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Ionomer Membrane and MEA Development for DMFC

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Abstract: Membrane-electrode assemblies (MEAs) have been prepared from different acid-base-blends consisting of different sulfonated arylene main-chain polymers and polybenzimidazole PBI and a microphase-separated arylene main-chain block copolymer consisting of a sulfonated and proton-conducting and a hydrophobic microphase. The MEAs have been prepared using 4 different methods: Method A: The membrane has been prepared first as a free film, and the electrodes have subsequently been coated onto the membrane; Method B: The membrane has been prepared first as a polyester-supported film, and the electrodes have thereafter been coated onto the membrane; Method C: The MEA has been built up from the anode; Method D: The MEA has been built up from the cathode. The MEAs have been tested under different temperatures and different meOH concentrations. Three different polyacid-PBI blend membranes could be identified which showed comparable or even better DMFC performance than Nafion®105: a sulfonated polyethersulfone-PBI blend membrane, a sulfonated polyetherketone-PBI blend membrane, and a partially fluorinated sulfonated polyether-PBI blend membrane. The proton-conducting block co-ionomer membrane initially showed an excellent DMFC performance due to reduced meOH permeability, compared to the polyacid-PBI blend membranes, which however degraded with time of the DMFC operation probably being due to irreversible morphology changes. Among all tested MEAs the MEAs prepared by Method B showed the best DMFC performance. The DMFC performance of the MEAs

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prepared by Method C and Method D was slightly worse than that of the MEAs made via Method B. The DMFC performance of a MEA from the sulfonated polyetherketone-PBI blend membrane which was built up using Method D improved steadily during 4 weeks of DMFC operation.

Keywords: blend membranes, DMFC, MEA

INTRODUCTION

Direct methanol fuel cells (DMFC) are an interesting alternative to other battery types as the energy source for small and portable electronics (1) such as notebook computers, mobile phones, and photodiode arrays because the fuel methanol shows a high energy density and can be easily stored. DMFCs have two main disadvantages, compared to H_2-polymer electrolyte fuel cells (H_2-PEFC):

1. the electro-oxidation of methanol is a complex reaction, leading to anode losses in the range of 0.2 to 0.4 V (2),
2. the perfluorinated ionomers of the Nafion® type show unacceptable high methanol (and water) transport over the membrane (3), leading to a reduction of fuel efficiency by direct oxidation of the permeated meOH molecules at the cathode catalyst Pt and to a lowering of the cathode potential by mixed potential formation.

To overcome these shortcomings of the H^+-conducting Nafion® type membrane in the DMFC application, many efforts have been undertaken in the past decade. The efforts include filling the perfluorinated ionomer membrane with inorganic nanoparticles such as SiO_2 (4) or layered zirconium phosphates (ZrP) (5) or the use of arylene main-chain ionomers such as sulfonated polyetherketones (6), polyethersulfones (7,8), poly(phenylsulfone)s (9,10), or other polyaromatics. The advantage of polyaromatic ionomers is their lower meOH and water permeability, compared to the perfluorinated ionomers, which is due to the less pronounced hydrophobic/hydrophilic separation and therefore narrower H^+ transport paths within the membrane matrix, compared to Nafion® type ionomers (11,12). One of the disadvantages of most of the polyaromatic polymers in the DMFC application is their high water uptake particularly at higher temperatures, which leads to a strong softening and weakening of the membranes which limits the DMFC operation temperature range. To overcome this problem, one possible measure is the synthesis of ionically and/or covalently cross-linked polyaromatic membranes which have been introduced by Kerres et al. (see the review papers (13) and (14). The water uptake of the membranes could be significantly

reduced by cross-linking, as reported in (15), and power densities of up to $0.28\,W/cm^2$ could be reached with an ionically cross-linked membrane at DMFC operation temperature of 130°C (14). In a recent paper, the DMFC performances of differently cross-linked composite membranes at DMFC operation temperatures of up to 60°C, which is an interesting temperature range for mobile DMFC applications, were determined and compared with the DMFC performance of a Nafion®105 membrane (16). Among the tested membranes, a covalently cross-linked membrane from sulfonated PEEK and sulfinated PSU (cross-linker for the sulfinated PSU: decafluorobiphenyl) showed the best DMFC performance at 60°C (320 mV at $240\,mA/cm^2$; Nafion®105: 300 mV at $120\,mA/cm^2$).

Another interesting approach for alternative DMFC membranes is the synthesis of morphologically controlled and microphase-separated sulfonated polymers, where both microphases should be continuous. In the multiblock *co*-ionomers, the sulfonated microphase overtakes the proton transport, and a hydrophobic microphase serves for limitation of swelling of the sulfonated microphase and thus for improved mechanical integrity, compared to homopolymers. Because of phase separation between the hydrophilic and the hydrophobic microphase, the SO_3H group concentration in the hydrophilic microphase should be higher than in homogeneous polymers of the same overall ion-exchange capacity, leading to higher proton conductivities in the multiblock *co*-ionomers, compared to the referring homopolymers. Moreover, due to the fact that the meOH permeability of ionomers is closely linked to the swelling properties because of the water-similarity of meOH, the meOH permeability of block *co*-ionomers should be lower than that of the corresponding homo-ionomers having the same overall SO_3H group content.

There are only a few examples in literature for the preparation of phase-separated sulfonated multiblock-*co*-ionomers for DMFC membranes. For example, Holdcroft et al. reported on highly fluorinated comb-shaped copolymers (17) and ionic graft polymers (18) in order to counterfeit the architecture of polyperfluoroalkylsulfonic acids with improved mechanical integrity at higher temperatures and lower to moderate glass transition temperatures, compared to Nafion®. McGrath et al. synthesized sulfonated-fluorinated poly(arylene ether) multiblock *co*-polymers which showed higher proton conductivities compared to random copolymers of the same IEC, particularly under reduced humidification conditions (19–22). The high proton conductivities were explained with a well-defined nanophase separation which was determined via AFM and DSC. Miyatake et al. compared the proton conductivity of sulfonated multiblock-*co*-imides with their corresponding homoionomers and could also confirm that the block *co*-polymers showed improved proton-conductivity, particularly at lowered humidity, compared to their

homopolymer analogues (23). Non-fluorinated sulfonated multiblock-*co*-poly(arylene ether ketone)s were synthesized and characterized with respect to potential use in fuel cell applications by G.G. Scherer et al. (24). They stated that these membranes are suitable alternative candidates to Nafion® in PEFC and DMFC. Meier-Haack et al. dealt with the synthesis of nonfluorinated sulfonated multiblock-*co*-polymers. They reported a clear reduction of meOH permeability of the block *co*-ionomers, compared to the corresponding random copolymers (25).

In the present paper two different classes of sulfonated ionomer membranes have been investigated to study their suitability for the DMFC application in the 25–60°C range:

- Different types of ionically cross-linked blend membranes from sulfonated polyarylene ethers and polybenzimidazole PBI Celazol®. The prepared polyarylene ethers are presented in Fig. 1.
- A morphologically controlled (microphase-separated) block *co*-polymer comprising sulfonated and hydrophobic microdomains. The synthesized block co-ionomer is shown in Fig. 2.

In order to consider the different methods of catalyst coating at membrane-electrode assemblies (MEAs) fabrication (26), one can coat the catalyst either onto the membrane or onto the gas diffusion layer (GDL). These procedures can be automated easily. It is important to automate the total MEA production including the membrane fabrication

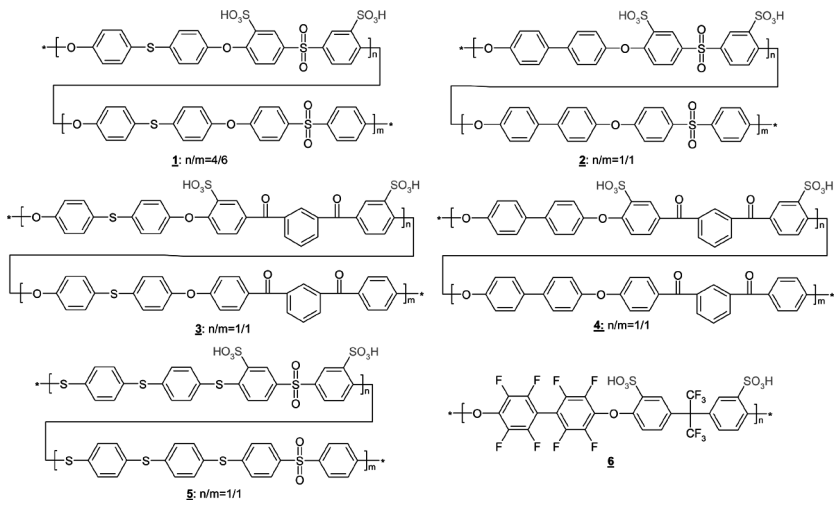


Figure 1. Synthesized sulfonated polyarylenes.

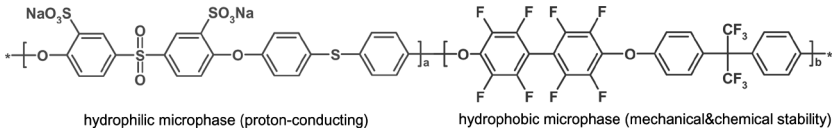


Figure 2. Synthesized multiblock copolymer 7.

with a minimum number of steps. The present work wishes to contribute to reach this objective.

Different building-up principles for MEAs have been applied to those membranes having the most promising DMFC performance:

A. Casting of a free film of the respective membrane, followed by solvent evaporation and application of the electrodes via spraying of the electrode ink
B. Filling of a thin polyester textile with the ionomer via spraying of the polymer solution onto the textile, followed by evaporation of the solvent and coating of the supported membrane with the electrodes via ink spraying

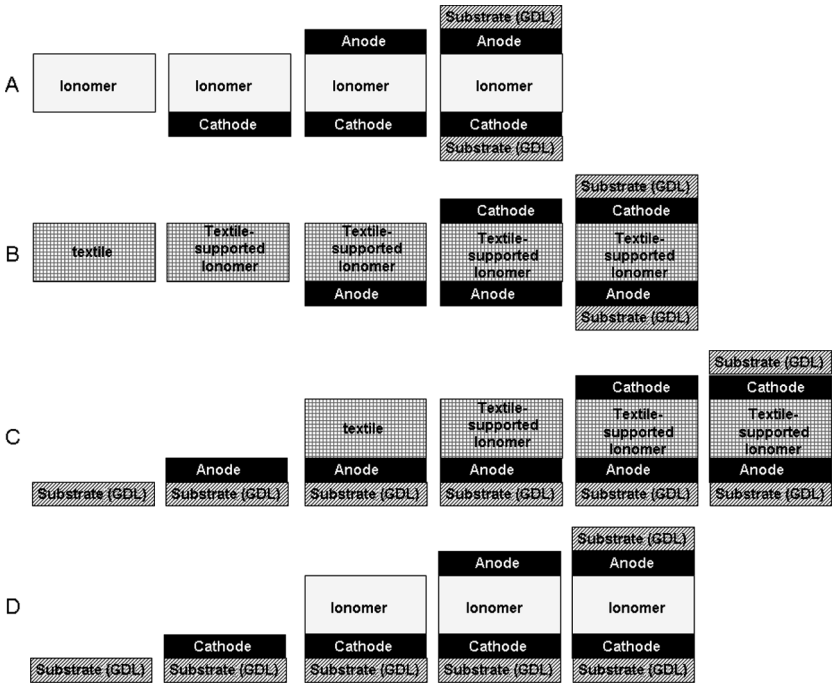


Figure 3. The applied MEA preparation methods.

C. Building up the MEA from the anode
D. Building up the MEA from the cathode

The four methods for MEA preparation are schematically represented in Fig. 3.

EXPERIMENTAL PART

Polymer Synthesis

The synthesis of the homopolymers **1** to **6** was performed via nucleophilic displacement polycondensation as described in previous articles (27–30). In the case of the polymers **1** to **5**, sulfonated monomers were used for the polycondensation reaction, while at polymer **6** first the polymer was prepared, and then it was sulfonated using H_2SO_4 with 60% SO_3. The multiblock-co-polymer **7** was prepared according to a further earlier paper by

1. separate preparation of the hydrophilic sulfonated oligomer and the hydrophobic oligomer and
2. coupling of the telechelics to the final multiblock copolymer (31).

Membrane Preparation

The nonsupported acid-base blend membranes have been prepared from their NMP/DMAc solution by casting of the polymer blend solution, which has been prepared using a procedure described in (16), onto glass or aluminium plates, followed by solvent evaporation at temperatures between 90 and 130°C. The block copolymer membrane was prepared by dissolving the polymer **7** in NMP to a 10% solution, casting of the solution into an aluminium bowl, followed by evaporation of the solvent at temperatures between 90 and 130°C. The textile-supported acid-base blend membranes were prepared by spraying the polymer solution onto the textile which was fixed onto a heated table. During the spraying process, the solvent was continuously evaporated by heating of the table. After the textile was completely covered with ionomer, the process was finished.

The membranes have been posttreated in the following manner:

1. for 48 h at 90°C in 10% H_2SO_4 (in the case of the block co-ionomer **7** HCl was used instead of H_2SO_4);
2. for 48 h at 60°C in deionized water. After that, they were stored in sealable plastic bags.

POLYMER AND MEMBRANE CHARACTERIZATION

Equivalent Weight (IEC) Measurement

The IEC was determined by immersion of 0.1 to 0.5 g of a sulfonated polymer or membrane sample (in H^+ form) in conc. NaCl solution, followed by titration of the released H^+ ions with 0.1N NaOH.

Molecular Weight of the Polymers

Gel permeation chromatography (GPC) was carried out with an Agilent Technologies GPC system (Series 1200) using the universal calibration method and the following detectors: refractive index detector (Shodex RI71), and light scattering detector. For GPC analysis, 2 wt% solutions of the polymers in DMAc with 5% w/w LiBr were prepared.

Membrane Resistance

The ex-situ proton conductivity of the membranes has been determined via impedance spectroscopy in 0.5 N HCl at room temperature, as described earlier (15). The MEA conductivity was determined directly in the fuel cell during operation by the cell impedance measurement at a frequency of 1 kHz.

Thermal Stability

Thermal stability of the membranes was determined by thermogravimetry (TGA, Netzsch, model STA 449 C) with a heating rate of 20°C/min under an atmosphere enriched with oxygen (65–70% O_2, 35–30% N_2). The decomposition gases were further examined in a coupled FTIR spectrometer (Nicolet Nexus FTIR spectrometer) in order to identify the splitting-off temperature of the sulfonic acid group ($T_{onset}^{SO_3H}$) for which the asymmetric stretching vibration of the S=O group at 1300–1400 cm^{-1} was used.

Membrane Water Content

The membrane samples were equilibrated for 48 h in deionized water at the temperatures 25–40–60–90°C. After this time, the samples were removed from the water bath, the surface water was removed with a

paper tissue, and the samples were weighed thereafter. Then the samples were dried at 90°C until constant weight was reached, and were weighed again. The water uptake (WU) was then determined via the following formula:

$$WU = [(m_{wet} - m_{dry})/m_{dry}] \times 100\ [\%]$$

Oxidation Stability of Polymers

There are two hypotheses for degradation mechanisms of fuel cell ionomer membranes found in literature: the first hypothesis is that the degradation occurs in the anode where the $HO^{\cdot}$ or $HO_2^{\cdot}$ radicals formed via O_2 diffusion crossover the membrane from the cathode (32,33); the other hypothesis is that the degradation occurs in the cathode, where the $HO^{\cdot}$ or $HO_2^{\cdot}$ radicals originate during O_2 reduction at the cathode side (34,35). The formation of $HO^{\cdot}$ or $HO_2^{\cdot}$ radicals is most probably the key reason for membrane degradation.

We used a 5%wt H_2O_2 solution at 60°C to simulate the fuel cell environment. The samples were dried, weighed, followed by equilibration in the H_2O_2 solution for different treatment times. After the respective treatment times the membrane pieces were removed from the H_2O_2 solution, washed with water, and dried. Then the molecular weight values of the polymer samples were determined using GPC.

MEA Preparation

MEA Type A. Membrane electrode assemblies were prepared by spray coating of unsupported noble metal catalysts directly on the ionomer membranes at room temperature using an ink made from catalyst powders and Nafion® solution in alcohols (15% by weight). A commercial Pt/Ru catalyst manufactured by Johnson Matthey at a loading of $5.2\,mg/cm^2$ has been used for the anode. The Nafion® content of the anode has been 15% by weight. The cathode was prepared from Johnson Matthey Pt at a loading of $6.4\,mg/cm^2$. The cathode Nafion® content has been 10% by weight. In order to avoid membrane rupture, the catalyst layers were not cured after deposition. The MEA active area was $25\,cm^2$ ($5\times5\,cm$) for the test of the membranes in the DMFC testing device and $36\,cm^2$ ($6\times6\,cm$) for the measurement at application conditions. Generally the Toray graphite paper (TGP 120) has been used as a gas diffusion layer. Unteflonized Toray paper has been used at the anode, 26% PTFE by weight has been used at the cathode.

MEA Type B. The textile-supported membrane was prepared by spraying the polymer solution onto a polyester textile (Sefar, 40 μm thick, mesh width 1μm), see section on Membrane Preparation. The electrodes were then coated onto the composite membrane as described in previous section.

MEA Type C. The porous substrate (Toray Paper TGP-120, 350 μ) was coated with a thin (10 μ) microporous Vulkan XC72/50% Nafion® layer. Onto this layer the anode catalyst layer was coated. Subsequently a barrier layer consisting of Vulkan72/50% Nafion® was coated onto the catalyst layer. As the next step, a 40 μm thick polyester textile was coated with the blend membrane solution and deposited onto the barrier layer. After evaporation of the NMP solvent at 100°C the cathode catalyst layer was deposited onto the reinforced membrane.

MEA Type D. As porous substrate a GDL 10BB of SGL Carbon was used, which comprises a very fine microlayer consisting of Carbon/5%PTFE. This cathode can be operated in relatively dry mode due to the lower hydrophobicity. The electrolyte layer was coated onto the cathode very slowly, interrupted by drying periods, while being placed onto the heating table (100°C). The anode catalyst was applied directly onto the electrolyte layer which is in the Na^+ form. Finally, the MEA was protonated in diluted H_2SO_4. The MEA was mounted into the DMFC in wet state.

DMFC Evaluation

The MEAs were characterized at temperatures from 25 to 100°C either in an electrically heated graphite cell housing with active area of 25 cm^2 or in a passive safety glass cell with an active area of 36 cm^2 at atmospheric pressure using aqueous methanol at different concentrations (1–4 mol/l). The cathode was supplied either with dry air at flow rate 0.6 L/min or with breath air.

The cells were operated in galvanostatic mode. The cells have been operated for a minimum of 24 h until constant membrane resistivity has been reached. Current-voltage curves have been recorded after a stabilization time of a minimum of 2 min per recording.

In order to assess methanol crossover, CO_2 evolution at the cathode has been measured via nondispersive infrared analysis of the dried exhaust gas stream. In order to assess the amperometric efficiency of the MEA, an equivalent methanol crossover current in mA/cm^2 has been calculated from the measured cathode CO_2 flow.

RESULTS AND DISCUSSION

Properties of the Sulfonated Polymers

The relevant properties of the applied sulfonated polyarylenes are presented in Table 1.

The characterization results of the polymers as presented in Table 1 are commented below:

- All the polymers have sufficient molecular weight to exhibit good film-forming properties. Molecular masses of at least 10,000 Dalton of aryl ionomers are in the most cases sufficient for good film-forming properties (29).
- The ion-exchange capacity of all polymers (apart from the multiblock copolymer **7**) leads to high water uptake values, particularly at higher temperatures, which makes the direct application of the pure polymers in a DMFC impossible. Therefore, all polymers have been blended with PBI to reduce the swelling and thus to improve the mechanical membrane stability by formation of acid-base interactions.
- The stability of the ionomers in terms of thermal splitting-off of the SO_3H groups, which is the first step of thermal decomposition in arylene ionomers (36), is comparable to each other and increases in the following series: block-*co*-ionomer **7** < polyetherketones **3**,

Table 1. Sulfonated polymer properties

Polymer [No.]	η_{rel} [a] [−]	M_n [Dalton]	PDI [−]	IEC [meq/g]	$T_{onset}^{SO_3H}$ [b] [°C]	WU 25°C/90°C [%]
1	1.18	n.a.	n.a.	1.65	248	49/590
2	n.a.	12,800	4.04	1.83	264	63/126
2_1	n.a.	12,396	1.48	n.a.	285	46/94
3	n.a.	19,900	3.37	1.6	235	58/786
3_1	n.a.	31,600	1.45	1.47	n.a.	n.a.
4	n.a.	13,700	4.01	1.62	235	42/95
5	n.a.	19,974	1.76	1.62	255	80/140
6	n.a.	46,500	3.53	2.45	257	n.d.[c]
7	n.a.	46,288	2.99	1.07	219	51/66

[a]0.3 g/dL in NMP, at 25°C.

[b]Determined from TGA-FTIR coupling experiment, appearance of traces of SO2 in TGA gaseous decomposition products.

[c]The swelling of this ionomer was, due to its high IEC, extremely high and could not be determined properly.

4 <polythioetherethersulfone **1** <partially fluorinated polyether **6** ≈ polyethersulfone **2**.

The TGA traces of the three ionomers having the best DMFC performance among the investigated membranes are shown in Fig. 4.

The stepwise thermal degradation of the ionomers is clearly visible in Fig. 4. In the temperature range up to ≈200°C the evaporation of water from the ionomers takes place, while the SO_3H groups are split off from the polymer backbone in the temperature range from about 250 to 400°C. At T > 400°C the decomposition of the polymer backbone is proceeding, as determined via the TGA-FTIR coupling experiment (36).

In order to investigate the oxidation stability of the ionomers **2** and **3**, they were immersed in a 5% H_2O_2 solution at 60°C for up to 48 hours. The oxidation stability of the ionomer **6** could not be determined via this method due to its extremely high water swellability. After the H_2O_2 treatment, the molecular weight degradation of the polymers was determined via GPC. The molecular masses of the ionomers after different times of treatment are presented in Table 2 (ionomer **2**) and in Table 3 (ionomer **3**).

When comparing the results from Table 2 and Table 3, it can be concluded that during the H_2O_2 posttreatment a relative shift of the number average molecular weight to lower values takes place which is more pronounced at the ionomer **3**. Moreover, the molecular weight distribution curves broaden with increasing H_2O_2 treatment time, as indicated in Fig. 5.

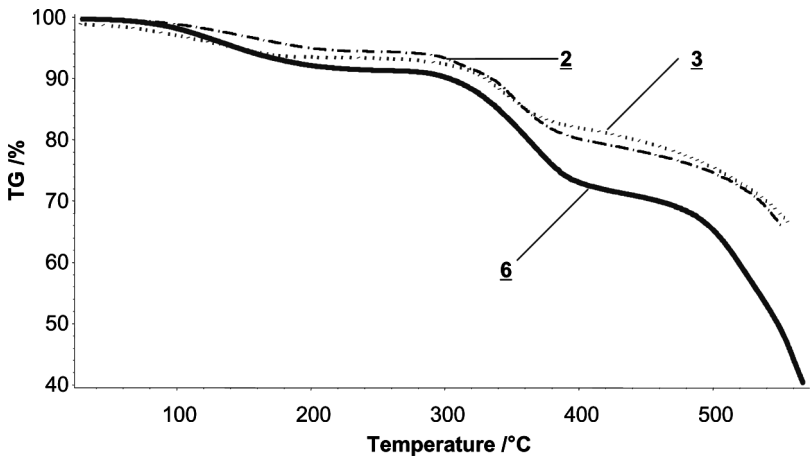


Figure 4. TGA-traces of the three best DMFC polymers.

Table 2. GPC determination of the molecular weight degradation of the ionomer 2

H_2O_2 treatment [h]	M_n	D	Comment
0	12,396	1.475	none
2	12,092	1.79	none
5,5	8,481	1.99	none
25	n.a.	n.a.	96% dissolved in H_2O_2/H_2O mixture
48	n.a.	n.a.	dissolved in H_2O_2/H_2O mixture

Properties of the Ionomer Membranes

The most important properties of the acid-base blend membranes of the ionomers **1** to **5** with PBI and of the block ionomer membrane **7** are summarized in Table 4.

Interestingly, the $T_{onset}^{SO_3H}$ temperatures of the acid-base blend membranes are higher than the $T_{onset}^{SO_3H}$ temperatures of the pure ionomers, which proves the stabilizing effect of the PBI blend component. The thermal stabilizing effect of the PBI blend membrane component in acid-base ionomer blend membranes has already been reported earlier for other acid-base blend membrane systems (29,30,36). Moreover, it was reported that the PBI blend component even improves the ionomer blend membrane stability against H_2O_2 and the radicals formed therefrom (28–30).

DMFC Application of the Ionomer Membranes

DMFC Screening of the Different Membrane Types

As the first step of the DMFC investigations, MEAs have been made from the polyacid-PBI blend membranes applying MEA preparation

Table 3. GPC determination of the molecular weight degradation of the ionomer 3

H_2O_2 treatment [h]	M_n	D
0	31,600	1.45
2	27,183	1.71
5.5	17,393	1.76
25	10,958	1.62
48	3,159	4.14

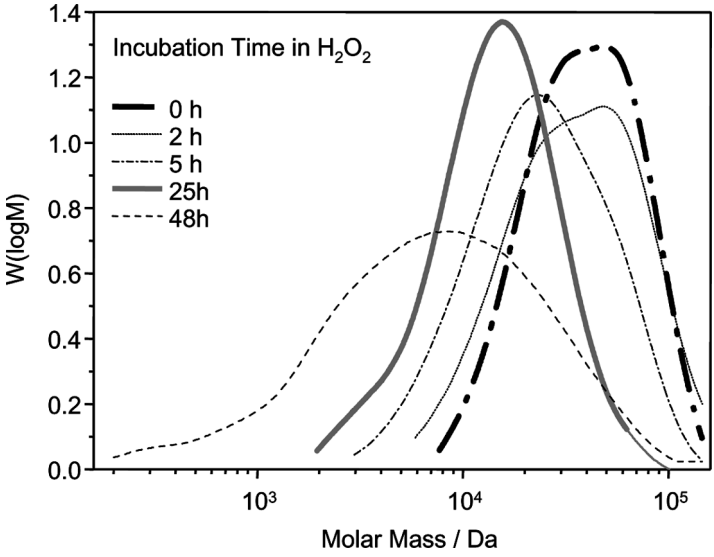


Figure 5. Molecular weight distribution curves after different H_2O_2 treatment times of ionomer 3 as determined via GPC.

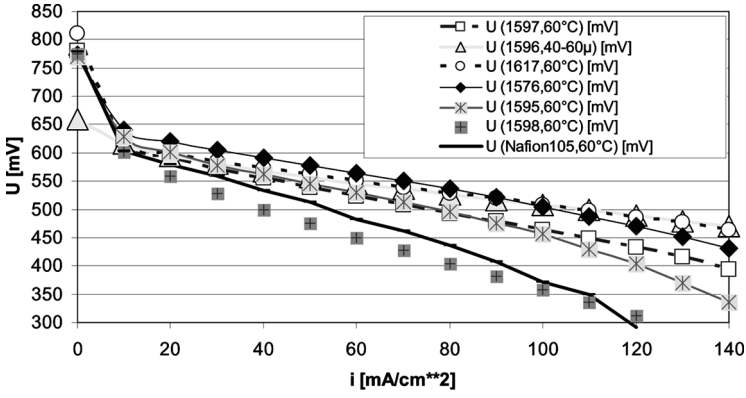
Method A. The MEAs have been tested under the same conditions to allow comparability between the different ionomer membrane types. The conditions applied for the screening tests are summarized below: $T_{cell} = 60°C$, $dbp_{air} = 0$ bar, $F_{air} = 0.688$ L/min (in the case of the M45-MEA $F_{air} = 0.44$–0.5 l/min) (dry air), $dp_{meOH} = 0$ bar, $F_{meOH} = 4$ ml/min, $c_{meOH} = 1.0$ mole/L, anode: JM PtRu 6 mg/cm^2(Lot: 04–00932), Toray Paper nonteflonated, cathode: JM Pt 6 mg/cm^2(Lot: CR0311), Toray Paper teflonated (26% PTFE). In Fig. 6, the i/U polarization curves of the acid-base blend MEAs are presented. For comparison, also a Nafion®105 MEA has been tested under the same conditions.

From Fig. 6 can be easily seen that most of the acid-base blend membranes show better DMFC performance than Nafion®105 which might be due to the lower meOH permeability of the arylene ionomer acid-base blend membranes (Fig. 6). The series of performance of the different membranes is as follows: $1596 \approx 1617 > 1576 > 1597 > 1595 >$ Nafion®$105 > 1598$. The DMFC performance of the 1596 membrane is comparable to that of a covalently cross-linked ionomer membrane (To27) published in a previous paper (16). In further DMFC tests at higher operation temperatures up to 110°C it showed, however, that the 1617 membrane degraded which is probably due to the lower chemical stability of the thioether linkages of ionomer **5**, compared to the other polyarylenes. An oxidation of the thioether linkages of the ionomer **5**

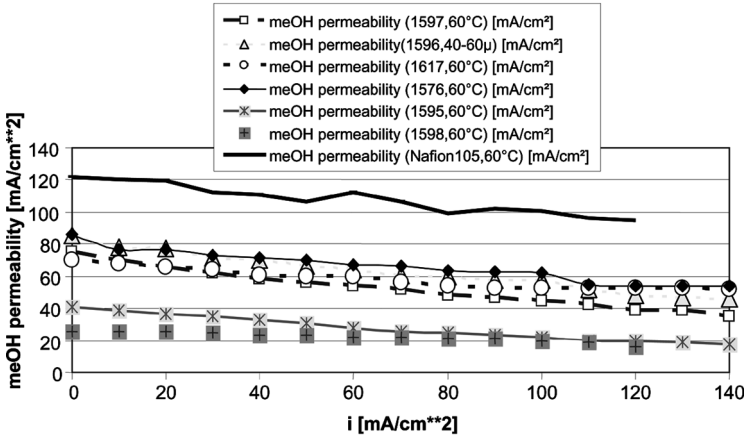
Table 4. Ionomer blend membrane properties

Membrane [No.]	Ionomer [No.]	IEC [meq/g]	WU 25/90°C [%]	R_a (in-situ)[a] [Ohm*cm^2]	$T_{onset}^{SO_3H}$ (membrane) [°C]	$T_{onset}^{SO_3H}$ (ionomer)[b] [°C]
1595	**1**	1.12	24/79	0.26	260	248
1596	**2**	1.31	35/56	0.46	266	264
1597	**3**	1.17	26/293	0.26	248	235
1598	**4**	1.21	32/70	0.64	250	235
1617	**5**	1.17	38/78	0.1	263	255
1576_2 (M45)	**6**	1.54	69/107	0.16	269	257
M53_3	**7**	1.07	51/66	0.22	219	219

[a]measured in the DMFC during operation, temperature 60°C.
[b]values taken from Table 1, for comparison.



(a)



(b)

Figure 6. Results of the DMFC screening of the acid-base blend membranes; Figure 6a: polarization curves of the different acid-base blend membranes (comparison Nafion®105); Figure 6b: meOH permeabilities of the acid-base blend membranes (comparison Nafion®105).

to sulfone linkages should markedly improve the chemical stability of this polymer (9).

In a further experiment the thickness of the best acid-base blend membrane MEA, the 1596 MEA was varied in order to answer the question which membrane thickness would be optimal for the DMFC experiment. The DMFC performance of a 170 µm thick 1596 membrane was compared to the DMFC performance of a 40–60 µm thick one. The applied DMFC conditions were the same as mentioned above. In Fig. 7, the i/U curves of these two membranes are shown.

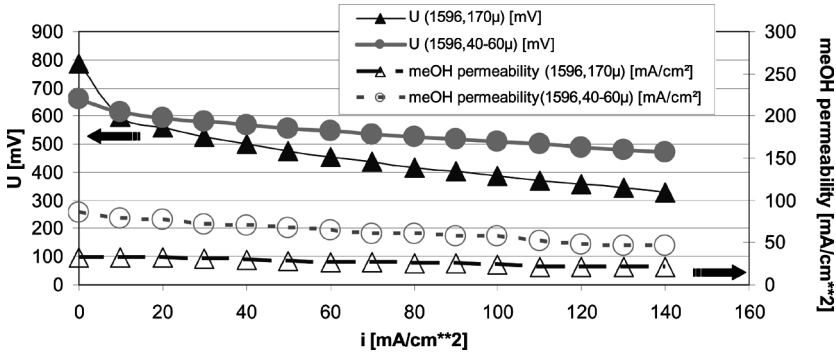


Figure 7. DMFC polarization curves of two 1596 membranes, 170 and 40–60 µm thick.

The influence of the membrane thickness onto the DMFC performance is clearly indicated: the thinner membrane shows a significantly higher meOH permeability than the thicker one, but also a markedly better polarization curve, which is due to the lower in-situ area resistance of the cell with thinner membrane (R_a (thinner membrane) = 0.15–0.16 Ohm * cm^2; R_a (thicker membrane) = 0.54–0.66 Ohm * cm^2). Obviously the higher proton conductivity of the thinner membrane overcompensates its higher meOH permeability which is indicated by the lower open current voltage (OCV) of the thinner membrane.

Comparison of a 1597 MEA With the Block *Co*-ionomer MEA (m53-3)

As a reduced meOH permeability of block *co*-ionomers, compared to the corresponding random copolymers, can be expected (25), we comparatively investigated the DMFC performance of the 1597 acid-base blend membrane and of the 53-3 block *co*-ionomer membrane. The results of this comparison are shown in Fig. 8. The applied DMFC operation parameters were: $T_{cell} = 60°C$, $p_{air} = 4$ bara, $F_{air} = 2.08$ L/min (dry air), $p_{meOH} = 1$ bara, $F_{meOH} = 4$ mLl/min, $c_{meOH} = 1.0$ mole/L, anode: JM PtRu 5.2 mg/cm^2 (Lot: 04-00932), Toray Paper nonteflonated, cathode: JM Pt 6.4 mg/cm^2 (Lot: CR0258), Toray Paper teflonated (26% PTFE). From Fig. 8 it can be seen that, as expected, indeed the meOH permeability of the block *co*-ionomer membrane is markedly lower than the meOH permeability of the acid-base blend membrane. However, after the block copolymer membrane has been operated at higher temperatures up to 110°C, its DMFC performance was much lower, and its meOH permeability significantly higher than initially. These findings indicate

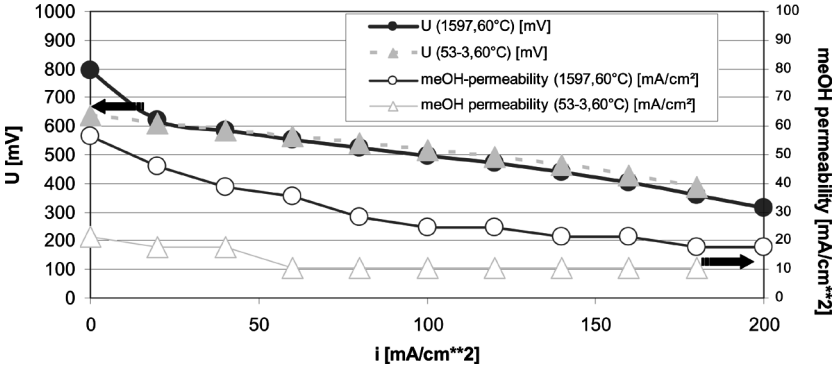


Figure 8. Comparison of the DMFC performance of the 1597 acid-base blend membrane with the block co-ionomer membrane M53_3.

that irreversible morphology changes, probably by irreversible swelling, are taking place in the block *co*-ionomer membrane during higher DMFC operation temperatures. It can be concluded from these results that the morphology of the block *co*-ionomers should be stabilized in order to allow stable long-term DMFC operation.

Temperature Dependence of the DMFC Performance

To investigate the temperature dependence of DMFC performance of the acid-base blend membranes, DMFC i/U polarization curves have been recorded of a MEA containing the unsupported 1576 (M45) ionomer membrane at different temperatures 25, 40, 60°C. The operation conditions have been: $p_{air} = 1$ bara, $F_{air} = 0.5$ L/min (dry air), $p_{meOH} = 1$ bara, $F_{meOH} = 4$ ml/min, $c_{meOH} = 1.0$ mole/L, anode: JM PtRu 6 mg/cm^2 (Lot: 04-00932), Toray Paper nonteflonated, cathode: JM Pt 6 mg/cm^2 (Lot: CR0311), Toray Paper teflonated (26% PTFE). In Fig. 9, the polarization curves at the three temperatures are presented. The performance of the M45 MEA increases with increasing operation temperature, which is mainly due to a decrease in membrane resistance with temperature (R_a (25°C) = 0.24 Ohm * cm, R_a (40°C) = 0.2 Ohm * cm, R_a (60°C) = 0.16 Ohm * cm), which is clearly seen in the diagram.

Comparison of the DMFC Performance of a 1597 g MEA with a Nafion®105 MEA

In Fig. 10 the i/U polarization curve of a 1597 g MEA is compared to a Nafion®105 MEA in an air-breathing DMFC. Both polarization curves

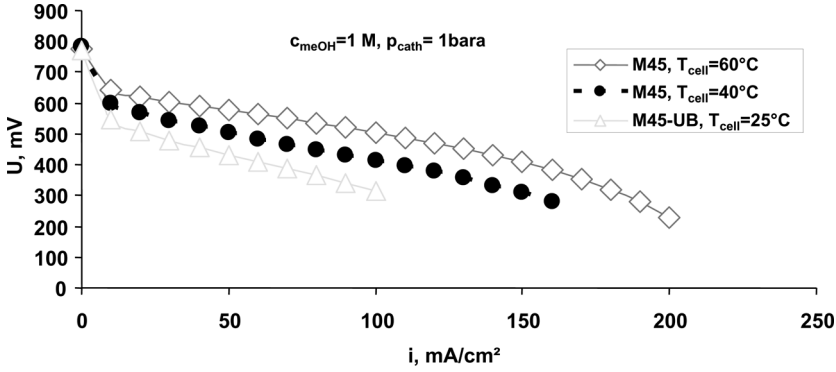


Figure 9. DMFC performance of the M45 membrane at different temperatures; operation conditions see text.

are similar; however, the 1597 g i/U polarization curve has been recorded at lower operation temperature than Nafion®105. Moreover, the 1597 g membrane is significantly thinner than the Nafion®105 membrane, and its OCV much higher and T_{cell} lower than that of the Nafion®105 membrane, indicating lower meOH permeation of the 1597 g membrane.

Comparison of a 1597 g MEA with a Nafion®105 MEA in Galvanostatic Operation Mode

In order to compare the DMFC efficiencies of a 1597 g MEA with that of a Nafion®105 MEA, both MEAs have been tested in an air-breathing

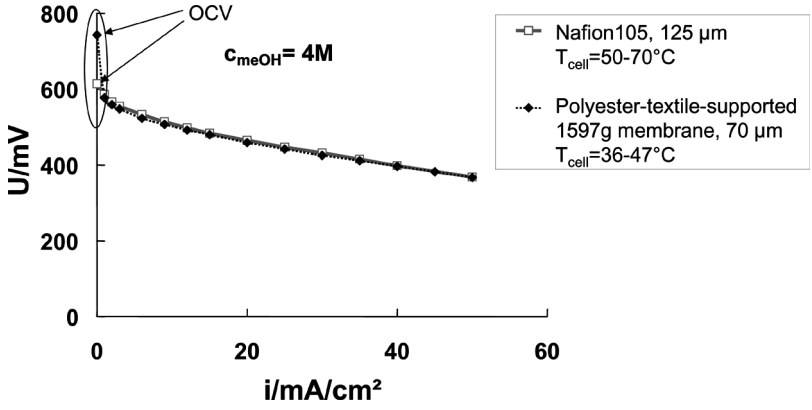


Figure 10. Comparison of the i/U polarization curve of the nonfluorinated 1597 g membrane with Nafion®105 (air-breathing DMFC).

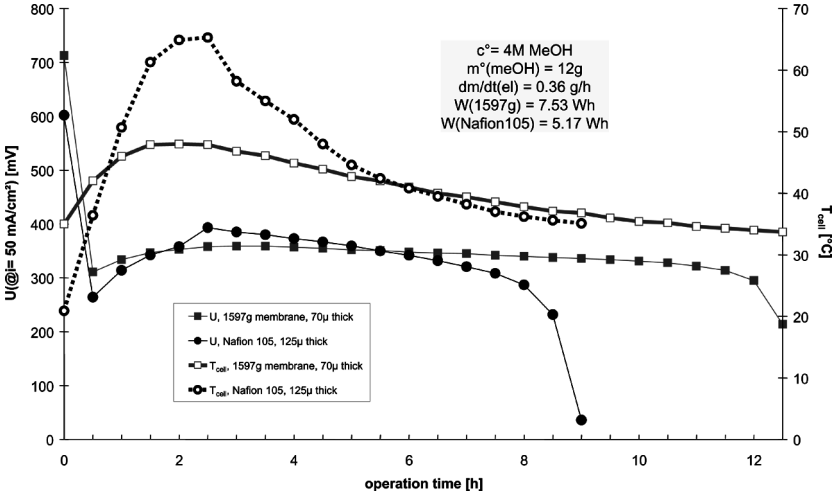


Figure 11. Voltage and cell temperature of a DMFC experiment during consumption of 12 g meOH at a DMFC current density of 50 mA/cm^2 of a 1597 g MEA and a Nafion®105 MEA in dependence of the operation time.

DMFC in galvanostatic operation mode. The meOH amount being consumed during the DMFC experiment was 12 g. In Fig. 11, the voltage and cell temperature at a current density of 50 mA/cm^2 are presented in dependence of the operation time. From Fig. 11 it can be seen that the cell temperature of the Nafion®105 MEA increases much more within the first 2 hours of operation, which is due to the higher meOH loss due to meOH crossover of the Nafion®105 membrane, which leads to a higher extent of direct exothermic reaction of the permeated meOH with the cathode catalyst. For the same reason the available meOH quantity is faster consumed in the case of the Nafion®105 MEA, compared to the 1597 g MEA, which ends up in a 45% higher power output of the 1597 g MEA, compared to the Nafion®105 MEA (1597 g: 7.53 Wh, Nafion®105: 5.17 Wh).

Comparison of the DMFC Performance of Different Types of 1597 MEAs

MEAs using the 1597 polymer electrolyte have been made via Method B (conventional, polyester-textile-reinforced), Method C (building up from anode), and Method D (building up from cathode). They were tested in air-breathing DMFCs with 1.5 M and 4 M meOH solutions at temperatures in the range 28–50°C. The best polarization curve of every MEA

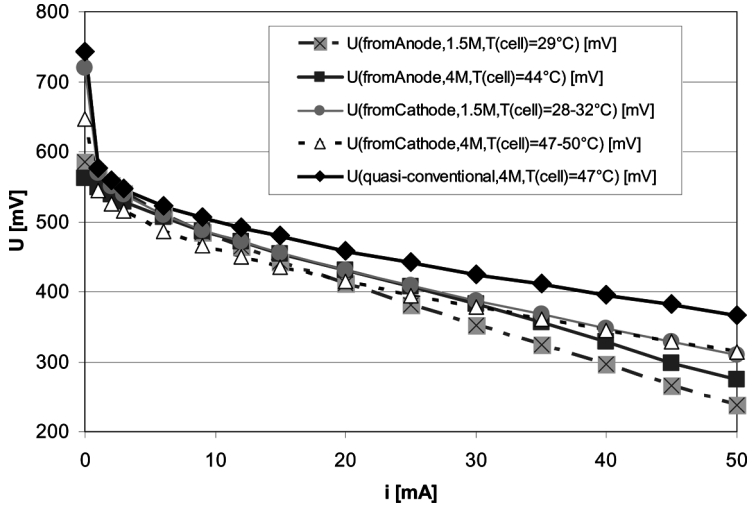


Figure 12. Air-breathing DMFC results using MEAs based onto the 1597 polymer electrolyte made via Method B (conventional, textile-reinforced), Method C (building up from anode), and Method D (building up from cathode).

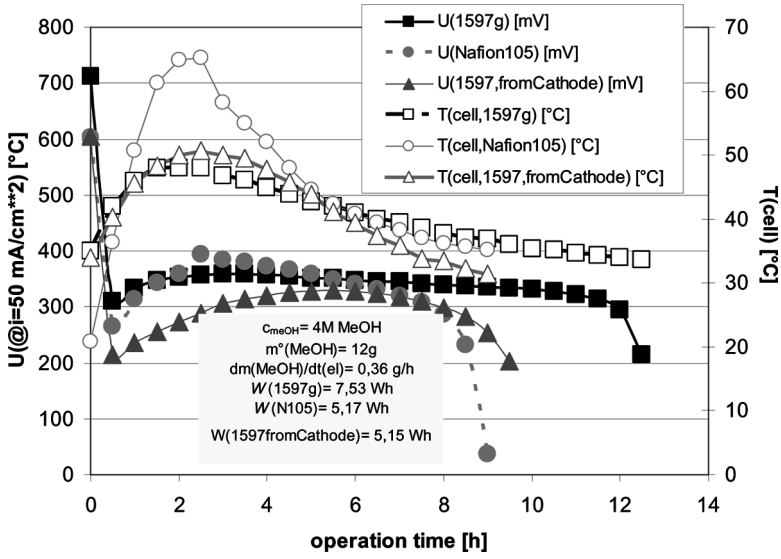


Figure 13. Voltage and cell temperature of a DMFC experiment during consumption of 12 g meOH at a DMFC current density of 50 mA/cm^2 of a 1597 g MEA, a 1597 MEA made via Method D and a Nafion®105 MEA in dependence of the operation time.

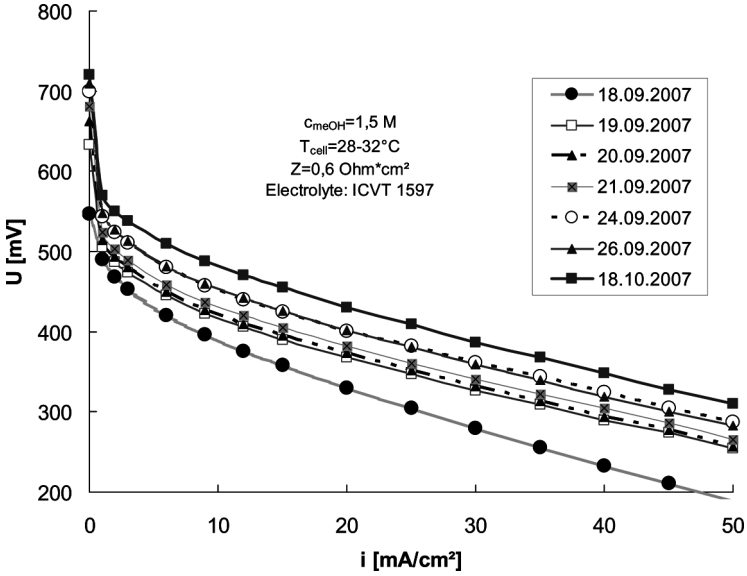


Figure 14. Polarization curves of the 1597 MEA built up using Method D at a meOH feed concentration of 1.5 M after different operation times within a 1 month time range.

type and meOH concentration are presented in Fig. 12. From Fig. 12 it can be seen that the MEAs built up from cathode or anode have slightly lower DMFC performance than the MEAs built up via Method B.

In order to compare the DMFC efficiencies of a 1597 g MEA with that of a 1597 MEA built up from cathode and with a Nafion®105 MEA, all three MEAs have been tested in an air-breathing DMFC in galvanostatic operation mode. The meOH amount to be consumed during the DMFC experiment was 12 g. In Fig. 13, the voltage and cell temperatures of the three MEAs at a current density of 50 mA/cm^2 are presented in dependence of the operation time.

One can see that the MEA from the 1597 g polymer electrolyte (prepared via Method B) shows the best utilization of the meOH amount fed to the DMFC. The MEA made by Method D shows a meOH utilization similar to Nafion®105. There is still optimization potential for the MEA preparation Method D using the 1597 polymer electrolyte.

Long-term DMFC Test of a Nonfluorinated Ionomer Membrane MEA

The long-term performance of the 1597 MEAs prepared by Method D was tested in a DMFC using 1.5 moles/L meOH solution (for 1 month)

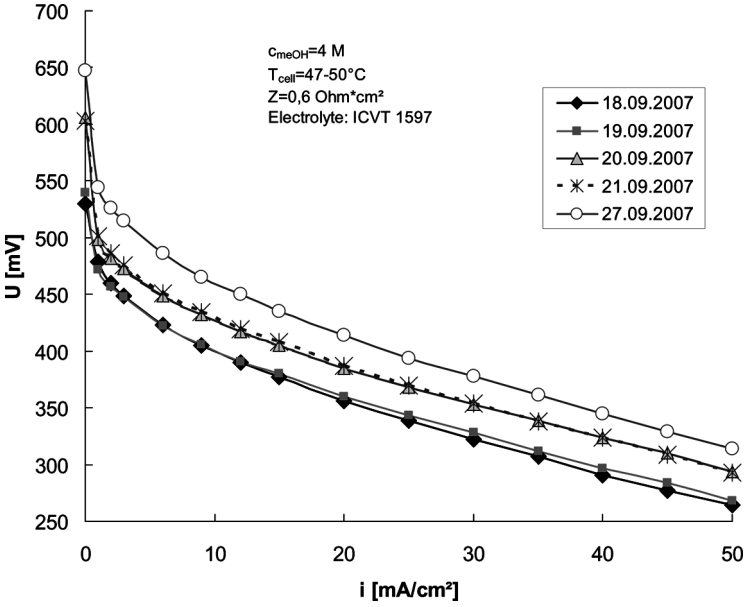


Figure 15. Polarization curves of the 1597 MEA built up using Method D at a meOH feed concentration of 4 M after different operation times within a 10 days time range.

and 4 moles/L meOH solution (for 10 days). The polarization curves recorded after different operation times are shown in Fig. 14 for the 1.5 moles/L meOH feed concentration and in Fig. 15 for the 4 moles/L meOH feed concentration.

One can clearly see that during the observed operation time range no MEA degradation at all takes place – in contrary the performance markedly improves during this time range which could be explained by washing out of solvent or other low-molecular matter from the MEA which was initially present from the MEA preparation process. Obviously the DMFC operation has a self-cleaning effect onto the 1597 MEA.

CONCLUSIONS

MEAs have been prepared from:

- acid-base-blends consisting of different sulfonated arylene main-chain polymers and polybenzimidazole PBI;

- a microphase-separated arylene main-chain block *co*-polymer consisting of a sulfonated and proton-conducting and a hydrophobic microphase.

The MEAs have been prepared using 4 different methods:

- Method A: The membrane has been prepared first as a free film, and the electrodes have been coated onto the membrane subsequently;
- Method B: The membrane has been prepared first as a polyester-supported film, and the electrodes have been coated onto the membrane subsequently;
- Method C: The MEA has been built up from the anode;
- Method D: The MEA has been built up from the cathode.

The MEAs have been tested under different temperatures and different meOH concentrations.

Three different polyacid-PBI blend membranes could be identified which showed comparable or even better DMFC performance than Nafion®105: a sulfonated polyethersulfone-PBI blend membrane, a sulfonated polyetherketone-PBI blend membrane, and a partially fluorinated sulfonated polyether-PBI blend membrane. The proton-conducting block *co*-ionomer membrane initially showed an excellent DMFC performance due to reduced meOH permeability, compared to the polyacid-PBI blend membranes, which however degraded with time of THE DMFC operation which is probably due to irreversible morphology changes. Among all tested MEAs the MEAs prepared by Method B showed the best DMFC performance. The DMFC performance of the MEAs prepared by Method C and Method D was slightly worse than that of the MEAs made via Method B, but it is expected that a fine-tuning of the MEA preparation conditions will lead to further improvement of Method C and Method D MEAs. The DMFC performance of a MEA from the sulfonated polyetherketone-PBI blend membrane which was built up using Method D improved steadily during 4 weeks of DMFC operation. It is thought that Method C and D MEA preparation procedures can be up-scaled to markedly reduce the MEA production costs.

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