

Development of ionomer membranes for fuel cells

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Received 18 January 2000; received in revised form 11 July 2000; accepted 11 July 2000

Abstract

In this contribution an overview is given about the state-of-the-art at the membrane development for proton-conductive polymer (composite) membranes for the application membrane fuel cells, focusing on the membrane developments in this field performed at ICVT.

For preparation of the polymers, processes have been developed for sulfonated arylene main-chain polymers as well as for arylene main-chain polymers containing basic N-containing groups, including a lithiation step. Covalently cross-linked polymer membranes have been prepared by alkylation of the sulfinate groups of sulfinate group-containing polymers with α,ω -dihalogenoalkanes. The advantage of the covalently cross-linked ionomer membranes was their dimensional stability even at temperatures of 80–90°C, their main disadvantage their brittleness when drying out, caused by the inflexible covalent network. Sulfonated and basic N-containing polymers (commercial polymers as well as self-developed ones) have been combined to acid–base blends containing ionic cross-links. The main advantage of these membrane type was its flexibility even when dried-out, its good to excellent thermal stability, and the numerous possibilities to combine acidic and basic polymers to blend membranes having fine-tuned properties. The main disadvantage of this membrane type was the insufficient dimension stability at $T > 70$ –90°C, caused by breakage of the ionic cross-links, where the ionic cross-links broke as easier as lower the basicity of the polymeric base was. Some of the acid–base blend membranes were applied to H₂ membrane fuel cells and to direct methanol fuel cells up to 100°C, yielding the result that these membranes show very good perspectives in the membrane fuel cell application. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Proton-conductive ionomer blend membranes; Membrane fuel cells; PEFC; DMFC; Covalent cross-linking; Ionic cross-linking

1. Introduction

Fuel cell technology is expected to become one of the key technologies of the 21st century both for stationary applications like block power stations and instationary applications like personal vehicles, trucks, buses, and locomotives, because the fuel utilization in fuel cell engines is markedly higher than in combustion engines. The proton-conducting membrane is the key component of a fuel cell system,

because only highly stable membranes can withstand the harsh chemical and physical environment in a fuel cell, which includes chemically active noble metal catalysts in the fuel cell electrodes, optionally chemically aggressive fuels like methanol and its partial oxidation products, aggressive oxidants like oxygen, formation of reactive radicals at the electrodes, especially at the cathode, and process temperatures which can exceed 100°C.

In this section the state-of-the-art in the development of proton-conductive polymer membranes and in the application of these membrane in membrane fuel cells is discussed. Among the membranes representing

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the state-of-the-art, the ionomeric membrane systems developed in our lab are mentioned.

1.1. Perfluorinated ionomers and its composites

1.1.1. Homogeneous perfluorinated ionomer membranes

Perfluorinated ionomers consist of a perfluoroalkyl side chain and a perfluoro alkyl ether side chain with a sulfonic acid group at its end. The mostly known materials of this class are the DuPont product Nafion[®] [1] and the Dow product Dow[®] membrane [2]. The difference between these two ionomer types is that the side chain of the Dow[®] membrane is shorter than the side chain of Nafion[®] [2]. The perfluorinated ionomers have an outstanding chemical stability, and excellent performance can be achieved when these membranes are applied in membrane fuel cells, especially in hydrogen fuel cells: longevities of up to 60,000 h were achieved with these materials at temperatures of 80°C. Their main shortcomings of these materials is their high price of minimum US\$ 800/m² [3] and the production process which includes strongly toxic and environment-unfriendly intermediates. A shortcoming of the perfluorinated ionomers especially related to their application in direct methanol fuel cells (DMFC) is their high methanol permeability which drastically reduces the DMFC performance [4].

1.1.2. Micro-reinforced perfluorinated ionomer composite membranes

The company Gore has developed micro-reinforced composite membranes with the trade name Gore-Select[®], which consist of a microporous stretched PTFE membrane whose pores are filled with perfluorinated ionomer [5,6]. By the PTFE host membrane the membrane is mechanically stabilized, compared to Nafion[®], and thus the membrane thicknesses could be reduced up to 5 μm, leading to a proton conductivity of the Gore-Select[®] membranes which is a factor of 10 higher than the proton conductivity of Nafion[®].

1.1.3. Composites of perfluorinated ionomers with heteropolyacids

Other Nafion[®]-containing composite materials are membranes which also contain polythiophene or different heteropolyacids like phosphotungstic acid,

phosphomolybdic acid or phosphotinic acid [7]. Via the addition of these materials the ion conductivity is significantly increased. The application of such composite membranes in membrane fuel cells is under active research.

1.2. Partially fluorinated ionomers

1.2.1. Grafted ionomer membranes

Partially fluorinated are under active research, for example in the group of Scherer at Paul Scherrer Institute, Villigen, Switzerland [8,9]. This ionomer membrane type is prepared in following steps: (1) perfluorinated/partially fluorinated polymer foils (e.g. poly(tetrafluoroethylene-*co*-hexafluoropropylene) FEP, poly(ethylene-*alt*-tetrafluoroethylene)) are γ-irradiated, and radical sites are formed in the polymer matrix; (2) the radical-containing foils are swollen with, for example, styrene/divinylbenzene, and the radical sites are starting styrene/divinylbenzene graft networks, forming interpenetrating polymer networks (IPNs) of poly(styrene-*co*-divinylbenzene) in the fluorinated polymer matrix; (3) after washing out of residual monomers, the styrene and divinylbenzene repeating units of the IPN are sulfonated by immersion of the foils in chlorosulfonic acid/dichloroethane mixtures. These proton-conducting membranes showed good performance when being applied in PEM fuel cells. Grafted ionomer membranes based on poly(vinylidene fluoride) have been developed by Sundholm [10]. A disadvantage of these membranes is the use of styrene and divinylbenzene monomers from which is known that their oxidation stability is limited, due to the tertiary C–H bonds present in the styrene/divinylbenzene graft chains which are sensitive to O₂ and hydrogen peroxide attack.

1.2.2. Ionomer types based on

poly(α,β,β-trifluorostyrene) and copolymers

The Canadian Ballard Company has developed a number of partially fluorinated proton-conducting membranes which consist of sulfonated [11] or phosphonated [12] polymerisates of unmodified α,β,β-trifluorostyrene and α,β,β-trifluorostyrene modified with radicals R. The sulfonated species show excellent performance in both oxygen and air membrane fuel cells [13], while the phosphonic acid-type membranes showed excellent performance only in oxygen

fuel cells [12]. Disadvantage of these membrane types is the complicated production process for the monomer α,β,β -trifluorostyrene [14] and the difficult sulfonation [11] and phosphonation [12] procedures for poly(α,β,β -trifluorostyrene)-homopolymers and -copolymers.

1.3. Nonfluorinated ionomers

1.3.1. Sulfonated phenol–formaldehyde resins and sulfonated vinyl polymers

The first ionomer membranes based on hydrocarbon polymers have been developed by General Electric: at first sulfonated phenol–formaldehyde resins in 1935 by Adams and Holmes [15], followed by sulfonated divinylbenzene-cross-linked polystyrene by D’Alelio [16]. It was, however, soon discovered that these membranes show insufficient chemical stability. Especially tertiary C–H bonds and benzylic bonds are easily attacked by oxygen, forming hydroperoxide radicals [17–19]. The hydroperoxide sites at the macromolecules can cause radical chain scission.

1.3.2. Phosphazene-based cation-exchange membranes

Recent papers of Pintauro and co-workers have shown that polyphosphazene-based cation-exchange membranes may be viable candidate materials especially for direct liquid methanol fuel cells. Sulfonated and cross-linked membranes had a high proton conductivity and low water/methanol diffusion coefficients [20,21].

1.3.3. Homogeneous partially sulfonated (het)arylene main-chain polymers

In the last decades numerous types of arylene main-chain polymers have been developed. Motivation for these developments was that these polymer family shows the best chemically and mechanically stabilities next to the fluorinated polymer classes. A huge number of these polymers have also been sulfonated in order to obtain proton-conductive membranes. Among the arylene polymers which have been sulfonated are the following polymer families: poly(phenylene ethers) (poly(2,6-dimethyl-1,4-phenylenether), poly(2,6-diphenyl-1,4-phenylenether) [13,22–24]), poly(ethersulfone)s [25,26], poly(etherketone)s [27], poly(phenyl-

enesulfide)s [28], poly(phenylquinoxaline) [29], poly(benzimidazole) [30], and different poly(imide)s and poly(etherimide)s [31,32]. Some of these ionomer membranes reached long life spans in membrane fuel cells: as an example, a sulfonated naphthalene-type polyimide reached a operation time of over 3000 h at 60°C [32].

A general problem of homogeneous sulfonated arylene main-chain polymers is that these ionomers begin to swell too strong and thus lose their mechanical stability when a certain sulfonation degree (ion-exchange capacity 1.4–1.6 meq SO₃H/g) or a certain operation temperature (60–80°C) is exceeded. Therefore, it is required to reduce the swelling degree of the membranes without lowering their proton conductivity too strong. These requirements are achieved by cross-linking of the ionomer membranes (see below).

1.3.4. Covalently cross-linked arylene main-chain ionomers and ionomer blends

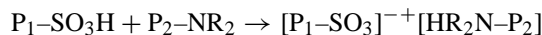
In the literature only few examples are found for covalently cross-linked ionomer membranes, apart from sulfonated poly(styrene-co-divinylbenzene) ionomer membranes. In [24] a covalent cross-linking procedure for sulfonated poly(ethersulfone) Victrex[®] was presented: a part of the SO₃H groups were first transferred to sulfonyl *N*-imidazolidine groups, and these groups have been reacted with 4,4'-diaminodiphenylsulfone, forming sulfonamide cross-linking bridges. It is, however, questionable whether the formed sulfonamide cross-linking bridges are stable in the strongly acidic environment of the fuel cell.

In our group, a novel cross-linking process for ionomer membranes has been developed, consisting of the alkylation of sulfinate groups with α,ω -dihalogenoalkanes [33–35].

The thermal stability of the covalently cross-linked ionomer (blend) membranes was quite high and ranged between 230 and 270°C. A problem occurring at these membranes was that they became very brittle when drying out, which is a severe problem when these membranes are applied to membrane fuel cells. The brittleness is possibly caused by the inflexibility of covalent networks. Because of this reason we began with the development of ionomer networks being more flexible, containing ionic cross-links (see Section 3.2).

1.3.5. Ionically cross-linked ionomer networks

Flexible ionomer networks can be built up via mixing of polymeric acids and polymeric bases, obtaining networks which contain ionic cross-links formed by proton-transfer from the polymeric acid onto the polymeric base:



It was observed that acid–base blend membranes show, when drying out, reduced brittleness, compared to uncross-linked or covalently cross-linked ionomer membranes, which is possibly caused by the flexibility of ionic cross-links. In our group we have already developed different types of acid–base blend membranes, consisting of sulfonated PSU Udel[®], sulfonated PES Victrex[®], and sulfonated poly(etheretherketone) Victrex[®] as the acidic compound, and of different commercially available polymeric bases like polybenzimidazole PBI Celazole[®], polyethylenimine PEI, and poly(4-vinylpyridine) P4VP as the basic compound [36–41]. Moreover, novel basic polymers have been developed, consisting of a PSU backbone which is modified with NR₂– groups (R = H, CH₃) [42,43] or with side groups including pyridine or tertiary amino groups [44]. The developed acid–base blend membranes show outstanding thermal stabilities of 280–350°C, determined by DSC and TGA. It could be shown that the acid–base blend membranes showed excellent performance in H₂ fuel cells and in direct methanol fuel cells [39–41].

1.4. High-molecular/low-molecular composite membranes

1.4.1. Polymer/inorganic mineral acid composite membranes

A well-known example for this class of composite membranes is polybenzimidazole PBI in which was deposited phosphoric acid (or sulfuric acid) as proton-conducting electrolyte [45–47]. The membranes can be prepared via two different routes: (a) preparation from a solution which contains PBI and phosphoric acid; (b) preparation by immersion of a preformed PBI membrane in, for example, 11 M phosphoric acid [48]. The membranes show excellent proton conductivities, especially at temperatures of up to 130–150°C [47], which is a temperature range

at which ionomers like Nafion[®] only show very low proton conductivities because of drying out [48,49]. The advantage of PBI/H₃PO₄ membranes, compared to Nafion[®], is, that they are much cheaper than Nafion[®]. Their main disadvantage is that the H₃PO₄ molecules can diffuse out of the membrane because they are in excess towards basic polymer sites (six H₃PO₄ molecules per PBI repeating unit). Due to their high proton conductivity at $T > 100^\circ\text{C}$ these membranes are especially suitable for the application in direct methanol fuel cells (DMFC). Nafion[®] membranes are not that suitable for the application in direct methanol fuel cells, due to their high methanol permeability, which leads to strong potential reduction [50]. A disadvantage of the PBI/H₃PO₄ membranes with absorbed, not deposited H₃PO₄, is that they can only be used with a feed of vaporized methanol. When liquid contacts the membrane, the phosphoric acid leaches out of the membrane and the proton conductivity drops precipitously.

Further H₃PO₄ composite membrane systems with high proton conductivities are so-called “hydrogels”, as, for example, poly(vinylalcohol)/H₃PO₄ blends [51], poly(ethylenoxide)/poly(methylmethacrylate)/H₃PO₄ blends [52], and poly(acrylamide)/poly(ethylenoxide)/H₃PO₄ blends [53]. However, so far no fuel cell results obtained with such membranes have been published. Their suitability for the fuel cell application is questionable due to the presence of easily oxidizable tertiary C–H bonds in the polymers forming the hydrogels.

1.4.2. Acidic polymer/low-molecular amphoteric composite membranes

Another type of proton-conductive composite membranes are blends of sulfonated polymers, for example sulfonated poly(etheretherketone) with amphoteric compounds like imidazole or pyrazole [54]. Imidazole and pyrazole can act both as bases and as acids: the proton is transferred from the acidic group to the basic N of these compounds. The formed imidazolium or pyrazolium cation can again deliver the proton, and thus water-free proton conductivity is possible with such composite membranes, which makes these membranes particularly interesting for the application in direct methanol fuel cells at temperatures of $>100^\circ\text{C}$. The problems with these composite membranes is

similar to the problem occurring at the PBI/H₃PO₄ composite membranes: the low-molecular amphoter can diffuse out of the membrane, because it is applied in excess towards SO₃H groups of the sulfonated polymer compound. To avoid loss in amphoteric compound it is required to develop composite membranes where the amphoteric compound is bound to the side group of a polymer backbone.

1.5. Organic/inorganic composite membranes

1.5.1. Ionomer/inorganic oxide particle composite membranes

In the literature a paper is found which deals with the development and fuel cell application of Nafion[®] membranes in which have been incorporated highly porous SiO₂ “Aerosil” particles (producer: Degussa) up to concentrations of 3% [55]. The SiO₂ works as water storage medium, enabling good proton conductivities even at temperatures of 145°C — Nafion[®] membranes containing no SiO₂ have only very low proton conductivity at this temperature. The DMFC application of such membranes yielded good performance. A maximum power density of 240 mW/cm² at 0.6 A/cm² and 0.4 V was obtained.

1.5.2. Ionomer/inorganic oxide particle composite membranes via sol–gel process

It would be advantageous to reduce the inorganic particle size in organopolymer/inorganic composites to molecular dimension, because the lower the particle size is, the higher is the particle surface and thus the better is the water-holding ability of the inorganic compound. Mauritz has done pioneering work in preparing ionomer/inorganic oxide “nanocomposites” via sol–gel techniques, where the inorganic compound is distributed molecular-dispersely in the ionomer matrix [56]. Core of the preparation process using sol–gel techniques is the hydrolysis of an element- or metalorganic precursor compound in the matrix of the ionomer, yielding a inorganic oxide or oxide/hydroxide network in the ionomer matrix. These systems are prepared in the following way: at first the ionomer membrane is swollen in water/alcohol mixtures, and then they are immersed in alcohol solutions containing the precursor, for example, tetraethoxysilane (TEOS). During immersion, the hydrolysis of the precursor takes place catalyzed by the sulfonic acid

groups in the ion-clusters of the ionomer membrane. Systems of this type are as follows:

- ionomer: Nafion[®]; precursor: TEOS; inorganic network: SiO₂/OH [57];
- ionomer: Nafion; precursor: Zr(OBu)₄; inorganic network: ZrO₂/OH [58];
- ionomer: Surlyn[®]; precursor: TEOS; inorganic network: SiO₂/OH [59].

Disadvantage of the above-mentioned nanocomposite membranes is that the sol–gel reaction takes place in a preformed membrane, and therefore the inorganic content in the composite membrane cannot be varied in a broad range. The nanocomposite ionomer membranes could be interesting candidates for fuel cell application, especially in DMFC at temperatures of >100°C.

1.5.3. Organic–inorganic hybrid polymers

Another class of ionomer membranes considered for fuel cell application are the so-called “ormolytes” (organically-modified silane electrolyte), for example, poly(benzylsulfonic acid siloxane) [60], which are produced by sol–gel process, followed by sulfonation in ClSO₃H/dichloromethane. These inorganic/organic hybrid polymer membranes can be cross-linked via hydrosilylation. The poly(benzylsulfonic acid siloxane) membrane shows an ionic conductivity of $1.6 \times 10^{-2}/(\Omega \text{ cm})$ [60] at ambient *T*. Fuel cell data of these membranes have not yet been published.

2. Novel polymer modification processes

2.1. Synthesis of sulfonated polymers via the metalation route

Polysulfone PSU Udel[®] is a commercial arylene main-chain polymer (producer: Amoco) which has a very good chemical stability, and thus is a suitable candidate for preparation of proton-conductive sulfonated ionomers which can be applied in fuel cells. Due to its composition, it can be substituted both via electrophilic and nucleophilic aromatic substitution: the bisphenol A-part of PSU (Fig. 1) is electron-rich and can thus be sulfonated via electrophilic sulfonation [61], while the diarylsulfone part of PSU is electron-deficient and can thus be reacted with metalorganic compounds like *n*-BuLi, forming

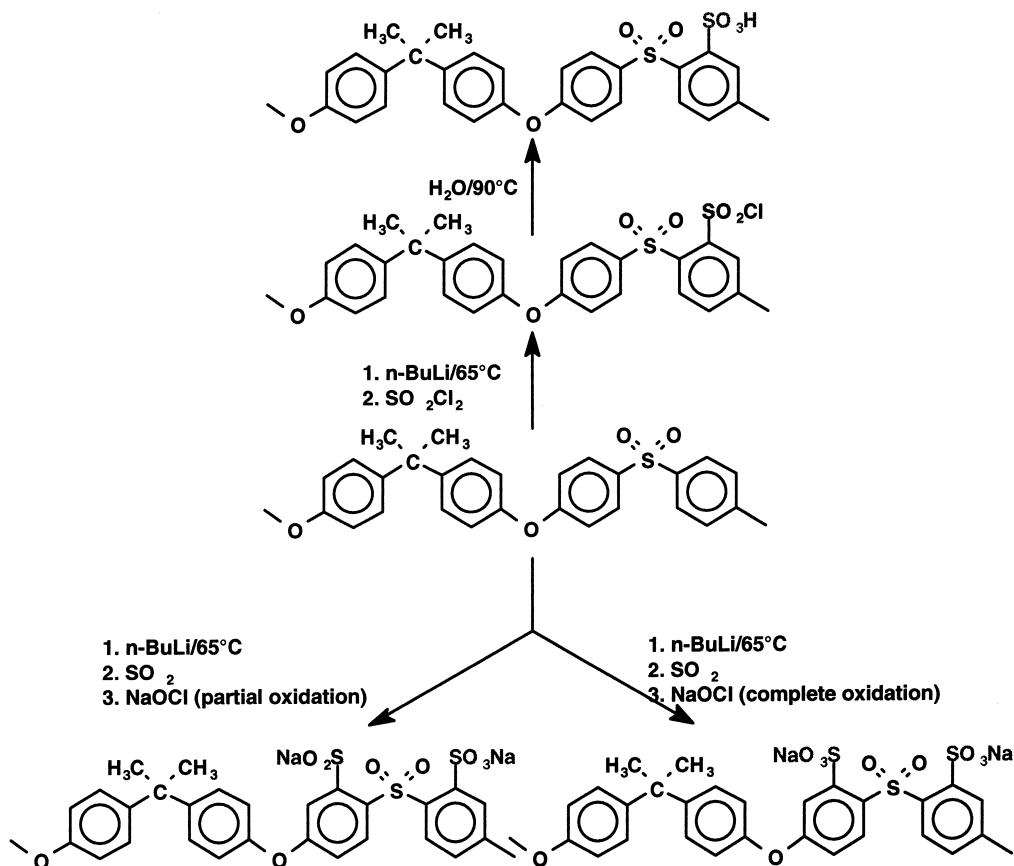


Fig. 1. Sulfonation of PSU via the metalation route.

PSU-Li which can be reacted with a great number of electrophiles [62]. In our labs a novel sulfonation procedure for polysulfone PSU Udel[®] has been developed which includes a lithiation step (Fig. 1). The lithiated PSU was reacted with (a) SO_2 , forming PSU- SO_2Li [63], and (b) SO_2Cl_2 , forming PSU- SO_2Cl [64]. PSU-sulfinate can be oxidized easily with KMnO_4 , NaOCl , or H_2O_2 , forming PSU-sulfonate, PSU-sulfochloride can be easily hydrolyzed to PSU-sulfonic acid. The advantages of this sulfonation process when applied to PSU are: (i) the sulfonate group is always introduced into the electron-deficient part of the repeating unit and is thus more stable towards hydrolysis; (ii) the intermediates PSU- SO_2Li and PSU- SO_2Cl can be isolated and thus be used for further reactions, e.g. for cross-linking (see later); (iii) the sulfonation yield is very high

(80–95%), and the sulfonation degree can be varied in a broad range from 0 to 2 sulfonate groups per repeating unit.

2.2. Preparation of basic PSU polymers

As mentioned in the introduction, the development of proton-conductive acid–base blend membranes is one of the research areas in our group. For the acid–base blend membranes we have prepared a number of PSU polymers containing basic groups also via the lithiation route [44,65]. Two types of reactions have been performed: (1) lithiated PSU is reacted with an aromatic aldehyde or ketone which contains tertiary basic nitrogen (Fig. 2), and (2) lithiated PSU is reacted with an aromatic carboxylic acid ester which contains tertiary basic N (Fig. 3), for example,

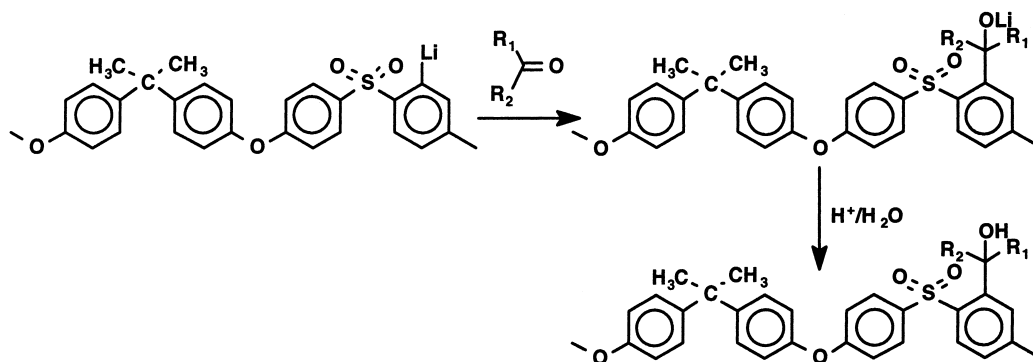


Fig. 2. Addition of an aromatic, basic N-containing ketone or aldehyde to lithiated PSU ($R_1 = \text{H}$ or aromatic group, $R_2 = \text{aromatic group}$).

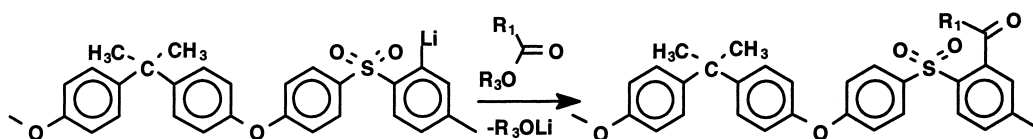


Fig. 3. Reaction of lithiated PSU with an aromatic ester ($R_3 = \text{alkyl}$, $R_1 = \text{aromatic group with basic N}$).

nicotinic acid ethyl ester or *N,N*-dimethylaminobenzoic acid ethyl ester (Fig. 4). At the second reaction, interestingly, the $>\text{C}=\text{O}$ bond formed by substitution of the ester's alcoholate group with the PSU carbanion does not react further with PSU-Li sites, forming

Li-alkoholate groups and thus cross-linked polymer, as it is the case if low-molecular Li-organic compounds are reacted with aromatic carboxylic acid esters [66]. This could be due to the low polymer concentration in the reaction mixture (1–3%), the low

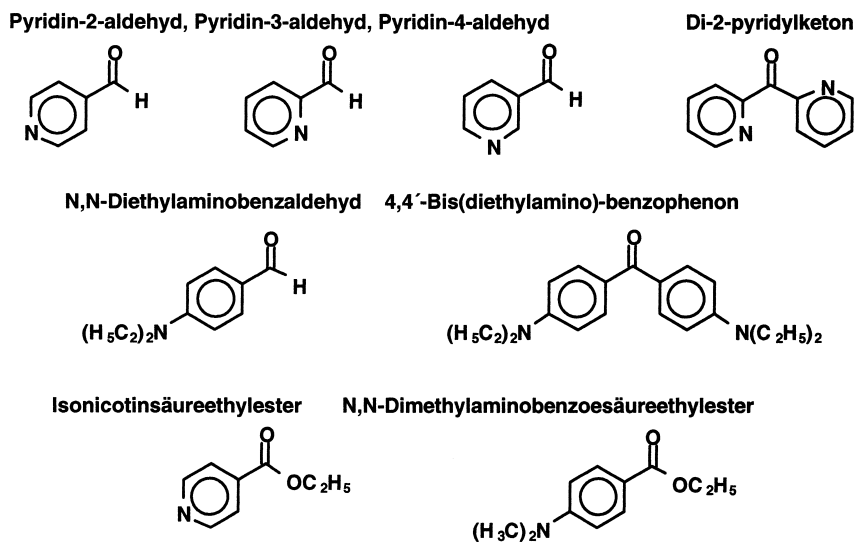


Fig. 4. Aldehydes, ketones and carboxylic acid esters used for reaction with lithiated PSU.

reaction temperature (-65 to -20°C), and the excess of carboxylic acid ester compound (three- to five-fold excess). The basic compounds reacted with lithiated PSU are shown in Fig. 4. At most of the reactions, substitution degrees of up to two basic aromatic groups have been achieved. Only at the reaction of lithiated PSU with 4,4'-*N,N*-diethylaminobenzophenone only a substitution degree of one group per PSU repeating unit could be obtained, which might be due to the bulkiness of 4,4'-*N,N*-diethylaminobenzophenone.

3. Development and characterization of novel proton-conductive membranes

3.1. Covalently cross-linked ionomer membranes via sulfinate alkylation

As mentioned in the introduction, a novel cross-linking procedure was developed in our lab, consisting of the alkylation of PSU-sulfinate with α,ω -dihaloalkanes having chain lengths of 3–12 CH_2 groups [33–35] (Fig. 5). Two different types of covalently cross-linked ionomer membranes have been prepared. The type I membranes were polysulfone PSU Udel[®] containing both sulfonate and sulfinate groups, wherein the sulfinate groups have been cross-linked as above-mentioned, resulting in ionomer networks in which all macromolecules are

involved [34]. The type II membranes were blends of PSU-sulfinate and PSU-sulfonate, again the sulfinate groups being cross-linked as above-mentioned, resulting in networks of cross-linked PSU-sulfinate in which the PSU-sulfonate macromolecules were entangled [35].

3.1.1. Type I covalently cross-linked PSU ionomer membranes

For preparation of PSU containing both sulfinate and sulfonate groups, PSU-SO₂Li was partially oxidized with NaOCl [34]. NaOCl is capable of oxidizing sulfinites very fast and with high yields [67]. In Table 1, the characterization data of cross-linked membranes (cross-linker: 1,4-diiodobutane) produced from PSU25BNa (SO₂Li content 1.7 groups per repeating unit) which has been oxidized from 37 to 100%, are presented. Interestingly, the theoretical and experimental IECs of the resulting membranes are lying very close together, indicating high cross-linking yield. As expected, the swelling of the membrane strongly increases, and, connected therewith, the ionic resistance strongly decreases when reducing the number of sulfinate groups in the PSU-sulfinate-sulfonate by growing oxidation degree.

The success of cross-linking reaction was also checked by FTIR. As analytical band, the symmetrical S=O stretching of the sulfinate group which occurs in aromatic sulfinites in the range between 960 and

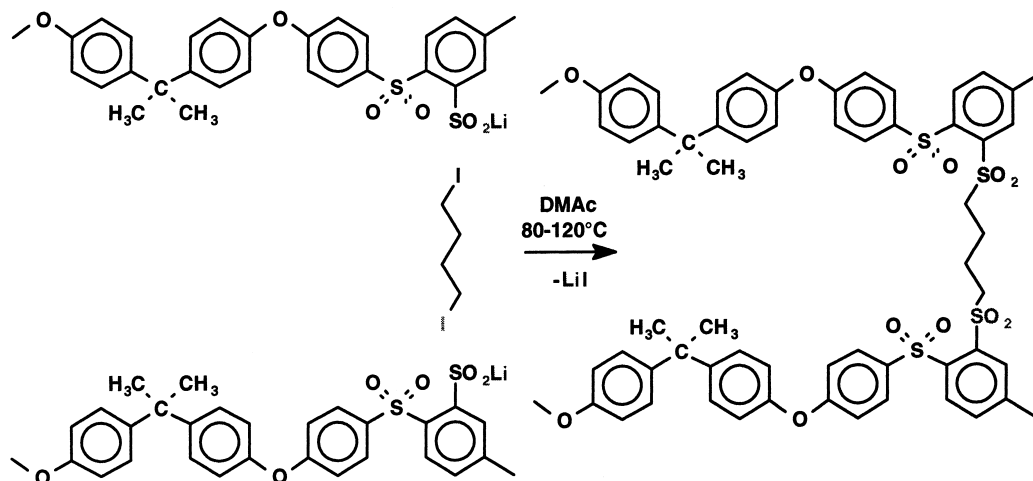


Fig. 5. Covalent cross-linking of PSU-sulfinate via alkylation with α,ω -dihaloalkanes.

Table 1

Characterization data of cross-linked membranes produced from PSU25BNa (SO₂Li content 1.7 groups per repeating unit) which has been oxidized from 37 to 100%^a

Membrane	PSU37	PSU50	PSU80	PSU100
Initial number of SO ₂ Li groups per PSU unit	1.7	1.7	1.7	1.7
Oxidation degree polymer (%)	37	50	80	100
IEC theoretical (meq SO ₃ H/g)	1.07	1.44	2.31	2.89
IEC experimental (meq SO ₃ H/g)	1.06	1.47	2.05	2.80
Swelling 25°C (%)	45	61	650	Water-soluble
R _{sp} (Ω cm) ^b	345	171	28	Water-soluble

^a The cross-linker used was 1,4-diiodobutane [34].

^b Specific ionic resistance, dc method, in 0.5N Na₂SO₄ solution.

980 cm⁻¹ [68] was used. In Fig. 6, the FTIR spectra of PSU, PSU-SO₂Li, PSU(SO₂Li)(SO₃Li), and of a cross-linked membrane made from the partially oxidized PSU-sulfinate, are shown. It results from Fig. 6 that no residual sulfinate groups were present in the membrane, indicating complete cross-linking.

It could be shown via swelling experiments that the swelling of the type I membranes does not increase strongly with temperature, indicating that the cross-linking bridges are hydrolysis-stable (Fig. 7). By

thermogravimetric experiments it could be shown that the chemical degradation of the cross-linked membranes starts at about 250°C [34].

The influence of the chain-length of the cross-linker on the membrane properties was also investigated. The results are shown in Fig. 8. It can be clearly seen that the swelling of the membranes strongly increases with the chain-length of the cross-linker; swelling degrees of <100% can only be achieved with 1,4-diiodobutane and 1,6-diiodohexane.

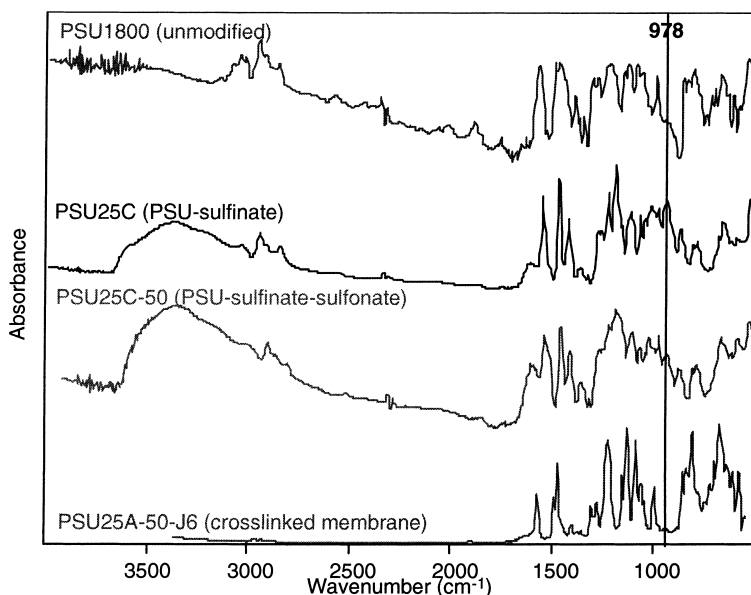


Fig. 6. FTIR spectra of unmodified PSU (P1800), two-fold sulfinated PSU (PSU-SO₂-25C), two-fold sulfinated and 50% oxidized PSU (PSU25C50) and of the cross-linked membrane PSU25A50-J6, produced from 1.9-fold sulfinated and 50% oxidized PSU (PSU25A50), cross-linked with 1,6-diiodohexane.

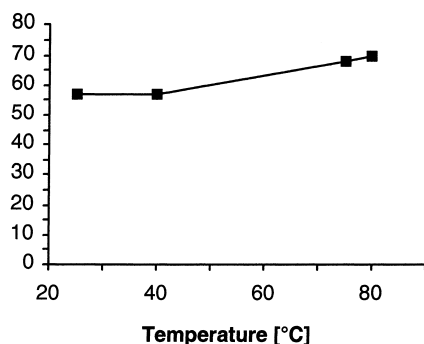


Fig. 7. The temperature dependence of swelling for the membrane PSU28Na50J4 (PSU-sulfinate-sulfonate; two sulfinate groups per repeating unit; oxidation degree 50%; cross-linker 1,4-diiodobutane).

3.1.2. Type II covalently cross-linked PSU ionomer membranes

For the preparation of the cross-linked type II PSU ionomer membranes, PSU-sulfinate and PSU-sulfonate both having one group per repeating unit was mixed in different ratios. As cross-linker, both 1,4-diiodobutane and 1,4-dibromobutane were used. The cross-linking success was controlled via determination of IECs of the resulting membranes, and

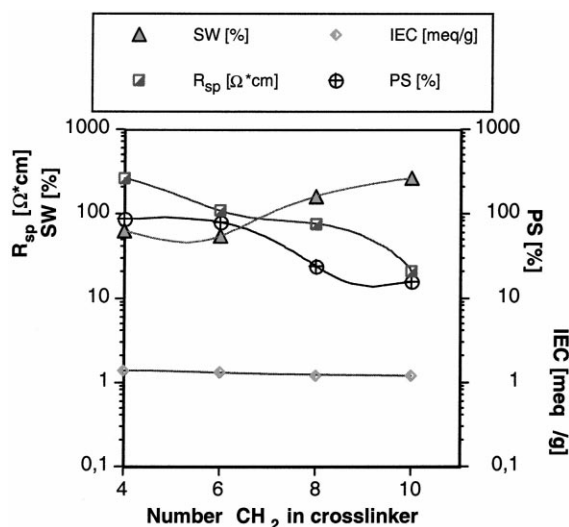


Fig. 8. Specific Na⁺ resistance, swelling and IEC of cross-linked membranes made from PSU25C50Na (PSU-sulfinate-sulfonate; two sulfinate groups per repeating unit; oxidation degree 50%) in dependence of the chain length of the diiodoalkane.

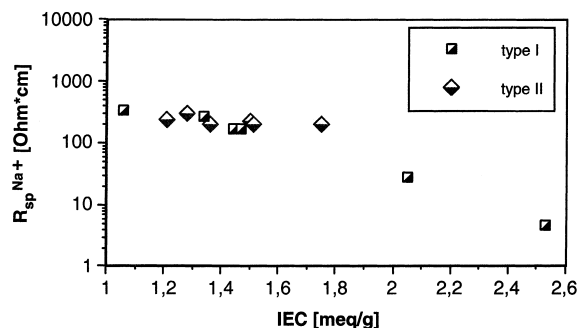


Fig. 9. $R_{sp}^{Na^+}$ in dependence of IEC at types I and II membranes, measured via direct current (dc) method in 0.5N Na₂SO₄.

via FTIR-analysis of the cross-linked membranes [35]. It was established that the cross-linking yield of the diiodo-cross-linker was higher than that of the dibromo-cross-linker, indicating a higher reactivity of iodoalkanes than bromoalkanes with sulfonates [35], which is consistent with the textbook finding that the iodide ion is a better leaving group at SN reactions at the saturated C than the bromide ion. FTIR spectra, recorded with cross-linked membranes, produced from one-fold sulfonated and one-fold sulfonated PSU, cross-linked with 1,4-diiodobutane, showed no sulfinate band, indicating complete cross-linking [35]. Via swelling experiments in diluted acid and water up to temperatures of 80°C over a time range of 63 days it could be shown that the PSU-sulfonate macromolecules are not dissolving out of the blend ionomer membrane network [35]. At 80°C, the pure type II blend PSU-sulfonate component is dissolving in water.

In Fig. 9 the dependence of specific Na⁺ resistance of type II membranes in dependence of their IEC is shown, compared to the specific resistance of selected type I membranes. It can be seen from Fig. 9 that both membrane types have similar electrical properties, indicating resemblance of their micromorphologies.

The thermal stability of the type II covalently cross-linked ionomer membranes is comparable to that of the type I membranes: the thermal degradation, determined via TGA and DSC, starts at 250°C [35].

3.2. Ionically cross-linked acid–base blend membranes

In this section some characterization results of acid–base blend membranes prepared in our lab are

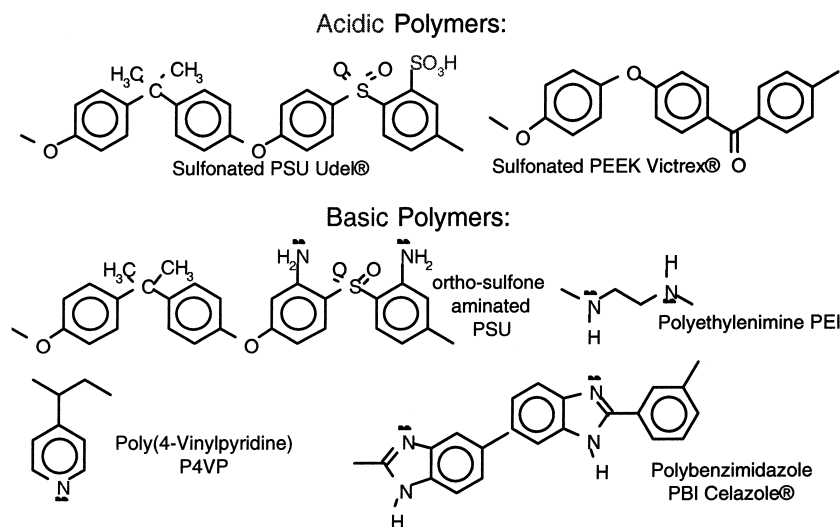


Fig. 10. Some acidic and basic ionomer blend compounds used in our studies.

presented. Acid–base blend membranes have prepared from sulfonated PSU and PEEK as the acidic polymers and from poly(4-vinylpyridine), polysulfone-*ortho*-sulfone-diamine, poly(ethylenimine), polybenzimidazole (Fig. 10) [36] and some polysulfone-based bases (Fig. 11) [44,65] as the basic polymers.

3.2.1. Ionic interaction

In acid–base blends two types of strong interactions between the acidic and the basic component are present: hydrogen bridges and electrostatic forces by proton transfer from the acidic to the basic group (Fig. 12). It is known from the literature that ionic interactions in blends of polymeric acids and bases can be observed via FTIR spectroscopy. For example, Eisenbach et al. reported about blends of partially sulfonated polystyrene and poly(10,12-docosadiynylene diisonicotinate), where the ionic interaction between the pyridine group and the sulfonate group could be observed via FTIR [69]: the band of the pyridinium cation of the blend in the acidic form was situated at 1637 cm^{-1} . This band disappeared when the blend was brought into the salt form by basic treatment. The same observations we have made at blend membranes of sulfonated PSU with poly(4-vinylpyridine): in the acidic form the pyridinium band was present, in the salt form (after treatment of the blend with aqueous NaOH) not. Also at blend membranes of sulfonated PSU/aminated

PSU [36] and at blend membranes of sulfonated PEEK and polybenzimidazole [39,41] bands resulting from the ionic interaction could be observed (Fig. 13).

The interaction between acidic and basic compound can also be determined indirectly via analysis of experimental and theoretically expected ion-exchange capacity. The theoretical IEC can be calculated from the molar ratio between acidic and basic groups. All acidic groups transferring their proton to a basic group, forming an ionic cross-link, can not longer contribute to the overall proton-conductivity of the blend membrane. The degree of formation of ionic cross-links should be due to the acid and base strength. The sulfonate group is a strong acidic group, and therefore all protons dissociate in aqueous environment, as it is the case in fully swollen membranes. Therefore, the strength of the ionic interaction in sulfonate acid–base blends is dependent on the base strength. The following was observed at acid–base blends containing sulfonated PSU and basic components of different base strength [36]: in the first case the basic component was polysulfone-*ortho*-sulfone-diamine, which is a weak base due to the strong electron-withdrawing power of the sulfone bridge of PSU (I effect, M effect), in the second case the basic component was polybenzimidazole — imidazole is a quite strong organic base. Both membrane types were acid-treated (10% HCl at 70°C) after preparation to generate the ionic cross-links. In

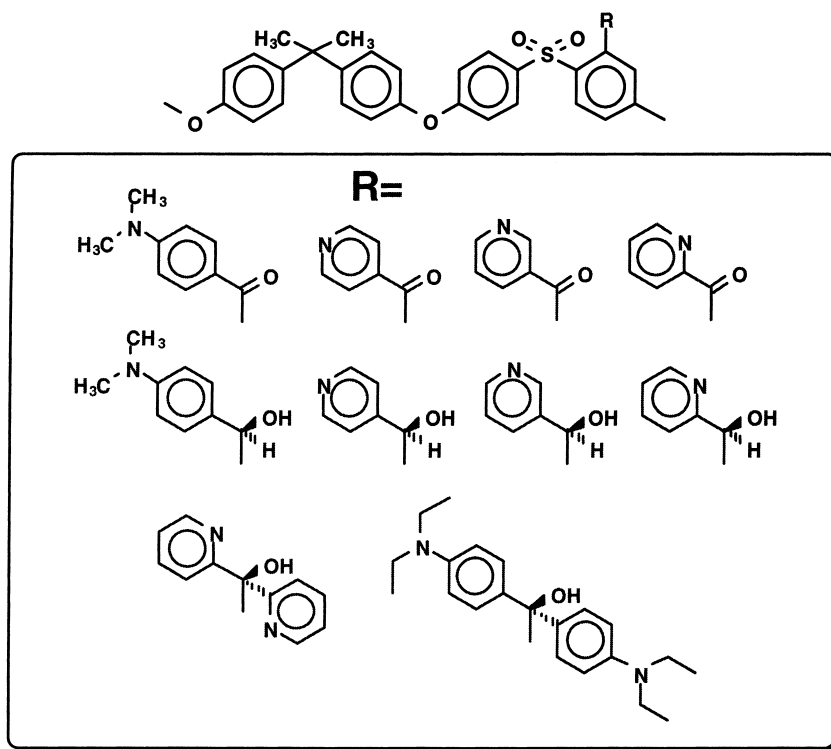


Fig. 11. Self-produced basic polymers from polysulfone PSU Udel®.

Fig. 14 the theoretical and experimental IEC of both membrane types are depicted.

It follows from Fig. 14 that at the PBI-containing blends the theoretical and IECs are lying very close together (the same was observed for sPEEK/PBI blends [39,41]), while at the PSU(NH₂)₂-containing blends the observed IECs were much higher than the calculated ones (the same was observed for sPEEK/

PSU(NH₂)₂ blends [70]). These findings can be explained in the following way: the ionic cross-links of the PSU(NH₂)₂-containing blends are obviously partially broken by the acidic post-treatment:

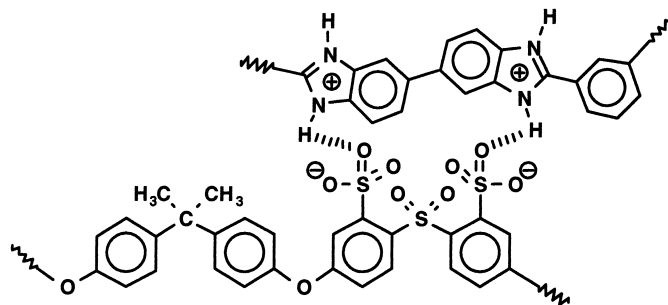
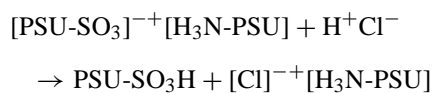


Fig. 12. Interactions between acidic and basic compound of blends of sPSU and PBI.

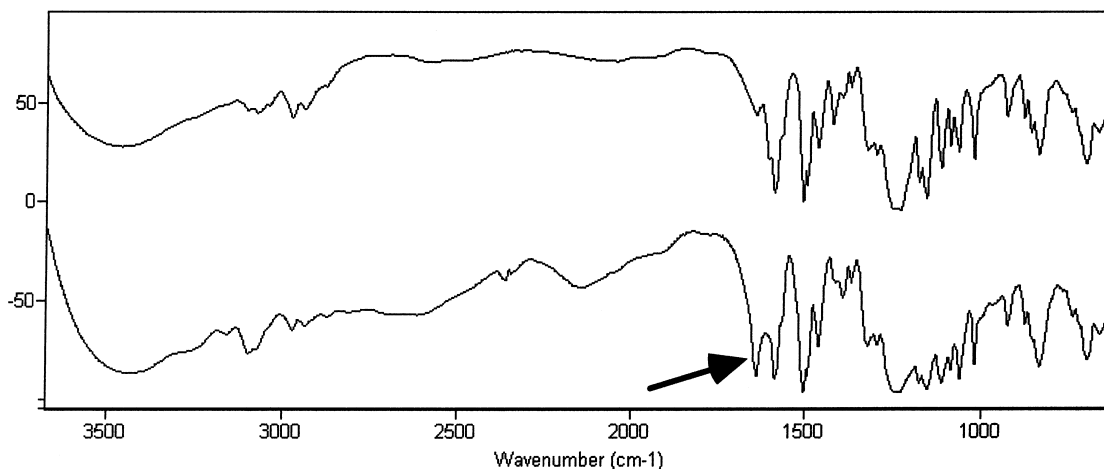


Fig. 13. FTIR spectra of blends of sulfonated PSU and poly(4-vinylpyridine). Upper spectrum: blend in the salt form; lower spectrum: blend in the acidic form. Arrow: pyridinium band.

Thus, the number of free sulfonic acid groups in the blend membrane again increases, and in addition, due to the low base strength of $\text{PSU}(\text{NH}_2)_2$, also the protons of the primary ammonium ions generated at the acidic post-treatment can again dissociate, contributing to the measured IEC.

3.2.2. Micromorphology

In ionomer blends two types of microphase separation can be present: microphase-separation between the acidic and the basic blend component if the interaction forces are not strong enough to lead to complete miscibility, and association of ionic groups, forming ion multiplets or ion clusters [1,71]. In our

studies we have investigated the micromorphology of a selection of acid–base blends via transmission electron microscopy (TEM) [39,41,43,64,65]. Prior to TEM investigation, the membranes were brought into the SO_3Ag form, because Ag gives good contrast in TEM. As examples we will present here the TEM micrographs of two blend membranes composed of sulfonated PEEK and the strong base PBI (S-1, M-170), and the TEM micrograph of a blend membrane composed of sulfonated PSU and PBI (S-2). The properties of these membranes are listed in Table 2.

In Fig. 15, the TEM micrograph of S-1 is shown ((a) 52,000 \times ; (b) 145,000 \times), in Fig. 16, that of S-2 ((a) 6600 \times ; (b) 205,000 \times), in Fig. 17 the TEM micrograph of M-170 is presented (105,000 \times). S-1 was made with water-insoluble sPEEK, S-2 with water-insoluble sPSU, while M-170 was made with water-soluble sPEEK. Therefore, the ionic cross-linking density is much higher for M-170 than for S-1, which leads to some polymer microphase-separation in S-1 (Fig. 15), while in M-170 only ionic association (Fig. 17) is observed. At S-2 it is even better seen that polymer microphase-separation as well as ionic association takes place (Fig. 16). When the base strength of the basic blend component is varied, also the micromorphology changes. Membranes made with weakly basic PSU-*ortho*-sulfone-diamine [64] or with different weak PSU-bases [65] show a higher extent

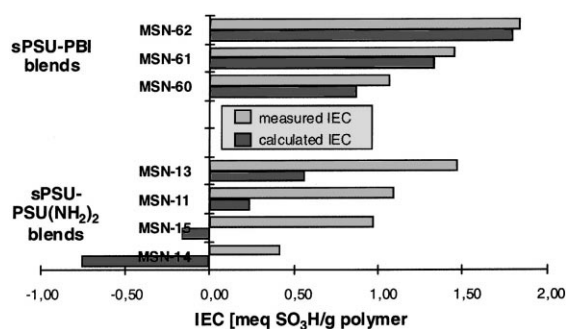


Fig. 14. Theoretical and experimental IECs of blends sPSU/PSU(NH_2)₂ and blends sPSU/PBI [36].

Table 2
Properties of selected acid–base blend membranes

Membrane no.	Composition	Capacity (IEC) (meq SO ₃ H/g membrane)	Thickness (μm)	$R_a^{H^+}$ (Ω cm ²)	$R_{sp}^{H^+}$ (Ω cm)
8H	85 wt.% sPEEK ^a , 15 wt.% PSU(NH ₂) ₂ ^b	1.34	59.8	0.109	18.2
9H	90 wt.% sPEEK ^a , 10 wt.% PSU(NH ₂) ₂ ^b	1.58	29	0.101	34.8
sPEEK-PSU-1	80 wt.% sPEEK ^a , 20 wt.% PSU(NH ₂) ₂ ^b	1.4	54	0.25	46.3
M-13	80 wt.% sPSU ^c , 20 wt.% PSU(NH ₂) ₂ ^b	1.47	82.5	0.24	29.1
S-1	90 wt.% sPEEK ^d , 10 wt.% PBI	1.26	36.9	0.106	28.7
S-2	95 wt.% sPSU ^e , 5 wt.% PBI	1.19	30	0.08	26.7
S-3	95 wt.% sPEEK ^d , 5 wt.% P4VP	1.48	65	0.247	38
S-4	95 wt.% sPSU ^e , 5 wt.% P4VP	1.36	76	0.196	25.8
M-23	95 wt.% sPSU ^e , 5 wt.% P4VP	1.02	41	0.204	49.8
M-69	95 wt.% sPSU ^e , 5 wt.% PBI	1.12	23	0.119	51.7
M-67	80.2 wt.% sPEEK ^f , 19.8 wt.% PBI	1.06	20	0.116	58
M-171	90 wt.% sPEEK ^f , 10 wt.% PBI	1.64	46	0.037	8.04
M-183	85 wt.% sPEEK ^f , 15 wt.% PBI	1.29	30	0.126	42.1
M-170	79 wt.% sPEEK ^f , 21 wt.% PBI	0.96	83	0.328	39.5
M-170/2	79 wt.% sPEEK ^f , 21 wt.% PBI	1.02	31.9	0.174	54.7
T17	95.3 wt.% sPEEK ^a , 4.7 wt.% PBI	1.37			75
442	89.6 wt.% sPEEK ^a , 4.5 wt.% PBI, 5.9 wt.% A95 ^g	1.18	95	0.34	36
504	sPEEK, PBI, A95 ^g	0.7	60	0.4	66.6
519	sPEEK, PBI, A91 ^h	1.2	90	0.22	24.6

^a Capacity: 1.75 meq SO₃H/g membrane.

^b *Ortho*-sulfone animated.

^c Capacity: 1.7 meq SO₃H/g membrane.

^d Capacity: 1.9 meq SO₃H/g membrane.

^e Capacity: 1.6 meq SO₃H/g membrane.

^f Capacity: 2.95 meq SO₃H/g membrane.

^g PSU modified with one group –C(OH)R₂, R = 1,4-phenylene-*N*(et)₂.

^h PSU modified with two groups –C(OH)R'₂, R' = 2-pyridyl.

in phase-separation than membranes made with the relatively strong base imidazole.

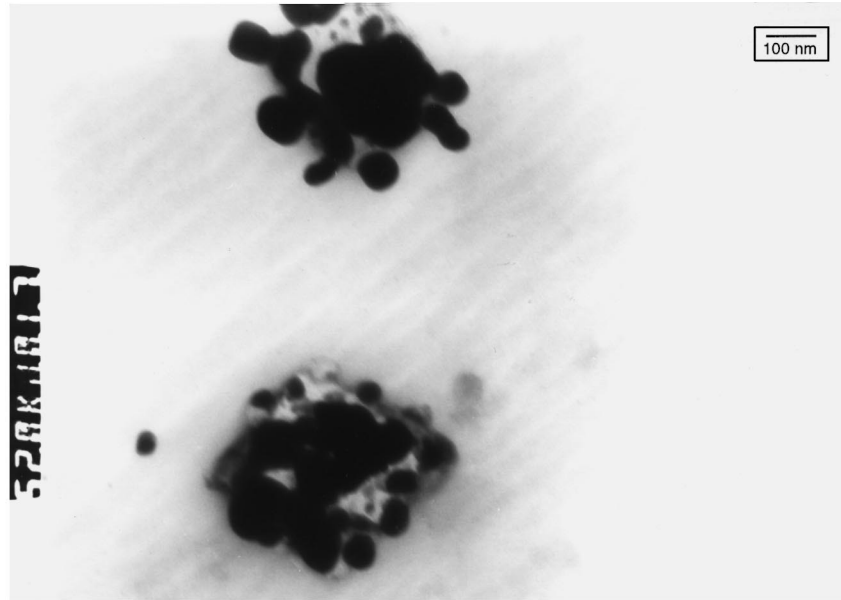
3.2.3. Thermal properties

The thermal properties of the acid–base blend membranes are better than the thermal properties of covalently cross-linked PSU-based ionomer membranes [34–36,39]. In Fig. 18, the TGA curves of a covalently cross-linked PSU ionomer membrane and of different acid–base blend membranes are shown. By DSC further information about the blend polymer membranes can be acquired apart from the thermal stability. For example, the glass transition temperatures T_g can be determined. The blending of sulfonated polymers with basic polymers has a strong impact onto T_g , as can be seen from DSC traces of sulfonated PSU, P4VP, and a sPSU/P4VP blend membrane with 5 wt.% P4VP (M-23, Table 2, [39,41]): the T_g of the sPSU sample is 178°C, the T_g of P4VP

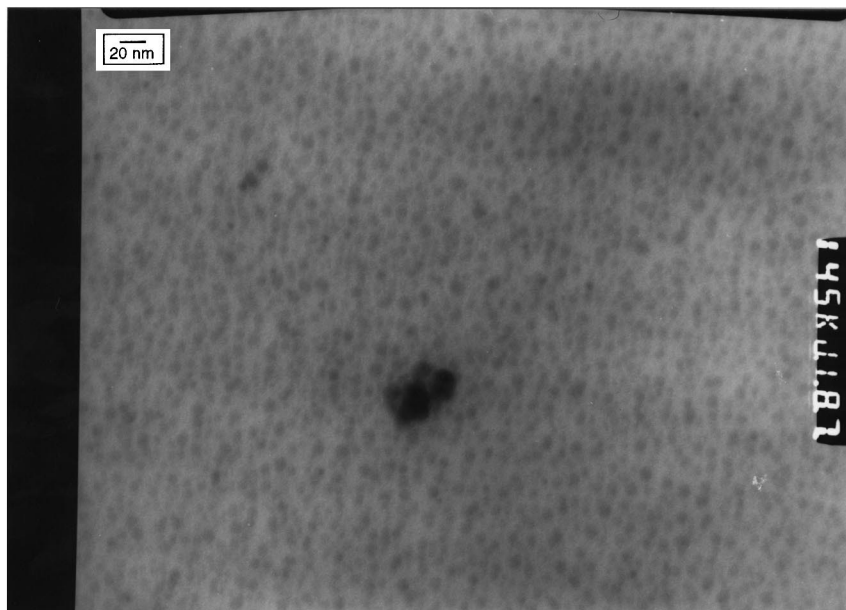
is 120.6°C, and the T_g of the sPSU/P4VP blend is 211.5°C. The strong T_g increase of 33.5°C from sPSU to the sPSU/P4VP blend is caused by the acid–base interactions between the acidic and the basic component of the blend. Similar findings we have already published for sPEEK/PSU(NH₂)₂ blends: the T_g of sPEEK is 205°C, the T_g of PSU(NH₂)₂ is 210°C, and the T_g of the sPEEK/PSU(NH₂)₂ blend membrane was determined to be 225°C [70]. The T_g of a sPSU/PBI blend membrane (S-2, Table 2), compared to T_g of pure sPSU, increased even still stronger: the T_g of S-2 amounted to be 228.5°C, which is an increase of 50.5°C towards the T_g of sPSU [39].

3.2.4. Proton-conductivity

In Fig. 19, specific H⁺ resistances of some types of acid–base blend membranes are shown. The following membrane types are depicted in Fig. 19 [36,39,70,72]: sPEEK-PSU(NH₂)₂ (type 1.1), sPSU-PSU(NH₂)₂

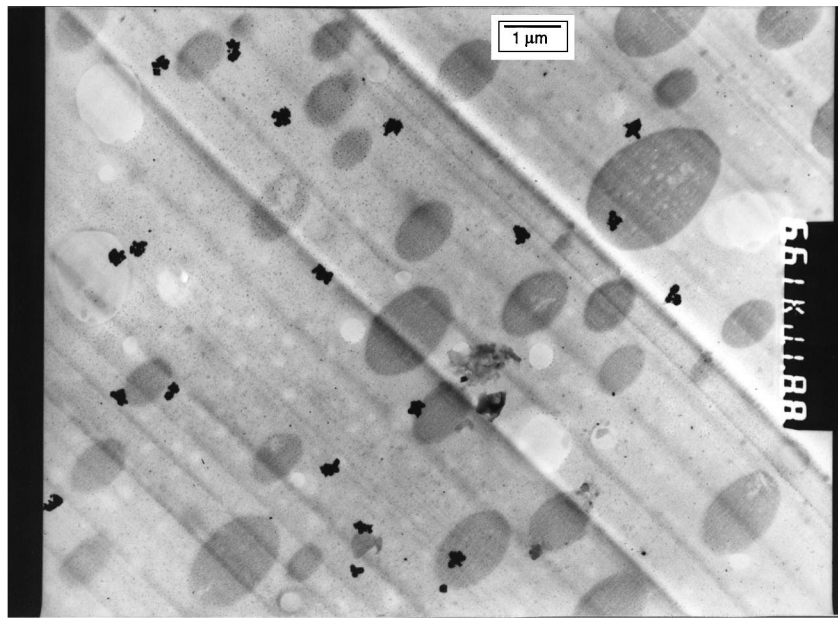


(a)

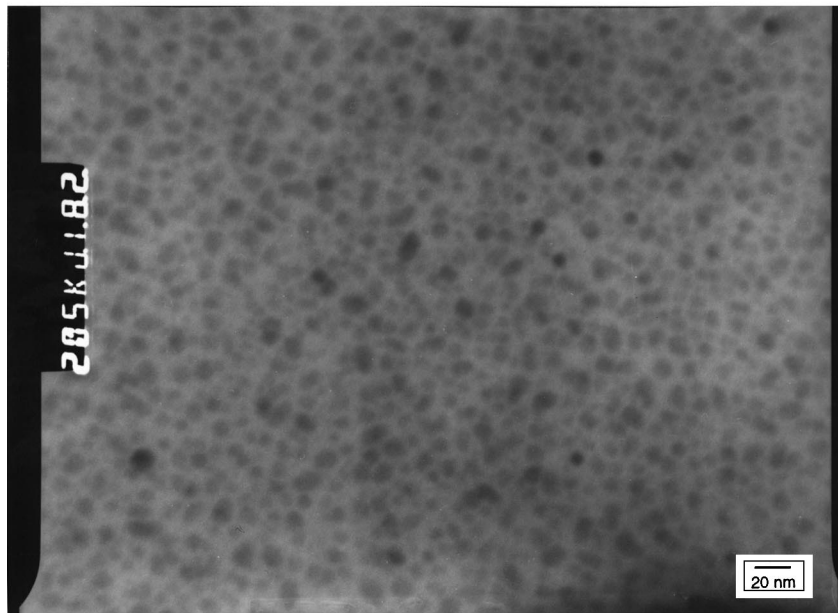


(b)

Fig. 15. TEM micrograph of S-1 ((a) 52,000 \times ; (b) 145,000 \times).



(a)



(b)

Fig. 16. TEM micrograph of S-2 ((a) 6600 \times ; (b) 205,000 \times).

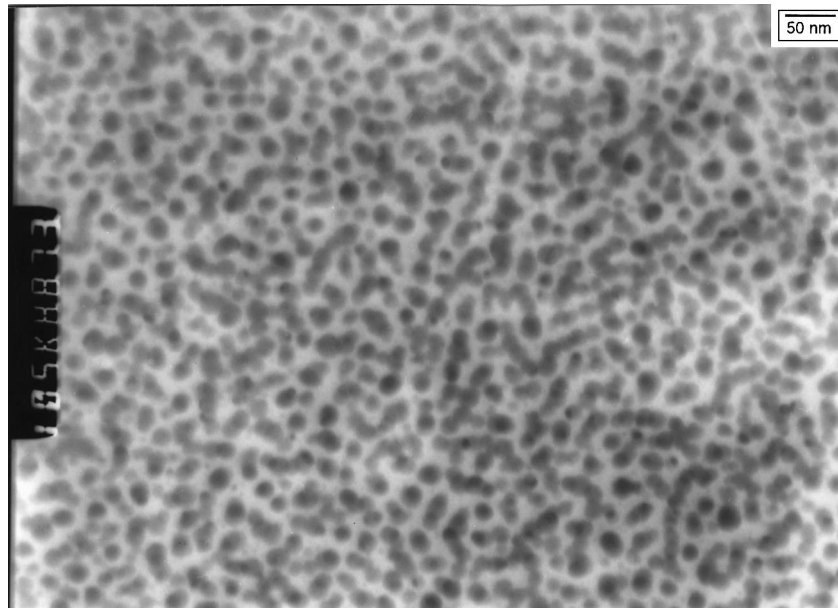


Fig. 17. TEM micrograph of M-170 (105,000 \times).

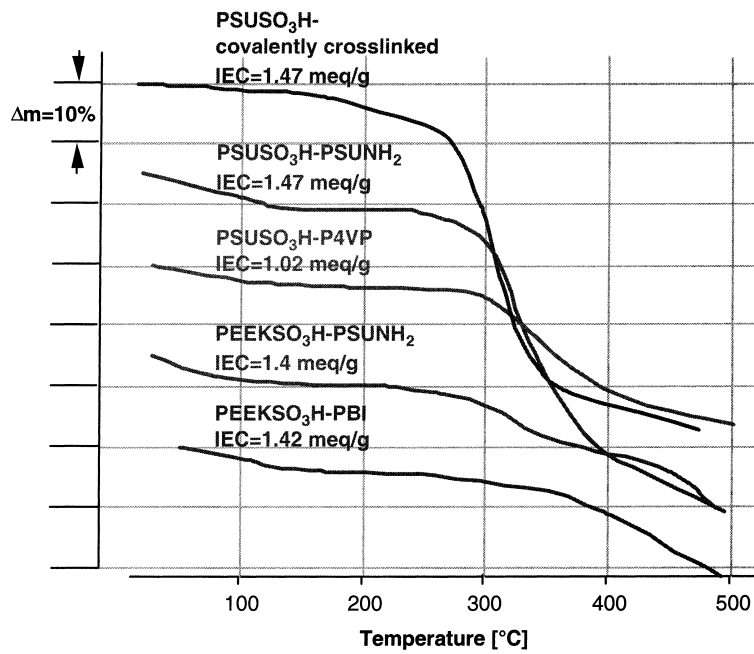


Fig. 18. TGA curves of a covalently cross-linked PSU ionomer membrane and of some acid–base blend membranes.

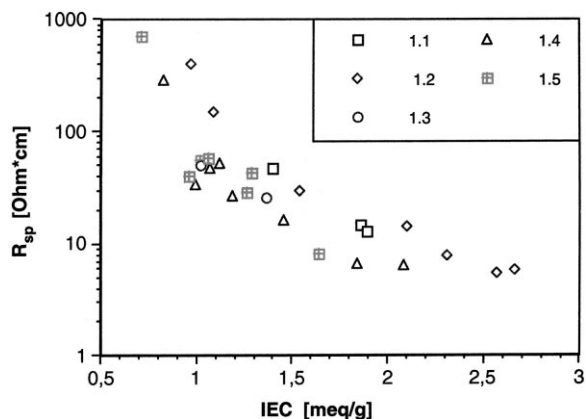
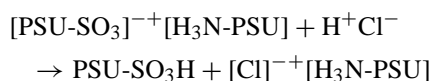


Fig. 19. Specific proton resistance in dependence of IEC at different membrane types: sPEEK-PSU(NH₂)₂ (type 1.1); sPSU-PSU(NH₂)₂ (type 1.2); sPSU-P4VP (type 1.3); sPEEK-PBI (type 1.4); sPSU-PBI (type 1.5).

(type 1.2), sPSU-P4VP (type 1.3), sPEEK-PBI (type 1.4) and sPSU-PBI (type 1.5).

It is obvious from Fig. 19 that the proton conductivities of the PSU-*ortho*-sulfone-(NH₂)₂-containing blend membranes are lower than the proton conductivities of the blend membranes containing PBI and P4VP at the same IEC. This can be explained with the fact that the IECs which have been measured from the PSU-*ortho*-sulfone-(NH₂)₂-containing blends also include the protons resulting from the partial splitting of the ionic cross-links by the membrane's acidic post-treatment (Section 3.2.1):



The protons situated at the ammonium group do not contribute to proton conductivity, are, however, recorded from the IEC-determination which is performed via acid–base titration.

4. Fuel cell application of the developed proton-conductive membranes

Both covalent and ionically cross-linked membranes developed in our lab have been applied to both PEM and direct methanol fuel cells. The covalently cross-linked membranes, however, showed limited

performance when applied in PEFC, which might be due to the membrane thickness of 100 μm, and to the poor contact between membrane and electrodes because the electrodes have only been mechanically cold-pressed onto the membrane [73]. At time improved, covalently cross-linked ionomer membranes are prepared and will be tested in both PEMFC and DMFC.

The application of ionically cross-linked ionomer membranes to membrane fuel cell yielded promising results. In the following a selection of these results which have been already published [36,37,40,41] will be presented.

4.1. Application in H₂ membrane fuel cells (H₂-PEFC)

Two acid–base blend membranes composed of sPEEK and PSU-*ortho*-sulfone-(NH₂)₂, indicated as 8H and 9H (properties, see Table 2), have been investigated in a H₂-PEFC. The polarization curves in air operation mode are shown in Fig. 20 [40,41]. The operation conditions are given in Fig. 20. Very good performance is performed. The curve of 9H shows markedly higher cell voltages than the membrane 8H at higher current densities. This is probably be due to the higher IEC of 9H and to the lower thickness, compared to 8H (Table 2) [41]. The operation of these two membranes in O₂ mode shows similar U/i polarization curve characteristics [40,41]. The application of a sPSU/PBI (M-69) and of a sPEEK/PBI (S-1) acid–base blend membrane (Table 2) to a H₂-PEFC

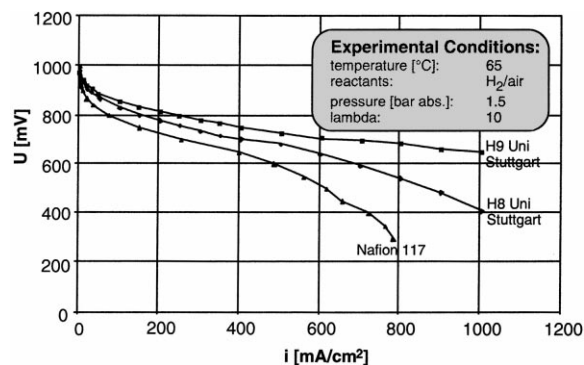


Fig. 20. U/i polarization curves of membranes 8H and 9H in a H₂-PEFC, air mode [40,41]; comparison: Nafion117.

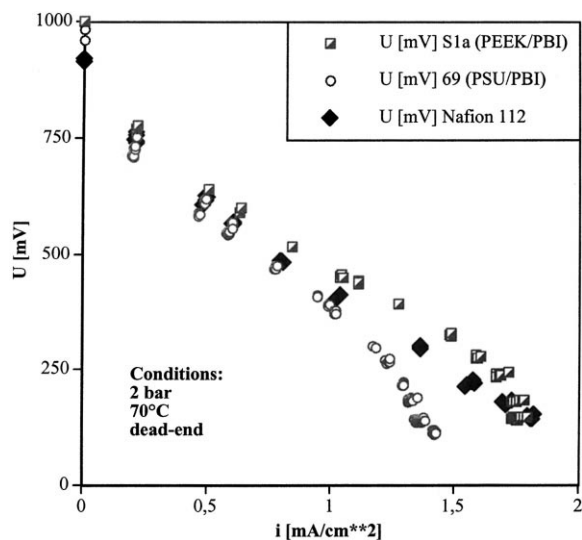


Fig. 21. U/i polarization curves of membranes M-69 and S-1 in a H_2 -PEFC, oxygen mode [36].

also yields U/i polarization curves comparable to that of Nafion[®] (Fig. 21). However, the U/i -curves of the membranes shown in Fig. 21 are worse than those presented in Fig. 20, which is due to the fact that the membrane-electrode assemblies used in Fig. 21 for recording of the U/i -curves have been produced by simply pressing of commercial etek electrodes onto the membranes. So far no long-term stability tests have been performed with our membranes in H_2 -PEFC, are, however, intended in foregoing research.

4.2. Application in direct methanol membrane fuel cells (DMFC)

In DMFC so far only few proton-conductive polymer membranes have been used. One of them is the perfluorinated Nafion[®] ionomer membrane. However, Nafion has a severe disadvantage when applied to DMFC: its high methanol permeability which leads to marked cell potential reduction via cross-potential formation at the fuel cell cathode [4,50]. Another polymer membrane system, PBI/ H_3PO_4 blend membranes, has also successfully been applied to DMFC [45–48], even at temperatures of 130–150°C (see also Section 1.4.1). One of the disadvantages of this composite membrane type is that the phosphoric acid

is not covalently bound to the polymer matrix which can lead to diffusion of phosphoric acid molecules out of the membranes particularly when the fuel cell temperature drops down below 100°C when liquid water is present in the membrane. Nonfluorinated sPSU and sPEEK ionomer membranes which are not cross-linked are instable in methanol [74]. Permeability investigations performed with the acid–base blend polymer membranes showed that these membranes show a markedly reduced pure methanol permeability, compared to Nafion[®] [75]. While Nafion[®] swells extremely strong in methanol, acid–base blend membranes show very good dimensional stabilities in MeOH [74]. Some of the acid–base blend membranes have been applied to DMFC and showed good performance, similar to Nafion[®] [40,41]. At this point it must be mentioned that the DMFC-applied acid–base blend membranes are much thinner than Nafion117[®] (Table 2). In Fig. 22, DMFC MeOH/air U/i polarization curves of the membrane 8H and Nafion117[®] are presented. It is obvious that 8H and Nafion117[®] show similar DMFC performance at a MeOH-concentration of 0.5 mol/l [40,41].

DMFC experiments with the acid–base blend membranes S-1, S-2, S-3, and S-4 (Table 2) have been performed up to $T = 100^\circ\text{C}$ [40,41]. The DMFC performance of these membranes was at 100°C even better than at 80°C, as can be seen from Fig. 23 [40,41]. During DMFC experiment, at some of the membranes the MeOH permeability has been determined via analysis of CO_2 amount developed at the cathode. Fig. 24 shows that the acid–base blend membrane T-19-III shows a markedly reduced MeOH permeability at $T = 110^\circ\text{C}$, compared to Nafion [77]. Another acid–base blend membrane, E-442, whose composition is given in Table 2, also shows a low MeOH permeability at $T = 110^\circ\text{C}$, which is shown in Fig. 25 [77]. In Fig. 26, the DMFC polarization curves of MEAs containing some of our recently prepared acid–base blend membranes at $T = 110^\circ\text{C}$ are shown [77]. For comparison, Fig. 26 also contains polarization curves of Nafion105 MEAs prepared via the same procedure. It can be seen that the electrochemical performance of MEAs made from acid–base blend membranes under conditions of high methanol concentrations and low current densities is superior to the Nafion105 reference material. At higher current

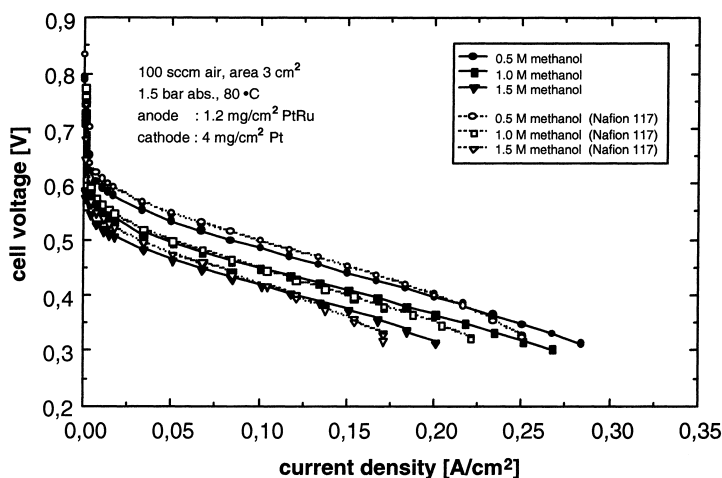


Fig. 22. DMFC U/i polarization curves of 8H membranes for MeOH concentrations of 0.5, 1.0, and 1.5 M. Comparison: Nafion117[®]. Experimental conditions: see diagram [40,41].

density, the performance of the MEA made from Nafion improved. This is most probably caused by the non optimized interface of the thin film electrode using recast Nafion as a binder [78] and the acid–base blend membrane.

Summarizing the findings presented in this section, the acid–base blend membranes show very good perspectives in DMFC application. One of the

important tasks for foregoing research is to perform long-term DMFC tests of our membranes which requires also catalysts which have good long-term stabilities. Moreover, the thin film electrode technique for preparation of the MEAs has to be tailored for the acid–base blend membranes, among others by using an arylene main-chain ionomer as a binder.

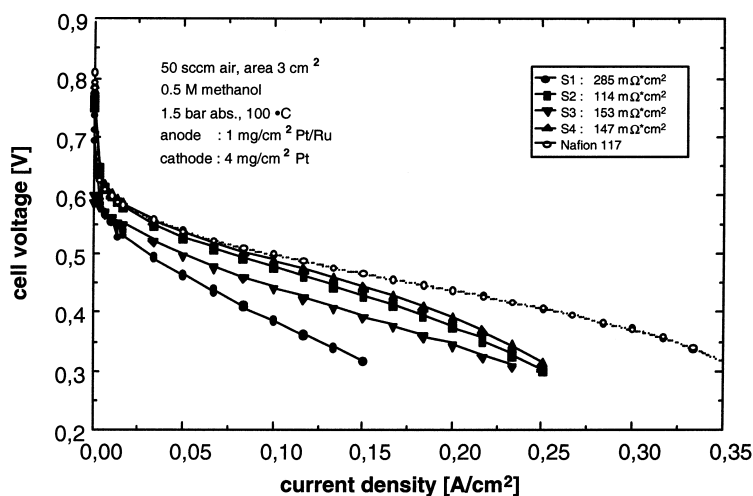


Fig. 23. DMFC U/i polarization curves of membranes S-1, S-2, S-3, S-4 and Nafion under air operation at the cathode for a MeOH concentration of 0.5 M at 100 °C. Experimental conditions: see diagram [40,41].

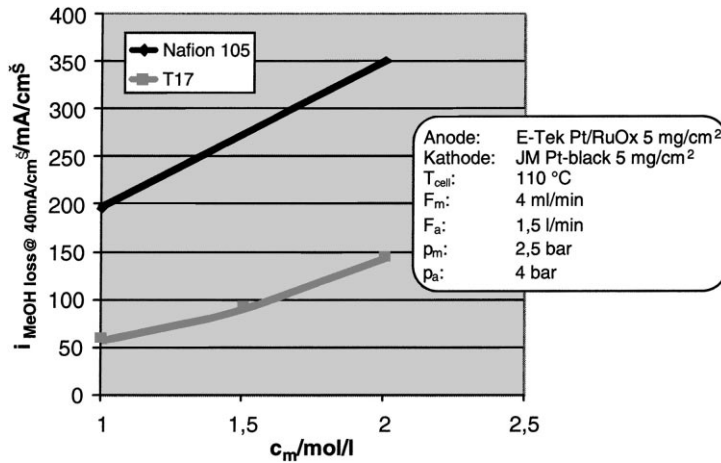


Fig. 24. MeOH loss (defined as current density loss caused by MeOH permeation) in dependence of MeOH concentration of membrane T17 and Nafion105 at $T = 110^\circ\text{C}$. DMFC experiment conditions: see diagram.

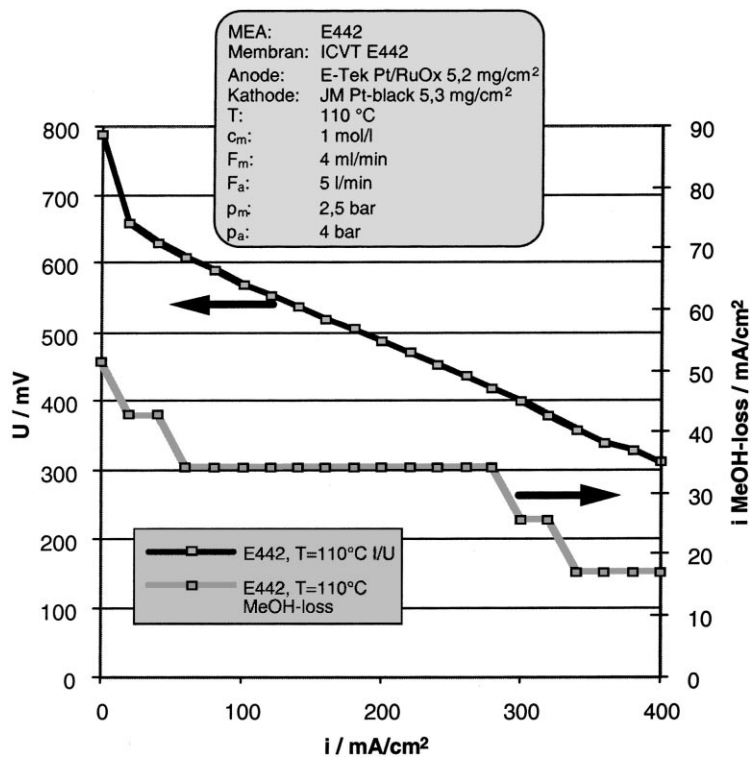


Fig. 25. U/i polarization curve and MeOH loss (defined as current density loss caused by MeOH permeation) in dependence of current density of membrane E442 at $T = 110^\circ\text{C}$. DMFC experiment conditions: see diagram.

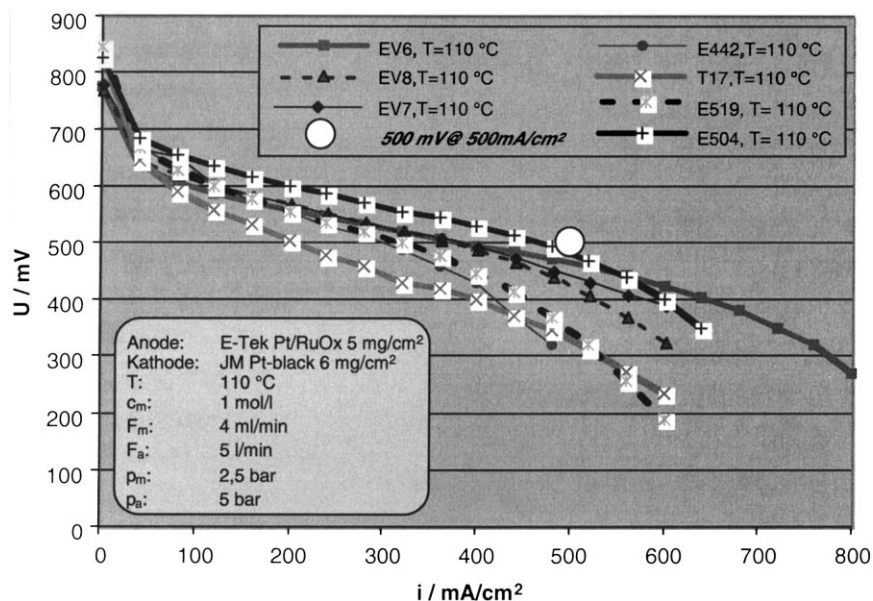


Fig. 26. U/i polarization curves of different acid–base blend membranes (properties, see Table 2) and of different Nafion MEAs (EV6, EV7, EV8) in a DMFC. Fuel cell experiment conditions: see diagram.

5. Conclusions

In our lab we have developed different types of covalently and ionically cross-linked ionomer membranes. Both the covalently and ionically cross-linked ionomer blend membrane types developed in our lab have advantages and disadvantages. In Table 3, the properties of both membrane types are compared

with each other, based on the findings presented in Sections 3.1 and 3.2. From Table 3 it follows that the main advantages of the covalently cross-linked ionomer membranes lie in their dimensional stability also at temperatures up to 80°C. Particularly the type I covalently cross-linked membranes where all macromolecules are involved in the covalent network show a high dimensional stability. The main

Table 3
Comparison and evaluation of the properties of covalently and ionically cross-linked ionomer membranes

Membrane type	Thermal stability	Ion-conductivity ^a	Stability in 10% HCl at 80°C ^b	Mechanical stability in wet state ^c	Mechanical stability in dry state
Covalent type I ^d	+	++	+++	++	–
Covalent type II ^d	+	++	++	++	0
Ionic very weak base ^e	++	+	0	+++	++
Ionic weak base ^f	++	++	+	+++	+++
Ionic medium base ^g	+++	++	++	+++	+++

^a At $1 < \text{IEC} < 1.5$ (meq $\text{SO}_3\text{H/g}$ dry membrane).

^b Dimensional/hydrolysis/bleeding-out stability.

^c At storage in liquid water at $T < 60^\circ\text{C}$.

^d See Section 3.1.

^e Type PSU-*ortho*-sulfone- NH_2 .

^f Type pyridine.

^g Type imidazole.

disadvantage of the covalently cross-linked membranes is their brittleness when drying out which is a very severe problem when they are applied to PEM fuel cells, because drying out of the membranes frequently can happen when the fuel cell is applied to cars where intermittent operation conditions are present.

The main advantage of ionically cross-linked ionomer membranes is their high mechanical flexibility even in dry state at temperatures of up to 80–100°C, because the ionic cross-links have a good flexibility and water-holding ability, which is due to the hydrophilicity of ionic cross-links which also involves hydrogen bonds from the ionic cross-links to the membrane-water. The good mechanical stability of the ionically cross-linked membranes was one reason for their good performance in PEMFC as well as in DMFC up to temperatures of 110°C. The main disadvantage of the ionically cross-linked ionomer membranes is that, particularly if the basicity of the basic blend compound is very low as it is the case at the PSU-*ortho*-sulfone-amine, the ionic cross-links can break at temperatures of >70°C. The stability of the imidazole group-containing acid–base blend membranes at higher temperatures is already improved (dimensional stability up to 80–90°C, depending on the ion-exchange capacity), but still insufficient at $T > 110^\circ\text{C}$ [76]. One of the challenges in foregoing membrane development for fuel cell applications is therefore to develop membranes showing dimensional stabilities and proton conductivities at temperatures higher than 110°C. For the fuel cell temperature range of >110°C, ionomer membranes having both ionic and (dissociation-stable) covalent cross-links are under development which are believed to show low MeOH permeability also at $T > 70\text{--}110^\circ\text{C}$.

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