer, showed very low radical concentration in the membranes which is comparable to the radical concentration observed in Nafion membranes placed in the same setup [85], suggesting good radical stability of these acid-base blend membranes.

Dependence of the DMFC Performance on DMFC Operation Parameters

Different ternary acid-base blend membranes, composed of sPEK, PBI and PSU-C(OH)(4-diethylaminophenyl)$_2$, were tested in a DMFC at temperatures of up to 130 °C. Good performance was detected at 110 °C, which was comparable to Nafion®112, reaching a peak power density of 0.25 W cm^{-2} in air operation [86]. However, the catalyst loading was 12 mg noble metal cm^{-2} membrane, which is much too high. One possibility to reduce noble metal loading of the electrodes is to increase the DMFC operation temperature, because higher operation temperatures led to improved catalyst utilization, and the other possibility is to reduce methanol permeability of the membranes. Therefore, the following DMFC operation conditions were applied [84]: the DMFC temperature was increased to 130 °C, and the noble metal loading was reduced by a factor of 4. Indeed, by application of these measures the power density of the fuel cell could even be increased, compared to the higher loading and lower operation temperature. Moreover, by a reduction of the air flow from 4 l min^{-1} to 0.3 l min^{-1} the methanol permeability of the membranes could be drastically reduced. In Figure 8, the current density/peak power density curves of the 565 acid-base blend membrane in the DMFC under these conditions are shown.

Dependence of the PEFC Performance on Operation Temperature

One problem of ionomer membranes requiring water for proton transport, like the sulfonated ionomer blend membranes, is, that at fuel cell operation temperatures approaching the boiling point of water, these membranes suffer from progressive drying-out, leading to a dramatic drop in proton conductivity and therefore loss in power density. Therefore it was investigated up to what temperatures our acid-base blend membranes can be used in PEFC. We selected again the above-mentioned ternary membrane type composed of sPEK/PBI/PSU-C(OH)(4-diethylaminophenyl)$_2$ for the test. The catalyst loading was 1 mg cm^{-2} per electrode. The operation temperature was raised from 85 °C to 100 °C. The result of the PEFC experiment was that the membrane operated well up to 100 °C. Even an increase of power density of the membrane from 85 °C to 100 °C could be detected [80]: at 85 °C, the maximum power density was 0.26 W cm^{-2} (@0.68 A cm^{-2}), at 90 °C 0.29 W cm^{-2} (@0.7 A cm^{-2}), and at 100 °C 0.33 W cm^{-2} (@0.8 A cm^{-2}).

2.3.2 *Covalently Cross-Linked Blend Membranes*

Dependence of the Membrane Properties on the Type of Cross-Linker

It was investigated whether the use of an aromatic cross-linker for sulfinate-S-alkylation in blend membranes of sulfonated poly(etherketone)s with sulfinated poly(ethersulfone)s leads to better thermal stability of the membrane. Therefore, blend membranes have been prepared from sulfochlorinated poly(etherketone) sPEK (*IEC* = 3.5 meq g^{-1}), sulfinated PSU (1 group per RU) and the cross-linkers 1,4-diiodobutane or bis(3-nitro-4-fluorophenyl)sulfone, respectively [87]. After hydrolysis of the SO_2Cl groups to SO_3H groups in the membranes, the following results were obtained: the proton conductivity of the two membranes was nearly identical, the water uptake characteristics were similar, and the thermal stability of the two membranes were nearly the same. In summary, the use of an aromatic cross-linker did not improve the thermal stability of the membranes.

Dependence of the Membrane Properties on Type of Cross-Linker (Different Aromatic)

A number of aromatic cross-linkers (Figure 9) have been tested for their suitability for the sulfinate S-alkylation reaction. When determining the properties of the membranes, we could see that all cross-linkers were capable of S-alkylating the sulfinate groups of the blend membrane. The properties of all prepared membranes were comparable [87, 88], their specific resistance being in the range 8–12 Ω cm, which is a value comparable to Nafion®. Moreover, their swelling at elevated temperatures (90 °C) was limited to 40–60%, which indicates a high degree of cross-linking. The cross-linking was also confirmed by extraction experiments of the membranes in 90 °C hot DMAc: the extraction residue agreed well with the mass share of the sulfinated and cross-linked blend membrane component. The thermal stability of all investigated blend membranes was in the same range.

Dependence of the Membrane Properties on the Covalent Cross-Linking Density

The water uptake (swelling) of ionomer membranes in fuel cells should be reduced to maintain good mechanical stability, and this if possible without reduction in H^+-conductivity. We prepared covalently cross-linked membranes which had the same calculated *IEC*, but a different cross-linking density. In Table 3, the composition and some properties of the two membranes are listed. Cross-linking polymer was sulfinated PSU Udel®, 1 sulfinate group per RU, cross-linker was 1,4-diiodobutane.

From Table 3 follows that the H^+-conductivity of both membranes is comparable, being in the Nafion range. Interestingly, the swelling value (SW) of the 1251 membrane is lower by a factor of 2 than that of the 1025 membrane; as shown by the SW90°C/SW25°C quotient (Table 3). From the results it can be concluded that the swelling values of the covalently cross-linked membranes can be varied independently from the proton conductivity of the membranes. The thermal stabilities of both membranes were nearly similar, as determined by TGA.

Dependence of the Membrane Properties on the Type of Sulfonated Poly(Etherketone)

The three different sulfonated poly(etherketones) sPEK, sPEEK and sPEKEKK have been used in covalently cross-linked blend membranes as the H^+-conductive component. It was found that the properties of the different membranes were very similar [87].

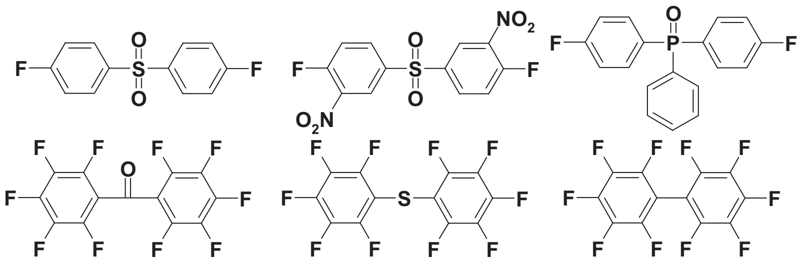


Fig. 9 Tested cross-linkers for sulfinate S-alkylation.

Dependence of the Membrane Properties on the Type of Sulfinated Poly(Ethersulfone)

The two different poly(ethersulfones) PSU and PPSU were used as the cross-linking component in the covalently cross-linked blend membranes. The membranes prepared from these polymers showed comparable properties. There are some indications that the thermal and the mechanical stability of the membranes of

Table 3 Covalently cross-linked blend membranes with different cross-linking density.

Membrane No.	*IEC* of sulfonated PEK	*IEC* exp. (theo.) / meq g^{-1}	R_{sp}^{H+} / Ω cm	Cross-Linking density / mmol CL g^{-1}	SW90°C / SW25°C[a] / –
1025	1.8 (water-insoluble)	1.07(1.23)	9.8	0.296	2.94
1251	3.5 (water-soluble)	1.21(1.23)	7.7	0.607	1.43

a quotient between water uptake at 90 °C and water uptake at 25 °C sulfinated PPSU is slightly better than the thermal and the mechanical stability of membranes using sulfinated PSU [88].

Dependence of the Membrane Properties on Membrane Type (Blend/not Blend)

Covalently cross-linked blend membranes like those described above have been compared to covalently cross-linked membranes prepared from sulfochlorinated PEEK which has been partially reduced using Na_2SO_3 to yield sulfonated-sulfinated PEEK [72] (cross-linker was 1,4-diiodobutane). The properties of the two membranes are gathered in Table 4.

Comparison of the properties yields two points of interest: the SW90°C/SW25°C quotient of the completely cross-linked membrane was markedly lower than the SW quotient of the blend membrane, and the extraction residue of the Zh31 membrane is 100%, indicating that all macromolecules of the Zh31 are integrated in the covalent network. Obviously it is an advantage when all macromolecules are integrated in the covalent network, because this efficiently limits the water uptake of the membranes, leading to improved mechanical stability. TGA investigations of both membranes indicated an improved thermal stability of the Zh31 membrane [89]

Dependence of the Membrane Properties on Membrane Type (Nonfluorinated and Partially Fluorinated Ionomer)

We have developed partially fluorinated covalently cross-linked membranes by reaction of disulfinated poly(ethersulfone)s with pentafluorobenzene sulfochloride and different cross-linkers [90]. The scheme for the preparation of such partially fluorinated covalent ionomer networks is given in Figure 10. The membranes obtained showed high H^+-conductivities and moderate SW. In Table 5, some of the properties of one novel membrane are compared with the properties of a nonfluorinated ionomer blend membrane [88].

Both membranes have comparable H^+-conductivities. The SW quotient of the partially cross-linked membrane is markedly reduced, compared to the nonfluorinated ionomer blend membrane. The reason for this finding is that at the partially fluorinated ionomer network all macromolecules are taking part in the covalent network, allowing for effective suppression of swelling. A comparative TGA investigation of both

Table 4 Comparison: ionomer membrane/ionomer blend membrane.

Membrane No.	Membrane polymers	*IEC* exp. (theo.) / meq g^{-1}	R_{sp}^{H+} / Ω cm	SW90°C/ SW25°C / –	Extraction residue exp. (theo.)[a] / %
1030	Sulfinated PSU+ sulfonated PEEK	1.14(1.23)	9.5	2.05	91.2(54.5)
Zh31	Sulfinated-sulfonated PEEK	0.84(1.26)	9.6	1.38	100 (100)

[a] the membranes were dry-weighed, followed by an 48 h immersion in DMAc at 90 °C. During this time, all non-cross-linked polymer dissolved in DMAc.

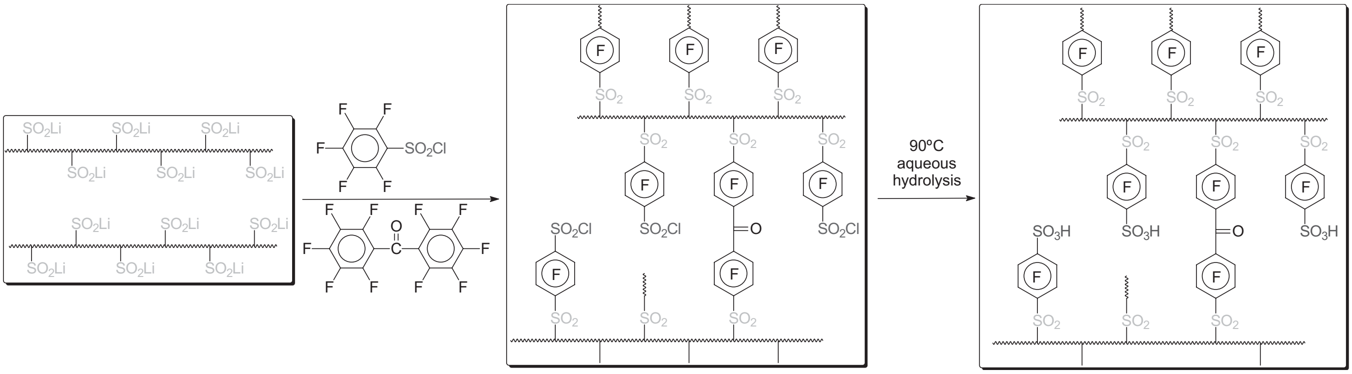
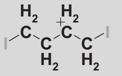
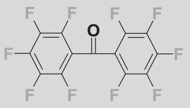
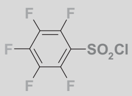


Fig. 10 Partially fluorinated ionomer network preparation.

Table 5 Properties of nonfluorinated and partially fluorinated ionomer membranes.

Membrane No.	Membrane polymers	Cross-linker	*IEC* exp. (theo.) / meq g^{-1}	R_{sp}^{H+} / Ω cm	SW90°C/ SW25°C / –
1030	monosulfinated PSU + sulfonated PEEK		1.14 (1.23)	9.5	2.05
1312	disulfinated Radel R	 	0.81	13.1	1.46

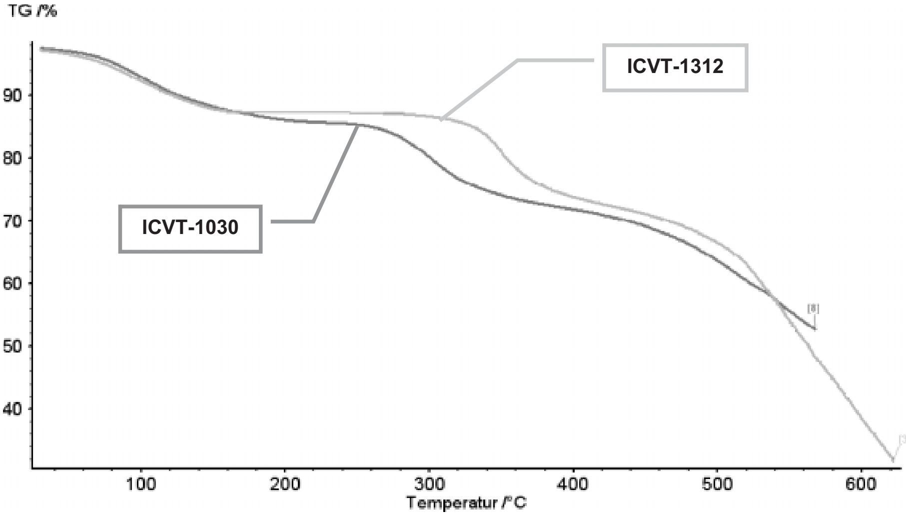


Fig. 11 TGA traces of the nonfluorinated 1030 and of the partially fluorinated 1312 membrane, respectively.

membranes suggests improved thermal stability of the partially fluorinated network membrane (Figure 11).

Dependence of the PEFC Performance on Operation Temperature

Some of the covalently cross-linked blend membranes were tested in a PEFC at different temperatures. The i/U polarization curves of one of these membranes, the 1251 membrane, are shown in Figure 12. It is obvious that the performance of the membrane is comparable to Nafion® up to temperatures of 100 °C. Above this temperature, however progressive drying-out of the membrane takes place, leading to a dramatic decrease in performance. The results suggest that it is required to improve the water-storage capacity of sulfonated ionomer membranes to ensure fuel cell-applicability in the mid-temperature range 100–150 °C.

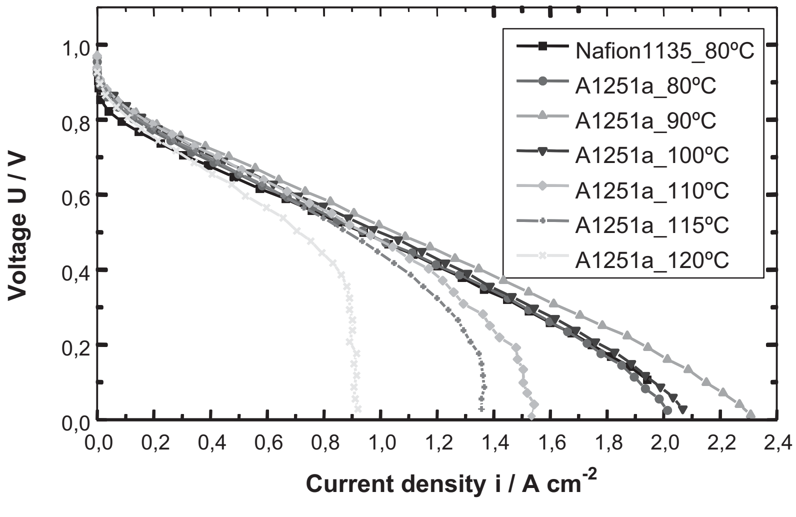


Fig. 12 i/U polarization curves of the 1251 membrane in a PEFC at T = 80–120 °C, O_2/H_2 operation, catalyst loading 2 mg cm^{-2}, pressure 2 bar.

2.3.3 Covalent-ionically cross-linked membranes

Comparison of the Morphology of Binary and of Ternary Covalent-Ionically Cross-Linked Membranes

As already mentioned, the ternary covalent-ionically cross-linked blend membranes show phase-separation, due to incompatibility of the sulfinate and the basic blend component. This problem was overcome by preparation of binary covalent-ionically cross-linked blend membranes: the polysulfonate was mixed with a polymer carrying both sulfinate and basic groups in statistical distribution on the same backbone. The TEM micrographs of the binary blend membrane clearly showed a homogeneous morphology of this membrane [80].

Comparison of the Properties of Binary and Ternary Covalent-Ionically Cross-Linked Membranes

The properties of a ternary covalent-ionically cross-linked blend membrane (ICVT-1028) were compared to the properties of a binary covalent-ionically cross-linked blend membrane (ICVT-WZ-054), both membranes showing comparable *IEC* and proton conductivity [79, 80]. The main difference in properties between the two membranes was their different swelling behaviour. In Figure 13, the water uptake (swelling) of both membranes' dependence on *T* is shown. The findings can be explained as follows: the membrane WZ 054 has a homogeneous morphology, the covalent network spreads all over the membrane matrix. Therefore, the water uptake of this membrane can be effectively limited. In contrast, the membrane 1028 is a phase-separated membrane, where the covalently cross-linked membrane phase is a discontinuous (disperse) membrane phase. Therefore, only the water uptake of the disperse phase is limited while the water uptake of the continuous membrane phase, in which most of the sulfonated macromolecules are placed, is not suppressed, leading to extreme membrane swelling at T > 60°C where the ionic cross-links are split off [86]. It is advantageous to ensure that covalent-ionically cross-linked ionomer membranes show a homogeneous morphology in order to efficiently suppress the water uptake of the membranes.

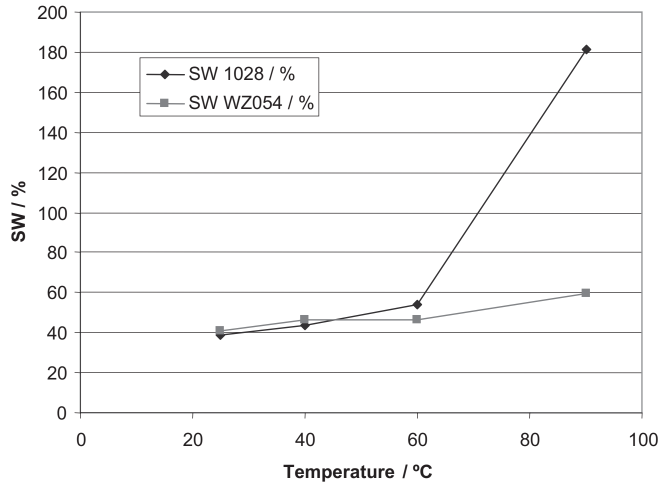


Fig. 13 Water uptake of ICVT-1028 (ternary blend) and ICVT-WZ-54 (binary blend) dependence on *T*.

2.3.4 Composite Blend Membranes

Composite Membranes by Introduction of Inorganic Powders

Our first approach for the preparation of hybrid membranes was the addition of inorganic particles to the polymer solutions, followed by solvent evaporation. The following inorganics have been added as μ-particles: SiO_2 (Aerosil 380®, Degussa) [79], Rutil TiO_2 (Aldrich 22,422-7) [80], and layered ZrP powder (Prof. Linkov, Univ. of the Western Cape, Cape Town, South Africa) [89]. Unfortunately, agglomeration of the inorganic particles in the membrane matrix took place, leading to large inorganic particles within the membrane morphology which were not effective in adsorption of water, particularly at elevated temperatures of > 80 °C. When applied to DMFC, a strong reduction of MeOH permeability could be realized by addition of SiO_2 particles, but the DMFC performance was also reduced. Consequently, the fuel cell performance of these membranes was not improved, in comparison to the pure organomembranes [80].

Comparison of Organo Blend Membranes with ZrP Hybrid Blend Membranes

By the application of the $ZrOCl_2$-H_3PO_4 procedure to the covalently cross-linked blend membranes, transparent hybrid membranes were obtained, indicating that the size of particles was well below the wavelength of visible light [88]. In Table 6, some of the properties of a covalently cross-linked blend membrane (ICVT-1228) and of the ZrP hybrid membrane based on this membrane (ICVT-1228ZrP) are listed.

Table 6 Some properties of ICVT-1228 and ICVT-1228ZrP.

Membrane No.	*IEC* exp. (theo.) / meq g^{-1}	R_{sp}^{H+} / Ω cm	SW90°C/SW25°C / –
1228	1.24 (1.23)	9.5	1.33
1228ZrP	1,21	19.6	1.24

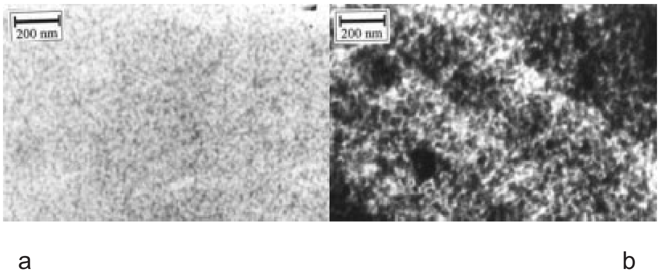


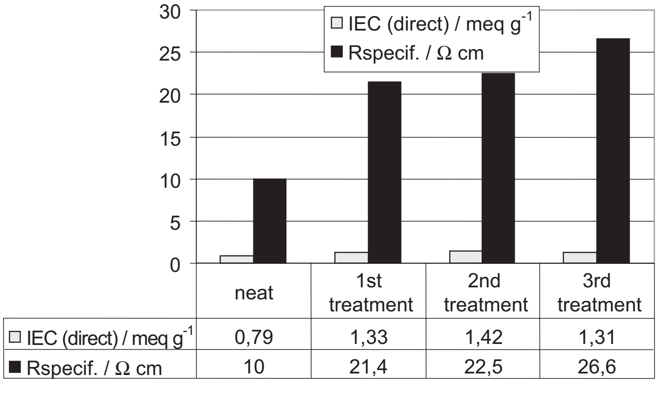
Fig. 14 TEM micrographs of ICVT-1228 (a) and ICVT-1228ZrP (b), sulfonate groups exchanged with Pb^{2+} for a better contrast, magnification 52,000X.

Interestingly, the room temperature proton conductivity of the composite membrane, compared to the organomembrane, was reduced by a factor of two. This finding can be explained by a structure of the ion-conducting channels and the growth of the inorganic phase, which preferably takes place in the vicinity of the SO_3H ion-aggregates. In Figure 14, TEM micrographs of the 1228 and 1228ZrP membrane are presented. The growth of the inorganic phase can be seen very clearly.

The even distribution of the ZrP microphase within the membrane matrix was proven by SEM-EDX mapping [88]. One of the ZrP hybrid blend ionomer membranes was tested in a PEFC up to temperatures of 115 °C and compared with a pure organomembrane. While the pure organomembrane showed a peak power density of 0.35 W cm^{-2} at 80 °C, the ZrP hybrid membrane had a peak power density of 0.6 W cm^{-2} at 115 °C, indicating that the ZrP phase had a positive impact on PEFC performance. The improvement of PEFC performance by the ZrP phase could be due to both improvement of water storage ability and by the contribution of the ZrP phase to proton transport at elevated temperatures as suggested by literature [38, 63, 65,]. However, for an in-depth clarification of the influence of the ZrP phase to PEFC performance of the hybrid membranes, further work has to be done.

Properties of Composite Membranes Repeatedly Treated with $ZrOCl_2$/H_3PO_4

Blend membranes from sulfonated PEKEKK Ultrapek (*IEC* = 3 meq g^{-1}) and sulfinated PSU Udel (1 group per RU),



	neat	1st treatment	2nd treatment	3rd treatment
☐ IEC (direct) / meq g^{-1}	0,79	1,33	1,42	1,31
■ Rspecif. / Ω cm	10	21,4	22,5	26,6

Fig. 15 *IEC* and H^+-conductivities of the 1202 membranes.

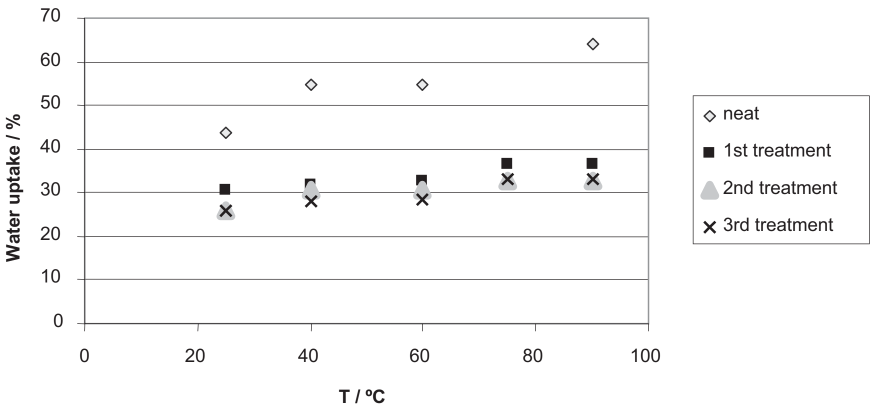


Fig. 16 Water uptake of the 1202 membranes dependence on *T*.

cross-linked with 1,4-diiodobutane (ICVT-1202), were repeatedly treated with $ZrOCl_2$-H_3PO_4. The change in membrane properties with the number of treatments of the ICVT-1202 membrane was monitored. In Figure 15, the *IEC* and H^+-conductivities of the membranes are presented. In Figure 16, the water uptake of the neat and of the $ZrOCl_2$-H_3PO_4-treated membranes are shown. From Figure 15 and Figure 16, the following can be read: using the ZrP treatment, the H^+ resistance is increased, supporting the aforementioned hypothesis that the deposit of ZrP in the ion-conducting channels narrows them, leading to hindrance of H^+-transport. Moreover the water uptake is reduced, which can be explained by (hydrogen bridge, dipole-dipole) interactions between the ZrP phase, which contains $Zr(HPO_4)_2$ groups [91], and the SO_3H groups of the organo-ionomer. Repeated treatment of ionically cross-linked blend membranes with $ZrOCl_2/H_3PO_4$ lead to similar results: the H^+-resistance of the membranes was increased, and their water-uptake was reduced [91].

Properties of Ionically Cross-Linked Membranes Containing Tungstenic Phosphoric Acid

Blend membranes from sulfonated PEKEKK Ultrapek®. PBI Celazole and tungstenic phosphoric acid (TPA) have been prepared [68]. Indeed, by introduction of TPA the proton conductivity of the membranes could be enhanced. We investigated the possible leaching-out of HPA molecules from the membrane matrix by post treatment of the pure organomembrane and the composite membranes, initially containing 10, 20 and 40 wt.-% TPA, in (i) 10% HCl at 90 °C for 48 h and (ii) water at 60 °C for 48 h, followed by investigation of the post treated membranes in TGA up to 600 °C. TPA remains as a residue when the organic membrane part is thermally removed. The pure organoblend membrane was completely decomposed after TGA, while the TGA of the composite membranes showed that only a part of the HPA was present in the membrane after the post treatment (Table 7).

Table 7 TPA loss in sPEKEKK-PBI-TPA membranes.

Content TPA / %	Calc. Residuals (dehydrated TPA) / %
0	0
10	8.56
20	17.12
40	34.24
100	85.6

The interactions present in the sPEKEKK-PBI-TPA membranes are not strong enough to prevent leaching-out of the TPA ions, and methods must be found for immobilisation of the heteropolyacids in the ionomer blend membrane matrix, which could be achieved by the generation of chemical bonds between the TPA molecules and the organomembrane.

2.4 Comparison of the Properties of the Different Ionomer Membrane Systems

To be able to assess the suitability of the differently cross-linked blend membrane types for fuel cell application, we compared representative membranes of the different types having comparable calculated *IEC*s.

2.4.1 Comparison of the Properties of Differently Cross-Linked Ionomer Membrane Types Having Comparable Calculated IEC

Differently cross-linked membranes having a calculated *IEC* of 1.2–1.3 meq g^{-1} were compared. The composition and characterization results are presented in Table 8. From Table 8 it can be concluded that the covalently cross-linked membrane 1398 showed the best properties in this series: this membrane has the lowest resistance and is the only one which does not dissolve when immersed in 90 °C hot water. Of the other membranes in this series the interactions between the acidic blend component and the other components are not strong enough to prevent dissolution in 90 °C hot water. In particular, the membrane 1397 showed a low *IEC* and a high H^+-resistance, indicating that a considerable amount of sulfonated macromolecules had already diffused out from the blend membrane matrix. The membrane 1397 is not transparent, indicating a microphase-separated morphology, which facilitates leaching out of the sulfonated blend membrane component.

The dissolution of the 3 membranes also reflects the undesirable property of sPEEK having an *IEC* of 1.8 meq g^{-1}: this ionomer itself dissolves in water at T = 90 °C. In the morphologically homogeneous- covalently cross-linked membrane, the strong entanglement of the sPEEK macromolecules in the covalent network obviously prevents their leaching-out. Interestingly, use of sPEK (*IEC* = 1.8 meq g^{-1}) instead of sPEEK (*IEC* = 1.8 meq g^{-1}) in ionically cross-linked membranes with PBI, having the same *IEC* as membrane 1389, prevents dissolution in water at T = 90 °C [84]. Obviously, in sPEK-PBI blends stronger interactions between the blend components are present than in sPEEK-PBI blends. The rea-

Table 8 Composition and characterization results of differently cross-linked membranes having comparable calculated *IEC* (comparison: pure PEEK-SO_3H, $IEC = 1.8$ meq g^{-1}).

Membrane No.	Type cross-linking	Composition	$IEC_{calc}(IEC_{exp})$ / meq g^{-1}	R_{sp}^{H+} (HCl)[I] / Ω cm	SW[II] 25-40-60-90 / °C
sPEEK	–	sPEEK (1.8)	1.8(1.54)	21.5	31-37-50-*[V]
1397	Van der Waals/ dipole-dipole	sPEEKCl (1.8)[III] PSU[IV]	1.23(0.82)	69.2	25-35-42-*[V]
1392	H-bridge	sPEEK (1.8) PEI Ultem®[VI]	1.23(1.01)	10.3	30-46-59-*[V]
1389	Ionic	sPEEK (1.8) PBI[VII]	1.3(1.12)	28.4	25-33-34-* [V]
1398	covalent	sPEEKCl (1.8)[III] PPSU-SO_2Li[VIII] B4FPhPhPO[IX]	1.23(1.18)	6.7	32-50-56-108

[I] measured in 0.5 N HCl
[II] measured in water of the respective *T*
[III] hydrolysis after membrane formation
[IV] unmodified PSU Udel®, producer Solvay
[V] dissolved at 90 °C
[VI] product of General Electric
[VII] PBI Celazole®, producer Celanese
[VIII] sulfinated PPSU Radel R®, 1 group per RU
[IX] cross-linker bis(4-fluorophenyl)-Phenylphosphinoxide

son for this finding is not yet clear. However, due to the higher concentration of carbonyl groups in sPEK, compared to sPEEK, one can speculate that the carbonyl group markedly contributes to the interaction between the macromolecular chains by dipole-dipole forces and H bridges.

For the application in fuel cells the thermal stability of ionomer membranes is also of great importance. Therefore, the membranes have also been investigated by TGA-FTIR coupling.

In Figure 17, the TGA traces of the above-mentioned membranes are presented. The temperature at which splitting-off of the SO_3H groups starts, which is the first step of membrane degradation [84], and the decomposition gases of the TGA were investigated by TGA-FTIR coupling. In Table 9, the starting temperatures of SO_3H splitting-off in the different membranes are listed.

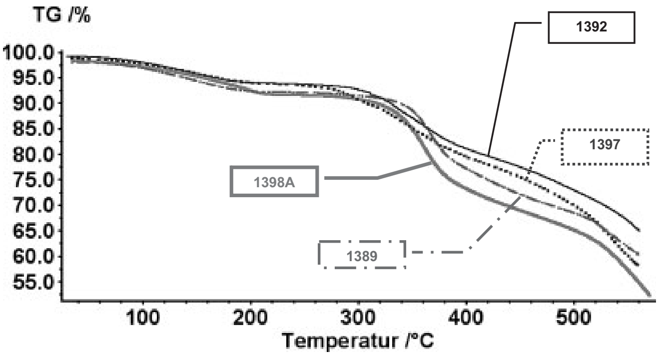


Fig. 17 TGA traces of the membranes 1397, 1392, 1389, and 1398A.

Table 9 Starting temperatures of SO_3H splitting-off at the different blend membranes (comparison with pure PEEKSO_3H, having *IEC* of 1.8 meq g^{-1}).

Membrane No.	Type cross-linking	Start-T SO_3H splitting-off / °C
PEEK-SO_3H	–	240
1397	Van der Waals / dipole-dipole	224.1
1392	H-bridge	228.1
1389	Ionically	239.2
1398	Covalently	232.6

The ionically cross-linked membrane showed the best thermal stability, being similar to the thermal stability of pure sPEEK, followed by the covalently cross-linked membrane. The thermal stabilities of the membranes 1392 and 1397 are markedly worse. The reason for this finding is not yet clear. In the literature it is reported that in polymer blends, in some cases, one blend component facilitates the degradation of the other blend component, as it was shown for PBI/polyarylate blends [92]. From the obtained results it can be concluded that the covalently and the ionically cross-linked blend membrane are interesting candidates for fuel cell application.

2.4.2 Comparison of the Properties of Covalently, Ionically and Covalent-Ionically Cross-Linked Ionomer Membranes Having the Same IEC

To find out which of the ionomer blend membranes, if any, are most promising for application in membrane fuel cells, we prepared a covalently, a covalent-ionically and an ionically cross-linked membrane having comparable IEC [86]. Membranes were obtained which showed almost identical H^+-conductivities and thermal stabilities. However, the membranes showed marked differences in swelling behaviour: the covalently cross-linked membrane (ICVT-1025) had a swelling value at 90 °C of 87%, while the swelling values of the ionically cross-linked membrane (ICVT-1029) was to 190% and that of the covalent-ionically cross-linked membrane (ICVT-1028) was 181%. As already pointed out, the unexpected high swelling of ICVT-1028 can be explained by ineffective covalent cross-linking taking place in the disperse blend membrane phase of the inhomogeneous ICVT-1028 blend membrane, while the high swelling value of ICVT-1029 is explained in the splitting-off of the ionic cross-links at elevated temperatures in water [86]. In 2M MeOH solution, the swelling behaviour of the three membranes is comparable to

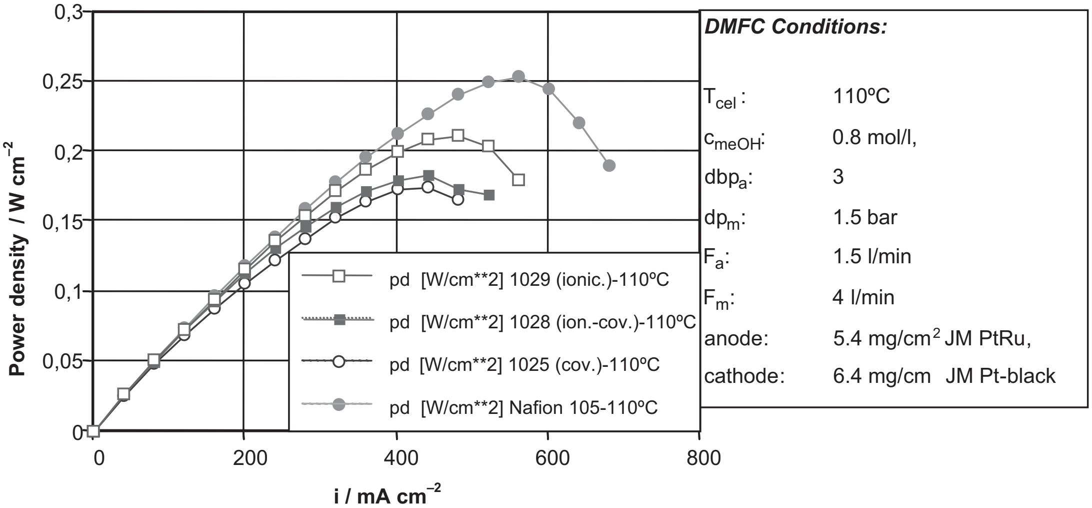


Fig. 18 Current density/power density curves of the membranes ICVT-1025, ICV.T-1028 and ICVT-1029 at 110 °C, comparison Nafion®105).

that in H_2O [93]: at 90 °C, the ICVT-1025 swells to 95%, while the ICVT-1028 has a swelling value of 150%, and the ICVT-1029 increases in weight by 195%. All three membranes were applied to a DMFC at temperatures from 25 to 110 °C [86]. The following current density/power density curves were obtained at 110 °C (Figure 18). From Figure 18 it can be seen that the performance of the three membranes is comparable, only slightly inferior than that of the Nafion®105 membrane. Therefore, from the DMFC test, no advantage of one of the three membrane types over the others could be observed, which is reflected by the fact that the H^+-resistance of the membranes, measured *in-situ via* impedance spectroscopy, was nearly the same: the ICVT-1029 had an area resistance of 0.13 Ω cm^2, while the ICVT-1028 had an area resistance of 0.16 Ω cm^2 and the ICVT-1025 an had area resistance of 0.17 Ω cm^2. The MeOH permeability of our membranes was lower than that of Nafion®105 by a factor 2–3 [86]. From this finding, one would expect that the performance of the cross-linked blend membranes is better than that of Nafion®105 under the same conditions. The reason why this is not the case lies in the bad connection between the polyaryl membranes and the catalytic electrodes which contain Nafion® as the binder and a H^+-conductive component: After the DMFC test, partial delamination between membranes and electrodes could be observed [86]. Substitution of Nafion® as a component by a polyaryl ionomer in the electrode did not lead to satisfying results up to now.

3 Conclusions

Commercially available arylene main-chain polymers have been used for modification with proton-conductive groups. We have developed blend concepts for low-temperature (< 100 °C) fuel cell ionomer membranes, blending differently modified polymers using cross-linking procedures (physical cross-linking, chemical cross-linking) because of the ease of mixing the different polymers in a common solvent, reduction of swelling by cross-linking, and the possibility of tailoring the membrane morphology and therefore the membrane properties by selective choice of type of blend components.

The developed membrane types had the following properties. The van-der-Waals-/dipole-dipole-blends and the hydrogen bridge blends showed a heterogeneous morphology, leading to extreme swelling at elevated temperatures. These membrane types are therefore not suitable for fuel cell application. In the acid-base blends a wide variability in properties could be reached by variation of the materials used for blending. The membranes showed good performance in PEFC up to 100 °C and in DMFC up to 130 °C, reaching peak power densities approaching 0.3 W cm^{-2} at reduced noble metal loadings of 3 mg cm^{-2}. A disadvantage of the ionically cross-linked membranes is that the ionic cross-links split off at $T > 70$–80 °C, leading to extreme swelling above this temperature range in liquid water. Covalently cross-linked (blend) membranes also showed a wide variability in properties, with good H^+-conductivities and stabilities. Leaching out of the sulfonated component could be avoided by preparation of covalently cross-linked ionomeric networks from polymers carrying both sulfonic and sulfinate groups on the same backbone. The covalently cross-linked membranes showed good performance in PEFC up to 100 °C and in DMFC up to 130 °C. A disadvantage of the covalently cross-linked membranes is that they tend to be brittle on drying out. Using covalent-ionically cross-linked (blend) membranes, a wide range in properties was achievable by variation of the acidic, basic, and cross-linking components. The problem of morphological heterogeneity and therefore extreme swelling of the ternary membranes at $T > 60$–80 °C could be overcome by blending of polymers carrying different types of functional groups onto the same backbone. The covalent-ionically cross-linked membranes showed good performance in DMFC up to $T = 110$ °C.

Cross-linked organic-inorganic blend composite membranes have been prepared from ionically or covalently cross-linked ionomer blend membranes by addition of μ-sized inorganic powders to the solution of the organopolymers, by addition of heteropolyacids to the solution of the organopolymers, and by ion-exchange of the formed organomembrane SO_3H protons with metal cations like ZrO^{2+}, TiO^{2+}, etc., followed by immersion of the membrane in phosphoric acid, leading to precipitation of metal phosphates or metal hydrogenphosphates within the membrane matrix. Blend membranes prepared by addition of inorganic powders to the polymer solutions give composite membranes containing large, agglomerated μ-sized particles, and no positive effect of the inorganic phase on the H^+-conductivity of the membranes could be found. Ionically cross-linked blend membranes by addition of heteropolyacids to the polymer solution showed strong heteropolyacid leaching-out during the membrane post-treatment which disqualifies this membrane type for application in fuel cells. Blend membranes having a layered zirconium phosphate "ZrP" phase were transparent, indicating nano-sized inorganic particles, and showed good H^+-conductivity, mechanical and thermal stability. Application of one of these composite membranes to a PEFC yielded good performance up to $T = 115$ °C.

In future work, membranes from arylene main-chain polymers carrying both sulfonate and sulfinate groups on the same backbone will be further developed, as well as partially fluorinated covalent ionomer networks which show improved chemical and thermal stability, compared to nonfluorinated systems. We will concentrate on the further development of blend membranes of sulfonated poly(etherketone)s with stable and strong polybases like poly(benzimidazole)s, due to their high durability, and on morphologically homogeneous ionomer membranes by preparation and further development of polyarylenes carrying several types of functional groups onto the same backbone to avoid phase-separation. Further development of differently cross-linked hybrid membrane systems having ZrP-type inorganic phases will also be made. Our objective is to obtain membranes whose inorganic phase is both proton-conducting and serves as water-storage to allow fuel cell operation in the temperature range 100–150 °C.

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