Tailoring the interface layer of the bipolar membrane

J. Balster [a,1], S. Srinkantharajah [a], R. Sumbharaju [a], I. Pünt [a],
R.G.H. Lammertink [a], D.F. Stamatialis [a,b,*], M. Wessling [a,2]

[a] *Institute of Mechanics, Process and Control–Twente (IMPACT), University of Twente, Membrane Technology Group,
Faculty of Science and Technology, PO Box 217, 7500 AE Enschede, The Netherlands*
[b] *MIRA Institute for Biomedical Technology and Technical Medicine, University of Twente, Membrane Technology Group,
Faculty of Science and Technology, PO Box 217, 7500 AE Enschede, The Netherlands*

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ABSTRACT

This work investigates various parameters affecting the water splitting of bipolar ion-exchange membranes. We show that the amount of functional groups and the water content of the interface layer have a strong influence on the bipolar membrane resistance. Use of anion exchange layers containing quaternary ammonium groups instead of bicyclic amines results in bipolar membranes with low electrical resistance. The influence of an iron and pyridine based catalyst in the bipolar membrane junction is investigated as well. We show that the pyridine based interface layer is a good tool to prepare tailor made bipolar membranes containing anion exchange layers with high base stability without having water splitting catalytic functional groups.

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1. Introduction

Bipolar membrane electrodialysis (ED-BPM) can be used to produce acids and bases from their corresponding salt solutions. A bipolar membrane (BPM) is a laminate of a cation and anion exchange layer and allows the dissociation of water into protons and hydroxyl ions under the influence of an electric field (Fig. 1). The three layers of a BPM, the anion exchange layer, the cation exchange layer and the bipolar membrane junction (interface between anion and cation exchange layer), play an important role in its performance in an electrodialysis process. The overall water dissociation reaction into hydroxyl ion and proton (hydronium ion) is described by [1].

$$2H_2O \rightleftarrows H_3O^+ + OH^- \tag{1}$$

The water dissociation rate in a BPM was found to be 50 million times faster than the ordinary water dissociation in aqueous solution [2]. The conditions for water dissociation in a bipolar membrane junction are very different to the dissociation in free water.

This is caused by the presence of a polymer phase, the fixed ionic groups, counter ions and the presence of an electrically charged environment between the cation and anion exchange membrane. Under operational conditions, this layer has low concentration of both counter and co-ions [3], but the current is carried by protons and hydroxyl ions which stem from dissociating water in the BPM junction. The water dissociation rate depends significantly on the characteristics of the bipolar junction interface layer [4–11].

Water splitting occurs already if a cation exchange and anion exchange membrane in loose contact with each other are placed in an electric field with the correct polarity and sufficient electric field strength [1]. The produced protons and hydroxyl ions are transported through the corresponding ion exchange layers, away from the interface (see Fig. 1). The water splitting region can be part of the either anion or cation selective layer at the contact interface of the two layers.

Ramirez et al. [12] explained the water dissociation reaction using the Donnan equilibrium and the Nernst–Planck equation. The water molecule is hypothesized to dissociate at an increased rate in accordance with the second Wien effect [2,12,13], which suggests that the degree of dissociation of weak electrolytes at high electric field is accelerated. However, Strathmann et al. [9,10] calculated that the increase in water splitting due to the second Wien effect is still at least three orders of magnitude smaller than the experimentally observed results.

Simons observed differences in the water dissociation behaviour between anion and cation exchange membranes and suggested that

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* Corresponding author. Tel.: +31 53 4894675; fax: +31 53 4894611.
E-mail address: d.stamatialis@utwente.nl (D.F. Stamatialis).
[1] Present address: Evonik Degussa GmbH, Process Technology & Engineering, Paul-Baumann Straße 1, 45764 Marl, Germany.
[2] Present address: RWTH Aachen University, Chemische Verfahrenstechnik (CVT), 52064 Aachen, Germany.
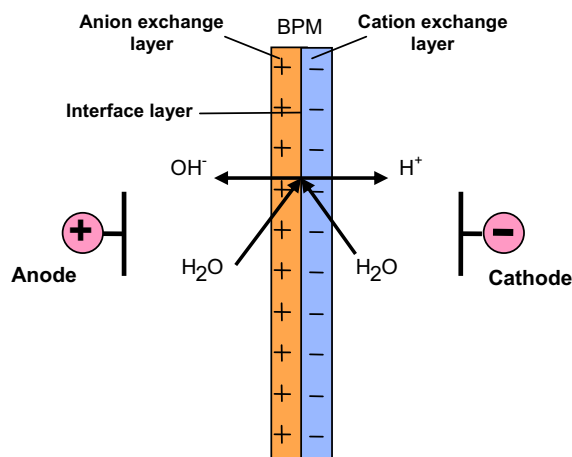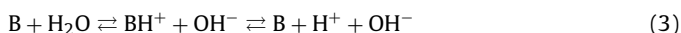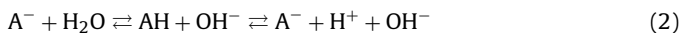
Fig. 1. Schematic drawing of the water splitting function of a BPM.

the water dissociation is caused by proton transfer between the fixed charged groups and water molecules existing in the interface [14,15]. The water dissociation is a proton-transfer reaction that is catalysed by weak acids and bases. With an immobile weak neutral acid AH or the corresponding acid BH^+ of a weak neutral base B as a catalyst, this reaction can be split into two consecutive reactions (simplified for the proton H^+ instead of the hydronium ion H_3O^+)[15]:

$$A^- + H_2O \rightleftarrows AH + OH^- \rightleftarrows A^- + H^+ + OH^- \qquad (2)$$

$$B + H_2O \rightleftarrows BH^+ + OH^- \rightleftarrows B + H^+ + OH^- \qquad (3)$$

In an electric field, the charged mobile ions OH^- and H^+ are removed from the reactive sites of the contact region. Their mobility is significantly accelerated due to the proton and hydroxide ion tunnelling similar to aqueous solutions [16].

As mentioned before, the ionic groups are extremely important in the water splitting mechanism. Investigation of membranes with sulphonic, carboxylic and phosphonic acid groups suggests that the decrease in the potential differences in the membrane is [3]:

$$SO_3H > -COOH > -PO(OH)_2 \qquad (4)$$

This decrease can be explained by the activation energy which is necessary for the interaction of the ionic group with the water molecule. In fact, the pK increases in the same order. In terms of catalytic activity, the ionic groups of bipolar membranes can be arranged in order of increasing rate constants for the water dissociation (see Table 1 [3]).

The dependence of activation energy for the dissociation of water on the nature of ionic groups is important evidence to support the catalytic mechanism inside the bipolar membrane for water splitting. The activation energy for membranes with a weak catalytic effect is lower than the activation energy in pure water ($56\,kJ\,mol^{-1}$). The phosphoric acid groups show the lowest value [3].

Despite the above, efficient water dissociation at the BPM does not occur if it is prepared with only lamination of anion and cation exchange layers containing ion exchange groups without catalytic activity. To improve the BPM performance, a thin interface layer, containing a water dissociation catalyst, is generally introduced

between the charged layers. Four parameters influence the water splitting performance of a BPM:

1. Amount of ionic groups at the interface layer [17–19],
2. Composition of the anion exchange layer [4–7,11],
3. Topology/roughness of the BPM junction [1,20], and
4. Water dissociation catalyst [21–28].

High concentrations of ionic groups at the BPM junction increases the polarity of the interface layer and enhances the water splitting reaction [19]. Besides, in this case the hydrophilicity of the BPM interface is higher. This in fact accelerates the water-splitting reaction because the hydrophilic polymer layer increases the water activity by attracting water from the ion exchange layers to the space charge region [17,18].

The composition of the anion exchange layer of a BPM plays an important role as well [7]. Anion exchange membranes have different water dissociation behaviour than cation exchange membranes due to the possible proton transfer between the fixed charged groups and the water molecules [14,15]. If the anion exchange layer contains secondary or tertiary amines, the water splitting reaction is catalysed (see Eq. (3)). Nowadays most of the commercially available anion exchange membranes contain quaternary ammonium groups which do not participate in the catalytic water splitting.

The structure of the BPM interface influences the resistance and the stability of the BPM. The electric resistance increases if a depleted film is developed between the two layers during operation. Therefore the interface of the BPM should be tailored to minimise electric resistance and to attain a firm bonding of the ion exchange layers. A firm bonding avoids the separation of the two layers (an effect also called "ballooning") if no sufficient current is applied [20].

Catalysts provide alternative reaction paths for the dissociation reaction by forming very reactive, activated complexes [15,27]. The best catalytic activities have been found for sufficient amounts of weak acids (and the corresponding base) such as amino groups, pyridines, carboxylic acids, and phosphoric acid groups [1,9,25,26]. Besides inorganic substances such as metal oxides and hydroxides [23] or heavy metal ion complexes (ruthenium trichloride, chromic nitrate, indium sulphate, and hydrated zirconium oxide) [19,21,24] are also good catalysts.

Theoretically, the potential difference across a 100% permselective BPM for the generation of one molar acid and base at 25 °C can be estimated to be 0.83 V [29]. Higher potential drops across the BPM are due to the electrical resistance of the cation exchange, anion exchange and interface layer.

The objective of this paper is to systematically investigate the influence of the interface layer on the water splitting performance of the BPM by addressing in detail all four parameters described earlier. Especially for the catalysts, different catalytic layers, based on iron and pyridine are introduced and their influence on the water splitting performance is investigated.

2. Experimental

2.1. Materials

The commercially available Neosepta CMX (from Tokuyama Soda Ltd.), or blends of sulphonated poly(ether ether ketone), S-

Table 1
Catalytic activity of different ionic groups.

Ionic group	$-N(CH_3)_3$	$-SO_3H$	$-PO_3H^-$	$=NH, -NH_2$	$\equiv N$	$-COO^-$	$-PO_3{}^{2-}$
$k\,[s^{-1}]$	0	3×10^{-3}	3×10^{-2}	10^{-1}	1	10	10^2

PEEK, and poly(ether sulphone), PES, were used as cation exchange layer of the BPMs. S-PEEK was prepared by sulphonation of poly(ether ether ketone) (PEEK) 450PF (Victrex) [30]. As precursor polymer PEEK 450PF from Victrex was used. PEEK is an amorphous polymer, with low water absorption and high solvent resistance. The polymer was dried for more than 24 h in a vacuum oven, at 100 °C. One litre of concentrated sulphuric acid (95–98 wt% extra pure, as received) was placed in a reaction vessel at 25 °C and 60 g polymer were added under stirring. The reaction mixture was stirred for several hours, at controlled temperature, to achieve the desired sulphonation [31,32]. Then, the reaction vessel was immersed in an ice bath to stop the reaction. The sulphonated polymer (S-PEEK) was precipitated in demineralised water of max 5 °C and washed until the pH was 7. The polymer was dried subsequently in air at room temperature and in a vacuum oven at 100 °C.

The S-PEEK/PES blends (indicated as S/P in the text) were prepared by adding 60% S-PEEK and 40% PES to the solvent N-methyl-2-pyrrolidinone, NMP, (in total 20 wt% polymer in solution), stirred for a minimum of 24 h and filtered over a 40 μm metal filter.

Neosepta AM-3 (from Tokuyama Soda Ltd.), IonClad R4030 (from Pall Gelman) or a tailor made membrane prepared from aminated polysulphone, Psf (FuMA-TECH GmbH, St. Ingbert, Germany, indicated as A-Psf in the text) in NMP (10 wt% polymer in solution) were used as anion exchange layers.

For the contact region of the BPM different materials have been used:

1. S-PEEK of various sulphonation degree (SD),
2. $Fe(OH)_3$ granular (0.2–2 mm) from Merck,
3. Poly(4-vinyl pyridine), P4VP, from Sigma–Aldrich ($M_w = 60,000$ g/mol),
4. Poly(acrylic acid), PAA, from Sigma–Aldrich ($M_w = 100,000$ g/mol), and
5. Poly(ferrocenyl dimethylsilane), PFS, an iron containing polymer prepared by the Materials Science and Technology of Polymers group of the University of Twente, Enschede (see Fig. 2).

The PFS polymer was dissolved in chloroform while all the other materials were dissolved in NMP.

2.2. BPM preparation

Single ion exchange membranes as well as the BPMs were prepared by the casting/evaporation technique [33]. In order to have a good contact between the different layers, the casting was as described in Fig. 3 [34] was used. The polymer layers were cast with the desired thickness and sequence onto a glass plate. After the solidification of one layer the next layer was cast on top of the for-
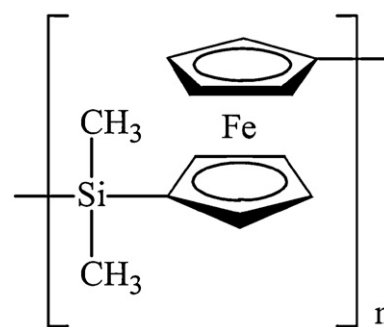

Fig. 2. Repeat unit of poly(ferrocenyl dimethylsilane), PFS.

mer, which then was allowed to dry. This procedure was repeated until all desired layers (cation exchange layers, CELs, Interface layers, anion exchange layers, AELs) were cast onto each other. If one of the layers was a commercial membrane, the other layers were cast on top of it, as described above. When two commercial ion exchange membranes were used, the membranes were just pressed together.

The tailor made membranes were dried in N_2 atmosphere at 40–80 °C for 1 week, then immersed in water and subsequently dried under vacuum at 30 °C for 1 week. The membranes were finally stored in a 2 M NaCl solution.

The $Fe(OH)_3$ at the interface layer of the BPM junction was added by two different methods: $Fe(OH)_3$ granular was dispersed in a S-PEEK solution and cast Electrodeposition. This was performed using a two compartment cell (with a membrane area of 3.14 cm², see Fig. 4, [24]). The concentration of $Fe(OH)_3$ immobilised at the junction was controlled over the applied current density and deposition time. After the electrodeposition, the membrane was washed in a 2 M NaCl solution for one day to remove excess of Fe^{3+} ions from the membrane.

2.3. Characterisation of the ion exchange membrane layers

The commercial AM-3 and CMX membranes and the tailor made ion exchange membrane layers were characterised by measurements of ion exchange capacity (IEC) and water uptake (w). These properties were used to calculate the sulphonation degree (SD) and the charge density (c_{char}) of the membranes [30,33].

The IEC was calculated as the ratio of total charge by the dry weight of the CEM. The degree of sulphonation was calculated according to [33]:

$$SD = \frac{M_{w,p} IEC}{1 - M_{w,f} IEC} \tag{5}$$

where $M_{w,p}$ is the molecular weight of the non-functional polymer repeat unit and $M_{w,f}$ is the molecular weight of the functional group including the counter ion ($-SO_3Na$).
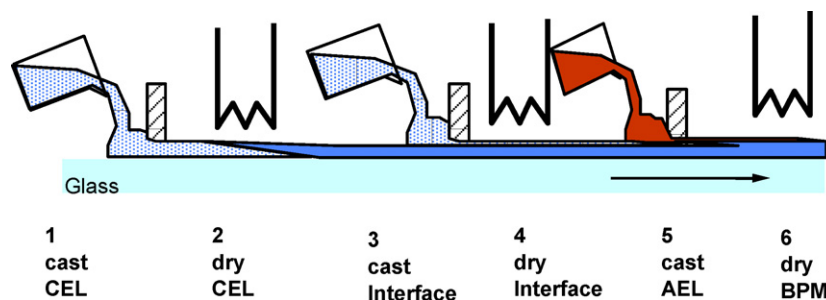

1	2	3	4	5	6
cast CEL	dry CEL	cast Interface	dry Interface	cast AEL	dry BPM

Fig. 3. Schematic drawing of the BPM preparation by casting.

Adapted from [35].

Table 2
Properties of the commercial and tailor made ion exchange membranes used as ion exchange layers of the prepared BPMs.

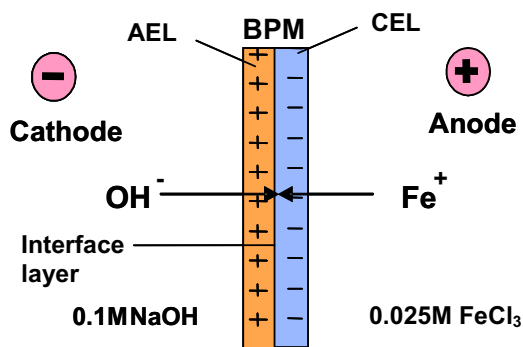| Membrane	Used as	Functional group	IEC [mol/kg$_{dry}$]	w [kg$_{water}$/kg$_{dry}$]	c_{char} [mol/L]
CMX	CEL	Sulphonic acid	1.65	0.26	6.4
S/P	CEL	Sulphonic acid	1.30	0.34	3.8
AM-3	AEL	Quaternary ammonium	1.65	0.20	8.3
R4030	AEL	Quaternary ammonium	0.81	0.19	4.3
A-Psf	AEL	Bicyclic ammonium	1.84	0.36	5.1

Fig. 4. Schematic illustration of the electrodeposition of iron hydroxides at the BPM interface.

The water uptake of the membrane is given by [33]:

$$w = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{6}$$

The charge density (c_{char}) of the membrane can be calculated [30]:

$$c_{char} = \frac{IEC}{w} \tag{7}$$

The properties of all membranes are shown in Table 2.

2.4. Characterisation of the BPMs

Many properties of a BPM can be determined from steady state current density–voltage drop (i–v) measurements (see Fig. 5) [35,36]. The central BPM is the investigated membrane, whereas the other membranes are auxiliary membranes, necessary to maintain well defined, constant concentrations in the two central compartments. During the experiment the temperature was held constant at 25 °C, the applied current density was increased stepwise and the system was allowed to reach steady state. The voltage drop across the membrane was measured with calomel electrodes at a fixed distance from the membrane surface by Haber–Luggin capillaries filled with concentrated KCl solution. Generally, in such measurements, the solution resistance is subtracted. However, the solution resistance close to the BPMs decreases at higher current densities due to the generation of H$^+$ and OH$^-$ (the conductivity next to the membrane increases). Therefore, the i–v curves were not corrected for the solution resistance.

Fig. 6 presents a typical steady state current density–voltage drop (i–v) curve of a BPM for a neutral salt solution (M$^+$X$^-$) [35,37]. Until the first limiting current density (i_{lim1}) is reached, the current is only transported by salt ions. At i_{lim1}, the electrical resistance is the highest since all salt ions are removed from the BPM junction. The magnitude of i_{lim1} is a measure for the selectivity of the BPM. Above i_{lim1}, the water splitting potential (U_{diss}) is reached leading to water dissociation. The water splitting products (J_{OH^-}/J_{H^+}) are now also available for the current transport [37].

In order to reduce the relative salt ion transport and have high water splitting efficiency the operating current density (i_{op}) should be as high as possible. Above the second limiting current (i_{lim2}), water diffusion limitations occur because the water transport toward the BPM junction is not sufficient to replenish the water dissociated at the interface, leading to drying out of the membrane [38,39]. The U_{diss} is strongly influenced by the thickness of the interface region and the catalytic activity of the groups present at the interface layer. The water splitting resistance (R_{diss}), which can be calculated from the current density increase in the water splitting
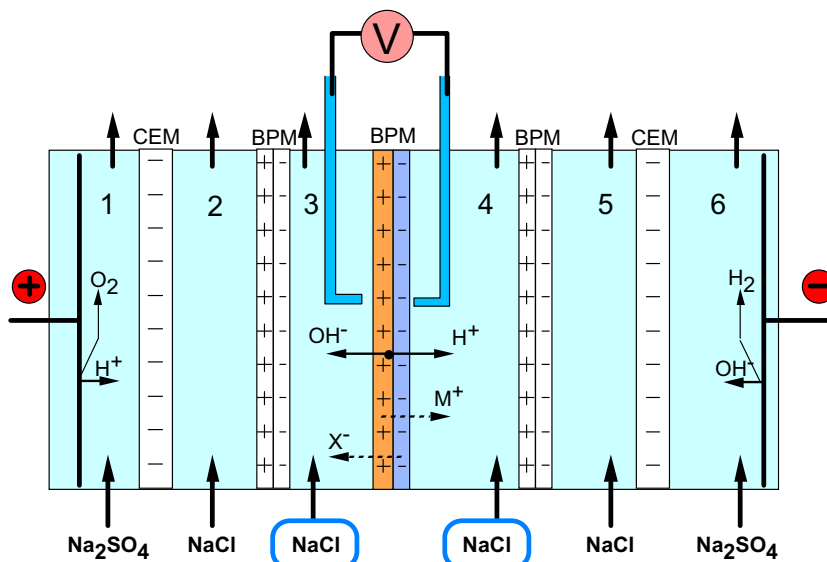

Fig. 5. Schematic drawing of a six compartment measurement module for i–v curve measurements.
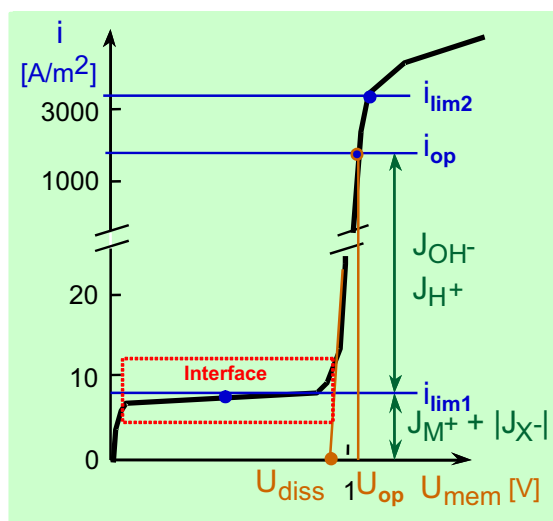
Taken from [35].

Fig. 6. Schematic i–ν curve of a BPM in a salt solution (M^+X^-). Adapted from [21,34].

region, decreases with increasing catalytic activity. Both parameters, U_{diss} and R_{diss} determine the operational area resistance of the BPM (R_{op}). All resistances (R) are calculated by Ohm's law ($R = U/i$).

3. Results and discussion

3.1. Influence of amount of ionic groups at the interface layer

Three different BPMs were prepared using a S/P layer (80 μm, IEC: 1.3 mol/kg$_{dry}$) as cation exchange layer and an A-Psf layer (10 μm, IEC: 1.8 mol/kg$_{dry}$) as anion exchange layer. As interface layer (10 μm) two S-PEEKs with different SDs (IEC: 1.8 and 2.1 mol/kg$_{dry}$, noted as S-PEEK 1.8 and S-PEEK 2.1 in the text) were used.

The presence of S-PEEK interface layer causes a decrease of the plateau length at i_{lim1} and therefore lowers the U_{diss} in comparison to a BPM with no interface layer (see Fig. 7). In addition, a steeper increase of current density with increased voltage is achieved leading to a lower R_{diss}. This reduction in U_{diss} and R_{diss}
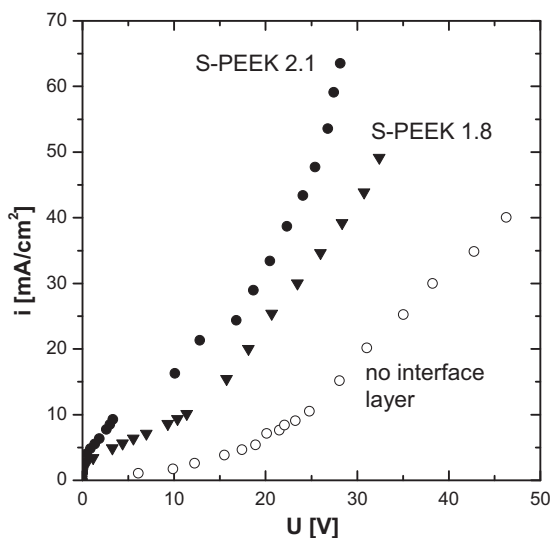
leads to a strongly reduced R_{op} of the membrane. The decrease of R_{op} is stronger for S-PEEK of higher IEC. As mentioned earlier, SO_3^- groups do not show catalytic water splitting activity, but the strength of the polarisation effect between cation and anion exchange layer increases, when additional SO_3^- groups are introduced [19]. In addition the hydrophilicity of the interface layer increases, leading to higher water content at the interface which shifts the water dissociation reaction to the right side (Eq. (1)) [17,18].

Fig. 7 shows a distinct limiting current density i_{lim1} for the BPMs having SPEEK interface layer. In contrast to prior knowledge, the co-ion leakage for the BPM without interface layer is lower than for membranes with S-PEEK interface layer. This discrepancy might be due to significant interpenetration of the anion exchange solution into the S-PEEK interface layer during casting. This seems to produce an anion exchange layer of lower thickness. Since the salt transport into the BPM depends on the layer thickness of the ion exchange layers [35,37], a thinner anion exchange layer causes higher co-ion leakage and therefore higher limiting current density. The influence of the compositions and thicknesses of the ion exchange layers to the co-ion leakage is thoroughly investigated in [40].

In conclusion focussing on the water splitting activity, our research suggest that a highly sulphonated layer at the BPM junction is preferable.

3.2. Influence of the composition of the anion exchange layer

As discussed earlier, the composition of the anion exchange layer of the BPM plays an important role in water dissociation [7]. If the anion selective layer contains secondary or tertiary amines, the water splitting reaction is catalysed (see Eq. (3)). Nowadays most of the commercially available anion exchange membranes contain quaternary ammonium groups, which are generally not catalytically active. However, under the influence of a strong electric field in alkaline conditions, the groups degrade to tertiary and secondary amines, which are then catalytically active [14].

Fig. 8 shows i–ν curves of BPMs prepared using the same S/P layer as cation exchange layer and S-PEEK 2.1 as interface layer, as described above. One was prepared by casting A-Psf (with bicyclic ammonium groups) and the other by laminating the Pall Ion-

Fig. 7. Effect of the S-PEEK interface layers with different SDs on the i–ν curve of tailor made BPMs measured in 2 M NaCl. The S/P and A-Psf layer were used as cation exchange and anion exchange layer, respectively.
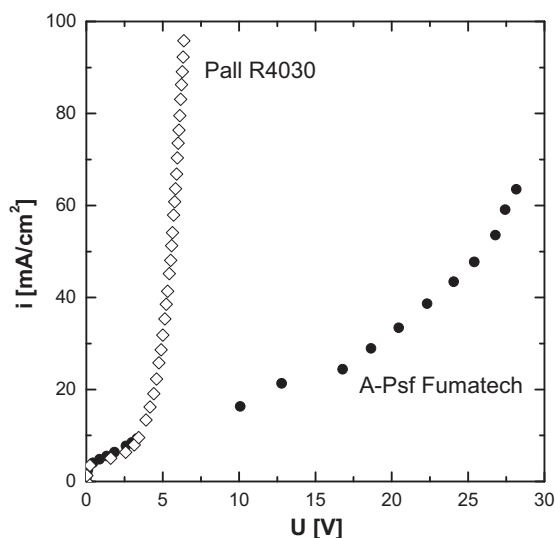

Fig. 8. Effect of the anion exchange layer on the i–ν curve of the prepared BPMs containing a S/P cation exchange layer and a S-PEEK 2.1 interface layer, measured in 2 M NaCl.

Table 3
Influence of the anion exchange layer on the properties of the prepared BPMs.

CEL	Interface	AEL	Symbol	U_{diss} [V]	R_{diss} [$\Omega\,cm^2$]	R_{op} [$\Omega\,cm^2$]
S/P	S-PEEK 2.1	A-Psf	◇	19.28	139.2	2822.7
S/P	S-PEEK 2.1	R4030	●	4.84	16.1	94.1

clad R4030 (with quarternary ammonium groups) anion exchange membrane onto the cation exchange layers.

The BPM prepared with the Pall R4030 membrane has lower resistance (R_{diss}, R_{op}). The U_{diss} and the activation energy to achieve water splitting is nearly 5 times lower (see Table 3), due to the presence of ionic groups which become catalytically active under strong electric field. Neither the quaternary nor the bicyclic ammonium groups can undergo any protonation or deprotonation reactions, which are necessary to catalyse the water dissociation reaction. However, as described before, the quaternary ammonium groups can degrade into tertiary and secondary amines [14].

The BPM junction under water splitting conditions is completely desalinated and to avoid high resistance, it should be as thin as possible. The morphology and the extent of the interface layer of the two prepared BPMs is likely to be different. The lamination of the S/P cation exchange layer and S-PEEK interface layer on the commercial R4030 membrane probably leads to a sharp BPM junction, because no penetration of the layers can occur since the polymer matrix of the R4030 membrane is perfluorinated and does not dissolve in NMP. Using A-Psf, penetration into the S-PEEK interface layer probably occurs due to casting. This leads to a firm bonding but less sharp BPM junction.

In the next section various catalysts will be investigated. For these tests we will prepare membranes with the non-catalytic A-Psf layers in order to compare purely the catalytic function of materials used to modify the interface.

3.3. Fe-based catalytic interface layer

One approach to enhance the water splitting ability of a BPM is the introduction of a Fe-based catalyst [21–24]. Therefore we introduce Fe additionally to the highly sulphonated S-PEEK layer into the prepared BPM (S/P 80 μm as cation exchange layer, S-PEEK 2.1, 10 μm as interface layer, and A-Psf, 10 μm as anion exchange layer). One BPM was prepared by dispersing $Fe(OH)_3$ into the S-PEEK solution prior casting of the interface layer. $Fe(OH)_3$ has a very low solubility and high catalytic water splitting capacity [1,23,24]. Next to $Fe(OH)_3$ a newly developed ionic Fe containing polymer (PFS, see Fig. 2) is tested as catalyst. A BPM (S/P 80 μm as cation exchange layer, S-PEEK 2.1, 10 μm as interface layer, and A-Psf, 10 μm as anion exchange layer) having 240 nm PFS as catalytic layer between the S-PEEK interface and the anion exchange layer was prepared. The thickness of the PFS layer was estimated from the height of the casting knife (12 μm) and the polymer content of the casting solution (2 wt%)

Fig. 9 presents the effect of the Fe based catalytic layers on the i–v curves of the developed BPMs. Addition of $Fe(OH)_3$ leads to a strong decrease of U_{diss} and R_{diss}, compared to the BPM without catalytic layer (see Table 4 and Fig. 9). Only by dispersion of 2 wt% $Fe(OH)_3$ into the S-PEEK interface layer, U_{diss} decreases nearly 4 times. This shows that much lower activation energy is needed for the water
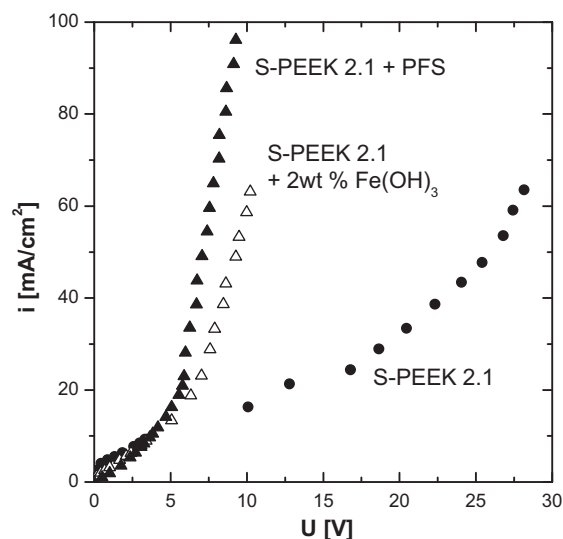

Fig. 9. Effect of the Fe based catalytic interface layers on the i–v curve of tailor made BPMs having intermediate S-PEEK layer, measured in 2 M NaCl.

dissociation reaction, because of the alternative paths for water dissociation created by $Fe(OH)_3$. The rate of the water splitting is much higher than without catalyst (R_{diss} decreased nearly 50%). In total R_{op} decreased more than 2 kΩ cm² by the introduction of $Fe(OH)_3$.

The application of PFS polymer onto the intermediate S-PEEK layer also leads to decrease of U_{diss} and R_{diss} and therefore R_{op} (see Table 4). In contrary to the BPM containing dispersed $Fe(OH)_3$, the ionic Fe is present in every repeat unit of the PFS polymer and therefore most likely homogenously distributed at the interface between cation and anion exchange layers. To the best of our knowledge, this is the first report demonstrating that a polymer backbone containing Fe can catalyse the water dissociation reaction at the BPM interface.

Both methods described above to incorporate Fe as catalyst into the BPM junction have disadvantages. The dispersion method may lead to inhomogeneous catalyst distribution (clustering of the particles), whereas the introduction of the specific PFS polymer does not allow variation of the Fe content at the BPM junction. Such variation is desired because the Fe content has a strong influence on the water splitting efficiency [24]. In order to achieve a good Fe distribution at the BPM junction the electro-deposition method described by Kang et al. [24] was also used. In the first experiments the commercial CMX (as cation exchange layer) and AM-3 (as anion exchange layer) membrane from Tokuyama Soda were pressed onto each other to form a BPM. The electro-deposition was performed as shown in Fig. 4 at current density of 10 mA/cm². The influence of deposition time and therefore of the amount of iron

Table 4
Influence of the Fe based catalysts on the BPM performance.

CEL	AEL	Intermediate layer	Catalyst	Symbol	U_{diss} [V]	R_{diss} [$\Omega\,cm^2$]	R_{op} [$\Omega\,cm^2$]
S/P	A-Psf	S-PEEK 2.1	–	●	19.28	139.2	2822.7
S/P	A-Psf	S-PEEK 2.1	$Fe(OH)_3$	△	5.74	71.6	482.0
S/P	A-Psf	S-PEEK 2.1 + PFS	Fe^{2+}	▲	4.98	56.4	336.9

Table 5
Effect of the electrodeposition time on the properties of the prepared BPMs.

CEL	AEL	Current density	Deposition time	Symbol	U_{diss} [V]	R_{diss} [Ω cm^2]	R_{op} [Ω cm^2]
CMX	AM-3	–	–	□	4.27	505.0	2664.0
CMX	AM-3	10 mA/cm^2	5 min	*	2.17	32.9	104.4
CMX	AM-3	10 mA/cm^2	15 min	☆	1.35	54.2	127.5

hydroxides on the performance of the BPMs is shown in Fig. 10. In comparison to the membrane without Fe, both BPMs prepared by electro-deposition have higher water splitting. R_{diss} is much lower after the introduction of iron hydroxides due to accelerated water dissociation leading to lower R_{op} (more than 2.5 kΩ cm^2) compared to the initial membrane (Table 5).

Fig. 10 shows that longer electro-deposition time (15 min instead of 5 min) does not improve water splitting. Longer electro-deposition time leads to higher amount of iron hydroxides at the BPM junction, resulting in lower U_{diss}, but also in higher R_{diss} of the prepared BPM (see Table 5).

Kang et al. [24] found that using electro-deposition with current density of ca. 5 mA/cm^2 for 10 min, between 2 and 3 mg/cm^2 of Fe(OH)$_3$ can be deposited at the BPM junction. Because we used current density of 10 mA/cm^2 for 5 min, the fluxes of Fe^{3+} and OH$^-$ into the BPM should be comparable and similar amount of Fe(OH)$_3$ should be deposited in our BPM. Electro-deposition longer than 5 min leads to deposition of more than 3 mg/cm^2 of Fe(OH)$_3$ and the thickness of the uncharged layer and the distance between the anion and cation exchange layer increases. This leads to a lower polarisation of the water molecules between the sulphonic acid groups of the cation exchange layer and the amine groups of the anion exchange layer [24] and therefore to higher R_{diss}.

It is important to note that electro-deposition of Fe(OH)$_3$ into the interface of BPM with S/P as cation exchange layer, S-PEEK 2.1 as intermediate, and A-Psf as anion exchange layer was not successful. Instead of a sharp layer of Fe(OH)$_3$ between the S-PEEK interface layer and the anion exchange layer, the Fe(OH)$_3$ precipitated in the S-PEEK intermediate layer and the S/P cation exchange layer. The S/P layer is monovalent ion selective [30] and hinders the transport of Fe^{3+} ions to the BPM junction. This effect in addition to high OH$^-$ leakage of the S-PEEK 2.1 layer resulted to immobilisation of the iron hydroxides on the surface of the cation exchange layer and in the S-PEEK 2.1 interface layer. The most effective catalytic water-splitting effects can be achieved if the iron hydroxides

are immobilised near the anion exchange layer [24]. It seems that electro-deposition is not suitable for the preparation of BPMs having S/P as cation exchange layer and S-PEEK 2.1 as interface layer and other techniques should be explored to improve water splitting of the BPM.

3.4. Pyridine based catalytic interface layers

Organic compounds containing weak ion exchange groups can be used as catalyst for the water splitting reaction [1]. Pyridine groups show the required dissociation constant (pK_a = 5.2 [41]) and have been used as catalysts for the preparation of BPMs [9,10,25].

In order to produce a BPM with low R_{op} in a simple procedure, P4VP layers were introduced as catalyst at the interface of the BPM by casting. The BPMs have an 80 µm S/P layer as cation exchange layer, 10 µm S-PEEK 2.1 as interface layer and 10 µm A-Psf layer as anion exchange layer. Fig. 11 shows the comparison of the BPMs with and without P4VP between the S-PEEK 2.1 and A-Psf layers. A thin layer of approximately 240 nm (estimated by the height of the casting knife, 12 µm, and the polymer content of the casting solution, 2 wt%) of P4VP between the S-PEEK 2.1 and the A-Psf layer leads to a strong increase in water splitting activity. The U_{diss} and therefore the activation energy for the water splitting reaction decreases more than 5 times (see Table 6).

The water splitting reaction is accelerated strongly by the presence of P4VP leading to 12 times lower R_{diss} compared to the BPM without P4VP layer. In total the P4VP decreases the R_{op} of the prepared BPM more than 2.7 kΩ cm^2.

Besides their catalytic activity the functional groups of P4VP also form complexes with the SO$_3^-$ groups of the S-PEEK 2.1 layer [42]. This result in lower penetration and firm bonding of the interface layers, leading to a sharp interface and high polarisation of the water molecules between the ionic groups of the anion and cation exchange layer. Nonetheless, the use of P4VP also leads to higher limiting current density (see Fig. 11). To use P4VP inside the BPM,
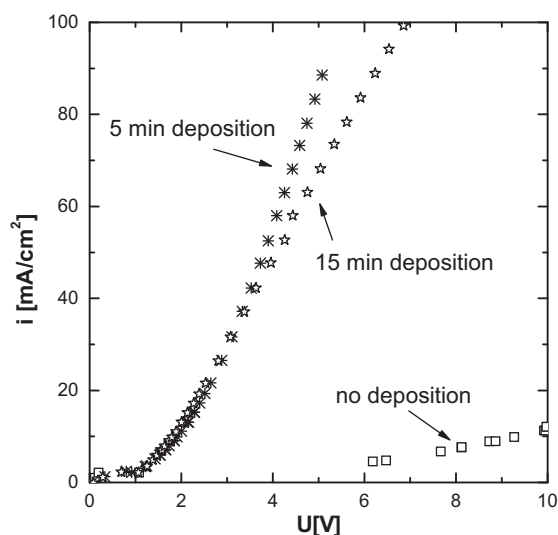

Fig. 10. Effect of the electrodeposition time on the i–v curve of prepared BPMs measured in 2 M NaCl.
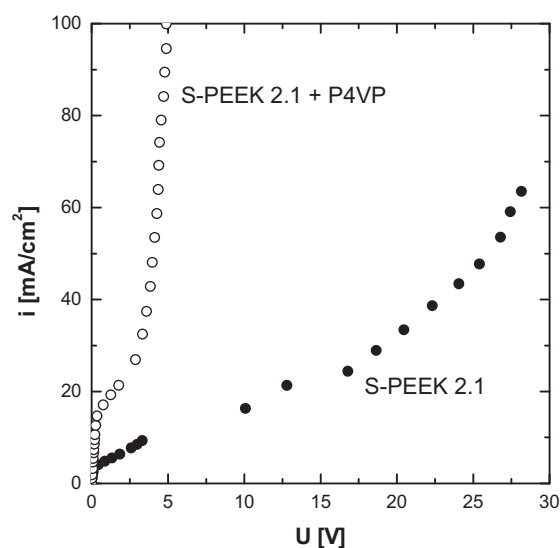

Fig. 11. Influence of the P4VP layer on the i–v curve of the prepared BPM in comparison to a BPM without catalytic layer, measured in 2 M NaCl.

Table 6
Influence of P4VP on the BPM performance.

CEL	AEL	Intermediate layer	Symbol	U_{diss} [V]	R_{diss} [$\Omega\,cm^2$]	R_{op} [$\Omega\,cm^2$]
S/P	A-Psf	S-PEEK 2.1	●	19.28	139.2	2822.7
S/P	A-Psf	S-PEEK 2.1 + P4VP	○	3.77	11.4	54.2

Table 7
Influence of the P4VP interface layer thickness on the BPM.

CEL	AEL	Intermediate layer	Symbol	U_{diss} [V]	R_{diss} [$\Omega\,cm^2$]	R_{op} [$\Omega\,cm^2$]
S/P	A-Psf	S-PEEK 2.1 + 80 nm P4VP	■	4.02	11.3	56.5
S/P	A-Psf	S-PEEK 2.1 + 240 nm P4VP	○	3.77	11.4	54.2

the casting sequence had to be changed. No firm bonding of the anion exchange layer onto the P4VP layer was possible by casting because of the reaction described above. Therefore, the 10 μm anion exchange layer was cast first onto the glass plate, followed by the P4VP, the S-PEEK and the S/P layer. Due to this, the P4VP solution penetrates into the thin anion exchange layer, reducing the effective anion exchange layer thickness. This results in higher co-ion leakage and higher limiting current density, as described already in Section 3.1. In order to investigate the influence of the amount of P4VP at the BPM interface, another BPM with a P4VP layer of 80 nm was prepared, too. Fig. 12 and Table 7 show no differences in the performance of the BPMs with these two P4VP layers. The $i–v$ curves are very similar showing that there is no difference in water splitting of BPM with P4VP layers in the range of 80–240 nm. Because the 240 nm layer is easier to prepare we will continue our investigations with this layer thickness.

In order to investigate the influence of the S-PEEK 2.1 interface, one BPM was prepared without the 10 μm S-PEEK layer, so that the P4VP layer was directly placed between the S/P cation exchange layer and the A-Psf anion exchange layer. In addition, a second BPM was prepared using a thin poly acrylic acid (PAA) layer of 120 nm instead of the S-PEEK layer. A combination of PAA and P4VP as BPM interface layer has been used by Strathmann et al. [9,10] with very good results. Fig. 13 shows a comparison of the $i–v$ curves of the prepared BPMs. Fig. 13a compares BPMs containing a 240 nm P4VP layer with and without the additional 10 μm S-PEEK 2.1 layer. The U_{diss} of both membranes is comparable, only the R_{diss} of the BPM without S-PEEK 2.1 interface is 7.8 $\Omega\,cm^2$ higher (see Table 8). This difference shows once more the importance of the hydrophilicity of

the S-PEEK 2.1 layer and of the amount of SO_3^- groups to the water splitting reaction. Because of the higher amount of SO_3^- groups (S-PEEK has an IEC of 2.1, the S/P cation exchange layer only of 1.3 mol/kg$_{dry}$), the polarisation of the water molecules is higher, leading to lower R_{diss} and R_{op} for this membrane.

The introduction of a thin PAA layer (120 nm) instead of the S-PEEK 2.1 layer leads to a BPM with higher R_{op} (Fig. 13b). The
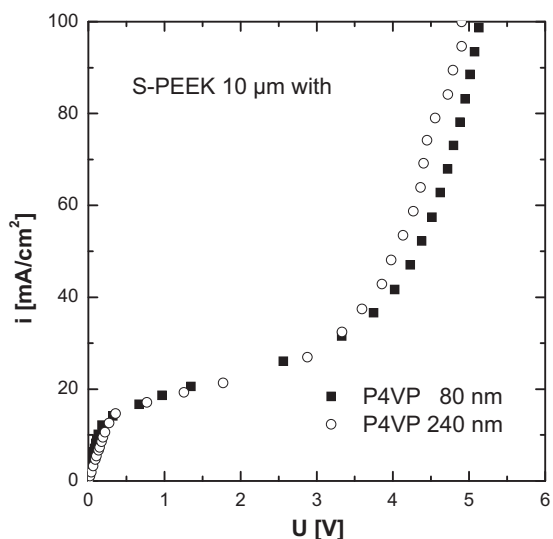

Fig. 12. Influence of the P4VP layer thickness on the $i–v$ curve of the prepared BPMs measured in 2 M NaCl.
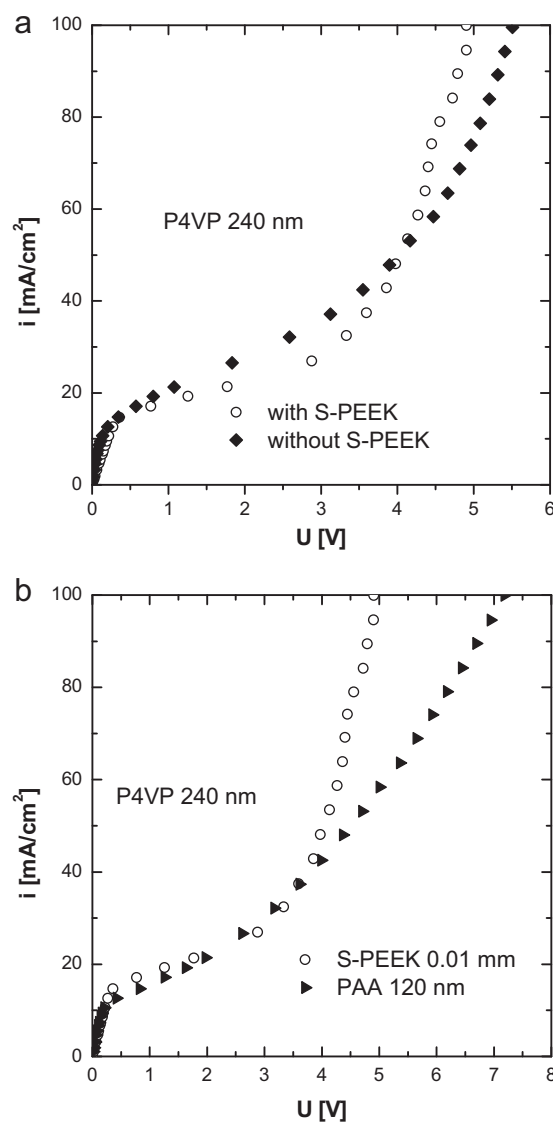

Fig. 13. (a) Influence of the S-PEEK 2.1 layer and (b) comparison of the effect of a S-PEEK 2.1 and PAA layer at the interface on the $i–v$ curve of the prepared BPMs, measured in 2 M NaCl.

Table 8
Comparison of different P4VP based catalytic interface layers on the water splitting performance of the prepared BPMs.

CEL	AEL	Intermediate layer	Symbol	U_{diss} [V]	R_{diss} [Ω cm^2]	R_{op} [Ω cm^2]
S/P	A-Psf	240 nm P4VP	♦	3.60	19.2	88.2
S/P	A-Psf	10 μm S-PEEK 2.1 + 240 nm P4VP	○	3.77	11.4	54.2
S/P	A-Psf	120 nm PAA + 240 nm P4VP	►	2.49	47.0	163.8
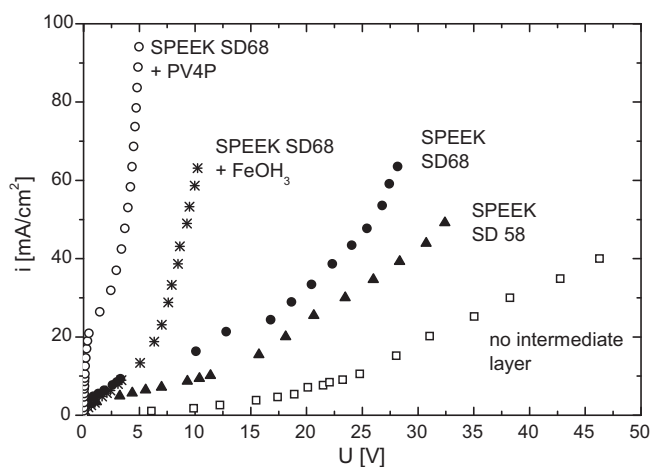
Fig. 14. Comparison of the i–v curves of all BPMs prepared in this work, measured in 2 M NaCl.

U_{diss} using PAA is lower because of the sharp interface between the ion exchange layers (see Table 8). When PAA comes into contact with P4VP an insoluble salt complex is formed directly, leading to a very sharp interface [1,2]. Because of this reaction, however, a lower amount of pyridine groups are catalytically active. In addition, the polarisation of the water molecules between the cation and anion exchange layer is lower using the PAA instead of the S-PEEK layer. The amount of SO_3^- groups of the S/P cation exchange layer (IEC = 1.3 mol/kg$_{dry}$) is lower compared to the S-PEEK 2.1 layer. This leads to a BPM with higher R_{diss} and R_{op} using a thin PAA layer instead of the 10 μm S-PEEK layer.

In conclusion, our results suggest that the BPM containing the 10 μm S-PEEK layer with the 240 nm P4VP layer shows the best water splitting performance.

3.5. Overview of prepared BPMs

Fig. 14 compares the BPMs prepared in this work. The membrane with no intermediate layer has the worst performance whereas the membranes with SPEEK interface are significantly better. Nonetheless, using catalyst is very critical to obtain a good BPM. The membrane with P4VP catalytic layer shows the best water splitting performance. The values of U_{diss}, R_{diss} and R_{op} are the lowest from all prepared tailor made BPMs. Besides, this membrane is easy to prepare without stability problems (ballooning). The thin P4VP catalytic layer combined with highly sulphonated S-PEEK layer seems to be the most promising interface for BPMs containing anion exchange layers without having functional groups that catalyse water splitting.

4. Conclusions

In this work, the effects of various parameters affecting the water splitting of a BPM were investigated. The amount of functional groups and the water content of the interface layer have big influence on the BPM resistance. The addition of highly sulphonated S-PEEK (IEC 2.1) at the interface layer decreases the U_{diss} and R_{diss} of the BPM due to the higher water content of the layer and the higher water molecule polarisation between the anion and cation exchange layer.

The use of anion exchange layer containing quaternary ammonium groups instead of bicyclic amines resulted in a better BPM. The R_{op} was strongly reduced due to the degradation of the quaternary amines into the catalytically active tertiary and secondary amines under the influence of a strong electric field in alkaline media. Using the bicyclic amine containing A-Psf as anion exchange layer no catalytic water splitting activity was observed.

Two different types of catalysts were tested, based on Fe and P4VP. Using the newly developed ionic Fe containing PFS polymer together with the S-PEEK 2.1 layer as interface resulted in a tailor made BPM with reduced U_{diss} and R_{diss} compared to the tailor made BPMs without catalytic layer. The combination of 240 nm P4VP as catalyst and 10 μm S-PEEK 2.1 as interface layers resulted in BPM with the lowest U_{diss}, R_{diss} and R_{op}. Besides this, BPM was easy to prepare without stability problems (ballooning). The pyridine based interface layer was proven to be a good tool to prepare tailor made BPMs containing anion exchange layers with high base stability without having water splitting catalytic functional groups.

Acknowledgments

Nomenclature

List of symbols

c_{char}	charge density [mol/L]
i	applied current density [A/m^2]
IEC	ion exchange capacity [mol/kg$_{dry}$]
M$^+$	salt or base cation (also as subscript)
m_{wet}	mass of the sample in wet state [kg]
m_{dry}	mass of the sample in the dry state [kg]
M_w	molecular weight [g/mol]
$M_{w,p}$	molecular weight of the polymer repeat unit [kg]
$M_{w,f}$	molecular weight of the functional group [kg]
pK_a	acidity constant
R	area resistance [Ω cm^2]
SD	sulphonation degree [%]
U	potential difference [V]
w	water uptake [kg$_{water}$/kg$_{dry}$]
X$^-$	salt or acid anion
AEL	anion exchange layer
BPM	bipolar membrane
CEL	cation exchange layer
NMP	N-methyl-2-pyrrolidinone
PAA	poly(acrylic acid)
PEEK	poly(ether ether ketone)
PES	poly(ether sulphone)
Psf	polysulphone
PFS	poly(ferrocenyl dimethylsilane)

P4VP	poly-(4-vinyl pyridine)
S-PEEK	sulphonated poly(ether ether ketone)
S/P	S-PEEK/PES blend, 60/40

Superscripts/subscripts

diss	dissociation
lim	limiting
op	operational
n	number of repeat units

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