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Blend membranes of polybenzimidazole and an anion exchange ionomer (FAA3) for alkaline water electrolysis: improved alkaline stability and conductivity

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Abstract

Anion exchange membranes (AEMs) conduct selectively hydroxide ions, while KOH doped polybenzimidazole is an ion-solvating polymer, conducting both potassium and hydroxide ions. In this work, meta-polybenzimidazole (mPBI) was blended with FAA3, a commercially available AEM, in the ratios of 2:1, 3:1, 4:1, 5:1 and 1:0. Doping was done by immersion in 0, 10, 15, 20, 25 and 30 wt% KOH solutions, giving rise to 30 membranes which were analyzed for their swelling behavior during doping, their composition (polymer, water, KOH), their mechanical properties and their through-plane conductivity in KOH solutions. Especially PF-41 showed higher tensile strength and Young's modulus than mPBI under all tested KOH concentrations. The highest conductivity of 166 mS cm^{-1} was observed for PF-51 doped in 25% KOH, 80% higher

than for mPBI. In an alkaline stability test, blend membranes showed higher tensile strength, Young's modulus and lower weight loss than mPBI after 4 weeks at 85 °C in 25wt% KOH solution. PF-31 and PF-41 were also tested in an electrolysis cell, where they showed cell resistance comparable to mPBI. Because systems without cathode feed can be quite efficient, the permeability of membranes for KOH solutions was investigated.

Keywords: polybenzimidazole; anion exchange membranes; blend polymers; alkaline electrolysis; alkaline stability

1. Introduction

Currently, about 96% of hydrogen is produced from fossil fuels, e.g. by steam reforming of methane.[1] Only a small fraction of hydrogen is produced by electrolysis of water, often for applications which demand ultra pure hydrogen, which is needed for example in the semiconductor industry and for fuel cells. This is expected to change over the next years, since hydrogen will play a key role for the transition towards renewable energies, as fuel for fuel cell vehicles, and as a means to chemically store energy produced by intermittent renewables such as wind and solar power.

Industrial alkaline electrolysis systems use a porous diaphragm, which is sandwiched between the electrodes and immersed in a concentrated alkaline electrolyte solution, typically aqueous KOH.[1] This cell setup is cheap, but has technological drawbacks, hindering the use of state-of-the-art electrolysis systems for storage of renewable energy in the form of hydrogen: a) The electrodes are far apart (e.g. the commercial separator Zirfon PERL UTP 500 has a thickness of 500 μm [2]), and usually a gap between the separator and the electrodes is provided, leading to a large area resistance,[3] which results in large Ohmic losses at high current density. b) Slow shut down and start-up: The operating parameters cannot be changed rapidly, because the anode and cathode pressure must be controlled to prevent gas crossover through the porous diaphragm. c) Crossover is a serious issue especially at low current densities for all electrolyzers because hydrogen crossover is a constant flow and practically independent of the current density; this leads to a high hydrogen concentration in the oxygen gas stream at low production rates (low current density).

An already quite well developed alternative is proton exchange membrane (PEM) electrolysis, where a thin, dense PEM is in direct contact with the electrodes. The dense, pore free membrane material allows to keep the hydrogen crossover within the operational range, even

when the distance between the two electrodes is reduced to $\sim 200\text{ }\mu\text{m}$. [4, 5] Therefore, these systems are suitable for dynamic operation conditions, show higher efficiency, and have a more compact design. Drawbacks of PEM electrolyzers are: a) The acidic environment limits the catalysts to noble metals (especially on the oxygen electrode where no alternatives to iridium have been found). Iridium is more rare than platinum, which practically excludes the very large scale roll out of PEM electrolysis. b) Cationic impurities leached from system components or present in the feed water are absorbed rapidly by cation exchange membranes like Nafion, reducing the number of mobile protons, and thereby increasing the resistance. c) Due to the expensive materials (Nafion, noble metals), PEM electrolysis has much higher installation costs than state-of-the-art alkaline electrolysis.

The technical solution for a next generation electrolyzer system is expected to be based on polymeric, dense alkaline membranes. Advantages are: a) Absence of pores, providing a tolerance towards differential pressure and enabling fast start/shut-down and compact design similar to PEM electrolysis. b) The increased pH allows the use of cheap, abundant non-noble metal catalysts [6]. c) Pure or low alkaline feed water, in contrast to 5-10 M KOH for standard alkaline systems, reducing corrosion of system components. The first such systems were reported around 2011/2012 and evaluated with either pure water [7-9] or with addition of alkaline solutions [10-12]. Notably, the ionomeric phase in gas diffusion type electrodes is challenging, and better cell polarization performance is generally observed with increasing hydroxide concentration [13, 14]. Impressive cell polarization was even achieved without anion-exchange ionomer in 1 M KOH, with Nafion as electrocatalyst binder [15, 16]. The major drawback of these systems is the low alkaline stability of anion conducting polymers, which mainly employ quaternary ammonium groups [17, 18], which consequently limit the feasibility of applying a supporting hydroxide electrolyte.

Another approach is the use of ion solvating membranes, which are between AEM (thin, dense membranes) and porous diaphragms (filled with KOH solution). The most well investigated system is KOH doped polybenzimidazole (PBI), particularly poly(2,2'-(*m*Phenylene)-5,5'-bibenzimidazole) (mPBI). Due to the amphoteric nature of imidazole, PBI gets deprotonated under alkaline conditions and virtually all physicochemical properties depend on the composition of the resulting membrane [19-21]. This electrolyte system has been extensively evaluated for hydrogen [19] and direct alcohol [22-24] fuel cells. Recently, membranes of various polybenzimidazole chemistries [25-29] and polybenzimidazole-based polymer blend membranes [30] have been investigated as separator in alkaline water electrolysis. The reported data indicate reduced ohmic losses in the higher current density range, which clearly

demonstrate the feasibility of the concept. However, an aging test at 88 °C indicated severe stability limitations of mPBI in KOH at higher KOH concentrations, as revealed by gradually decreasing molecular weight due to chain scission [31]. Furthermore, the degradation rate was increased during cell operation [28]. The assumed degradation mechanism is attack of hydroxide on the C2 position of imidazole, leading to ring opening and ultimately chain scission.[27, 32]

Improving the long-term stability of the membrane remains one of the most critical challenges for making this electrolysis concept viable. It has been clearly shown in the literature that the stability of PBI in aqueous KOH significantly improves as the KOH concentration is reduced. Therefore, a rational strategy to mitigate degradation is to modify the membrane towards enhanced ion conductivity at reduced KOH concentration. One strategy is to break-up the dense packing of PBI polymer chains, so that PBI can absorb water and KOH more easily, e.g. by blending with another polymer. Ionic crosslinking between cationic groups of one polymer and the imidazolid anions of deprotonated PBI could enhance stability. In this work, this is addressed by blending mPBI with a commercially available anion exchange ionomer (FAA3i). We will show how this concept influences the membrane conductivity and cell resistance of an alkaline electrolyzer system, and that it improves the mechanical strength and alkaline stability.

2. Experimental

2.1 Materials

All materials, reagents and solvents were used without further purification. Dapozol® PBI (mPBI, specified as Mw: 51.000) was purchased from Danish Power Systems and linear (non-crosslinked) Fumion FAA3 ionomer shredded film (FAA3i, IEC = 2.4-2.9 mmol Cl⁻ g⁻¹) was purchased from Fumatech. Anhydrous *N,N*-dimethylacetamide (DMAc, 99.8%) was purchased from Sigma. Trimethylamine (TMA) 30 wt.% solution in water was obtained from Junsei. Aqueous solutions of potassium hydroxide (KOH) were prepared by dissolving KOH flakes (Daejung Chemicals and Metals Co., Ltd, 93 wt.%) in deionized water.

2.2 Membrane Preparation

A 10 wt% solution of mPBI was prepared by dissolving the polymer fibers in DMAc under argon atmosphere during vigorous stirring at 70 °C overnight. A 10 wt% FAA3i solution was

made by dissolving the commercially available polymer flakes at room temperature under ambient atmosphere in a sealed flask for at least 4 hours. To prevent gelation when both solutions are mixed, 0.5 ml trimethylamine (TMA) per 1 g of polymer were added to the FAA3i solution, and the solutions were stirred further overnight. Casting solutions with concentrations of 10 wt% were made by mixing PBI and FAA3i solutions together under slow stirring. The composition of the membranes was controlled by changing the ratios of the two solutions (see **Table 1**). The membranes were cast on a glass plate using an automatic casting machine and a Doctor Blade with a either 300 or 400 μm gap. After casting, the membranes were dried in a vacuum oven at 60 °C for at least 15 h. After drying, the membranes were peeled off from the glass plate in DI water, and further treated in DI water for 24 h in order to remove residual solvents. Membranes were air-dried and obtained as a film with a thickness of 17 – 30 μm , depending on gap width during casting.

Table 1. Prepared membranes and their composition.

Membrane name	Blend ratio PBI:FAA3i (weight based)	mPBI [%]	FAA3i [%]
FAA3i	0:1	0	100
PF-21	2:1	67	33
PF-31	3:1	75	25
PF-41	4:1	80	20
PF-51	5:1	83	17
PBI	1:0	100	0

All membranes were equilibrated in an aqueous potassium hydroxide solution with a concentration of 10, 15, 20, 25 and 30 wt.% for 15 hours at 85 °C in an oven using polypropylene vials.

2.3.1 Swelling, composition and morphology

For determining the swelling S during doping the membranes were dried overnight in a vacuum oven at 60 °C before doping. The area and thickness were noted before (dry dimension d_{dry}) and after doping (wet dimension d_{wet}) . For each data point at least three samples were used.

$$S = \frac{d_{wet} - d_{dry}}{d_{dry}} \quad (\text{Eq.1})$$

Membrane compositions were determined gravimetrically, with an estimation of weight fractions of a polymer, water and potassium hydroxide using the method developed by Aili et al. [26]. For calculations the equations listed below were used.

$$WF_{polymer} = \frac{m_{dedoped}}{m_{wet}} \quad (\text{Eq.2})$$

$$WF_{water} = \frac{m_{wet} - m_{dry}}{m_{wet}} \quad (\text{Eq.3})$$

$$WF_{KOH} = \frac{m_{dry} - m_{dedoped}}{m_{wet}} \quad (\text{Eq.4})$$

Here $WF_{polymer}$, WF_{water} , WF_{KOH} is weight fraction of polymer, water and potassium hydroxide respectively. m_{wet} is the weight of a freshly doped sample after removing from alkali solution and careful blotting with a tissue. m_{dry} is the weight of membrane dried in a vacuum oven for 4 hours at 110 °C. $m_{dedoped}$ is the weight of a sample after storing in DI water for 24 hours with several refreshments of water until a neutral pH was obtained, followed by drying at 110 °C for 4 hours in a vacuum oven. For each data point at least three samples were used.

To check for phase separation between PBI and FAA3, samples were prepared by microtome cutting and analyzed by cryogenic transmission electron microscopy (Cryo-TEM) on a FEI Tecnai F20 G2.

The degree of crystallinity was calculated from WAXS curves, obtained with a Rigaku MiniFlex II with CuK α source in the 5-70° range at a 7° 2 θ /min speed. The broad signal centered around 2 θ $\approx$ 27° was assigned as the amorphous regions, and the sharp peak around 2 θ $\approx$ 21-22° was assigned to the crystalline phase.

Gel permeation chromatography (GPC) was performed on a Breeze HPLC with NMP + 0.05M LiBr as eluent. The system was equipped with 2 Styragel HR columns and a Waters 2414 refractive index detector and calibrated against PMMA standards. LabSolutions GPC software was used for analysis of the data.

2.3.2 Mechanical properties

The mechanical properties of membranes were determined with a Cometech Universal Material Testing Machine (model QC-508E). For each material at least 5 samples were tested. All membrane samples were cut manually using a sharp blade. The size of each specimen was 5 mm in width, the gap length between the grips was 20-28 mm. The thickness of membranes depended on the state of doping, and was in the range of 23 μ m to 60 μ m. The temperature was 20-23 °C, and the relative humidity was 10-14 %. The maximum load of the machine was 50N or 5 kg and the crosshead speed 10 mm min⁻¹.

2.3.3 Alkaline stability

For the alkali stability evaluation of the blend membranes, they were cut into 4 cm $\times$ 4 cm pieces. The dry weight of samples was recorded after drying in a vacuum oven overnight at 60 °C. Membranes were submerged in a 25 wt.% potassium hydroxide solution using polypropylene sealed vials and stored in an oven at 85 °C. Sampling was done after 15 hours, 2 weeks and 1 month. For measuring the weight loss tested samples were stored in deionized water for 48 hours with a constant refreshing of water and dried in a vacuum oven at 60 °C overnight.

Infrared spectra were obtained with a Lambda Scientific Pty Ltd FTIR 7600 in attenuated total reflectance (ATR) mode and analyzed using the spectrometer software (FTIR 3.4.0).

2.3.5 Ion conductivity

Through-plane ion conductivity of doped membranes was measured by impedance spectroscopy (Biologic potentiostat SP150). The membranes were fixed between two gaskets, leaving an active area of 1.767 cm². The distance between the electrodes (gold coated copper discs) was 1.59 mm. The space was filled with the respective doping solution. The resistance of the membrane (R_m) was obtained by subtracting the resistance of the solution filled cell without membrane from the resistance obtained with membrane. Then the conductivity σ_m was calculated according to equation 5. The standard deviation of the conductivity values were relatively high, in the range of 20%. The main reasons are different doping and/or storage times of samples, high variation of the thickness when samples have wrinkles, and possibility of gas bubbles in the cell (in the case of the lowest measured values).

$$\sigma_m = \frac{\text{membrane thickness}}{R_m \cdot \text{electrode area}} \quad (\text{Eq. 5})$$

2.3.6 Electrolyzer test

Electrolyzer tests were done in a lab scale alkaline electrolyzer setup with an active area of 11.6 cm². The lab cell is visualized in Figure S12. Membranes for cell tests were doped at room temperature for at least 48 hours prior to cell test. Nickel foam (American Elements) pressed to about 250-300 μm was employed as anode and cathode. 300 μm PTFE gaskets were used at each electrode, and a 50 or 100 μm PTFE sub-gasket was used around the membrane, resulting in a total gasket thickness slightly larger than the membrane-electrode-assembly to prevent short circuiting through the thin membranes. The flowfield plates were made from Ni-coated stainless steel and employed an elongated pin-type flowfield. Cells were assembled by careful horizontal alignment and mounted in the setup. The setup is schematically illustrated in Figure S13. Heating was done directly in the flowfield plates. KOH solution was circulated by a set of gear pumps (polysulfone/hastelloy) at 60 ml min⁻¹ such that the electrolyte was briefly mixed between the degassing vessels and the pumps. The doping solutions for the different membranes were used as electrolyte in their respective electrolyzer tests (250-300 ml). The temperature was kept at 60°C.

Constant current operation and polarization measurements were performed by an Elektro Automatic EA-PS 5040-40 A power supply unit controlled by a LabView interface, and

electrochemical impedance spectroscopy (EIS) were recorded with a VersaStat 4 by quickly switching the wiring to the cell. The cells were activated at 100 mA cm^{-2} for 30 min. Following this impedance and polarization curves were recorded pair-wise at 3 times; after activation, after 2 days, and after 4 days. Polarization curves were recorded by stepwise galvanostatic measurements for 2 minutes at each setpoint. Between EIS and polarization measurements, the cells were operated at a constant current density of 200 mA cm^{-2} . EIS were recorded at 20, 40 and 100 mA cm^{-2} , with an amplitude of 10% of the current density and at 15 points per frequency decade. Water was added daily to maintain the electrolyte concentration.

2.3.7 Permeation test

To estimate the flux of KOH solution through doped membranes a 20 ml vial (25 mm diameter) with a small hole on the bottom to adjust the pressure was filled with 10 ml KOH solution. (see **Figure S11**) A 8.5 mm diameter hole was drilled through the screw cap, a hole was punched into the sealing gasket, and the membrane samples were sandwiched between the sealing and the cap, and sealed with a double sided adhesive tape. For measuring KOH permeation, the vials were stored upside down in an environmental chamber at 50°C and 50 % relative humidity. Permeation of KOH solution through the membrane was measured gravimetrically at certain time intervals.

3. Results and Discussion

3.1 Membrane fabrication

Both polymers (mPBI and FAA3i) readily dissolved in DMAc to give visually homogeneous solutions. However, gelation rapidly occurred upon mixing of the polymer solutions. Neither addition of solvent nor heating led to a significant reduction of the viscosity. This was likely due to crosslinking between mPBI and residual bromomethyl groups in the commercial FAA3i. Therefore, TMA was added to the FAA3i solutions in order to quaternize the residual bromomethyl groups before mixing with mPBI. Indeed, the addition of TMA allowed for visually homogenous casting solutions.

Figure 1. Cryo-TEM images of a PF-31 membrane (dark shadow and wavy lines are artefacts from microtome cutting during sample preparation).

After casting, all blend membranes appeared optically homogeneous. In order to reveal more information about the eventual phase-separation on smaller length-scales, the PF-31 membrane was investigated further by TEM (**Figure 1**). The micrographs showed some artifacts stemming from the microtome cutting, but showed no apparent signs of phase separation on the nanometer scale, indicating good miscibility between the two polymers in this ratio.

For doping with KOH, the membranes were immersed in KOH solutions at 85 °C for 15 hours. As seen in **Figure 2**, the volume swelling increased with the KOH concentration of the doping bath, up to a concentration of about 20 wt% KOH, after which the volume swelling started to decrease again. A similar behavior is observed for the weight gain during doping (**Figure 3**). Since the fraction of KOH in the membrane increases continuously with the KOH concentration in the doping solution (**Figure 4e**), the observed decrease in weight and volume is related to the water content, which decreases for most materials at high KOH concentrations (**Figure 4c**). A similar behavior was reported for pure mPBI membranes.[20] Interestingly, this is not related to osmotic pressure, as is typically observed for ion exchange membranes. As shown in **Figure S1**, the apparent KOH concentration of the KOH solution inside of the membranes is usually higher or same as the concentration in the doping bath, and increases continuously with increasing concentration in the doping bath.

The large weight gain observed for FAA3i (**Figure 3**) is mainly due to water (**Figures 4b** and **4c**), and decreases with increasing concentration of KOH in the doping solution, because of the increasing osmotic pressure between membrane and solution. The value at 0% KOH (DI water) was obtained for FAA3i in the bromide form, because the hydroxide form rapidly dissolved at 85 °C. Analysis of the KOH uptake shows that it varies between 15 and 23% in the range of 10-30% KOH in the doping solution. In comparison, for PF-51 the KOH uptake increases continuously from 13 to 76%.

When the polymer weight fraction of the doped membranes is plotted against the mPBI contents in the blends, a local minimum around 83% (PF-51) and a local maximum around PF-41 can be observed (**Figure 4d**). A comparison with **Figure 4f** shows that the polymer fraction in the doped membranes roughly correlates with the degree of crystallinity of undoped membranes (estimated by deconvolution of XRD curves, **Figure S2**), which indicates that highly crystalline areas may resist doping (which is expected [33]).

Figure 2: Volume (a), thickness (b) and area swelling (c) of membranes during doping with KOH. Data is also listed in the supporting information (**Table S1**).

Figure 3: Weight gain during doping at 85 °C for 15 hours; all membranes were used in the bromide form, which subsequently was exchanged into the hydroxide form when KOH was present.

Figure 4: Composition of polymers after doping (a-e) and degree of crystallinity before doping (f). Data is also listed in the supporting information (**Table S2**).

3.2 Mechanical Properties

The mechanical robustness of the KOH doped membranes was assessed by measuring stress-strain curves. In general, mPBI was the most stretchable membrane, showing elongation at

break values of up to 154% (**Figure S3**). The highest tensile strength and Young's modulus were obtained for the PF-41 membrane (**Figure 5** and **S3**), which probably can be assigned to its high degree of crystallinity. The second strongest material was PF-31. For a given polymer material, doping with KOH decreases the tensile strength and young modulus. In general, all 25 KOH doped materials showed a tensile strength between 18 and 93 MPa, and values for PF-31 and 41 never went below 33 MPa. For comparison, the tensile strength of Nafion 212 membranes is specified as 32 MPa, and that of Fumasep FAA3-50 membranes from Fumatech is specified as 25-40 MPa. The Young modulus of these commercial membranes is in the range of 0.26 GPa for N212 and specified as 1.0-1.8 GPa for FAA3-50. In summary, it can be stated that blending of PBI with FAA3i anion exchange polymer increases the mechanical properties of the KOH doped membranes. Recorded strain-stress curves are available in **Figure S4**.

Figure 5: Tensile strength (a) and young modulus (b) for a series of polymers doped in different KOH solutions, data for other materials and elongation at break is shown in **Figure S3**.

3.3. Conductivity

In previous work, it was shown that the conductivity of KOH doped mPBI peaks at KOH concentrations of about 20-25%. [19, 20, 27, 28]. After doping at 25wt% it reached about 0.1 S cm^{-1} [25], which was confirmed in the present work (**Figure 6a**). For mesPBI doped in 20wt% KOH, a much lower conductivity of $20\text{-}30 \text{ mS cm}^{-1}$ was obtained at 20°C . [26] While PF-21 membranes showed surprisingly low conductivity values over the whole tested range, all other membranes exceeded the conductivity of mPBI at a doping bath concentration of 20wt% KOH. Especially the PF-41 membrane reached a conductivity above 120 mS cm^{-1} . While some data points in **Figure 6** were measured only once (PF-21, and most values at 10% KOH), the values at 20% KOH were measured repeatedly for mPBI (3 samples), PF-51 (3 samples), PF-41 (7 samples) and PF-31 (10 samples). The highest conductivity of 166 mS cm^{-1} was observed for PF-51 membranes doped in 25% KOH. This makes the PF-31, PF-41 and PF-51 membranes very attractive for testing in the electrolysis cell. With increasing KOH concentration, the decreasing water content of the absorbed KOH (**Figure S1**) reduces the conductivity of the blend membranes.

When the conductivity is plotted against the PBI concentration for various doping solutions (**Figure 6b**), two things are observed. With the exception of 25wt% KOH, PF-41 shows higher conductivity at all doping concentrations than PF-31 and PF-51. This is unexpected, because PF-41 showed higher crystallinity and higher polymer contents than PF-31 (**Figure 3**). The second observation is again that PF-31, PF-41 and PF-51 show higher conductivity than mPBI in 20% KOH solution, and that PF-51 also shows higher conductivity in 25% KOH solution, but that mPBI is still better at all other conditions. One reason for PF-51's high conductivity is the exceptionally high ratio of KOH/polymer (**Figure 6d**). However, at the highest ratio (in 30% KOH), the conductivity decreases again. This could have to do with the conductivity of free KOH solution, which is highest around 25-35 wt%, and then decreases again. [34] In 30% KOH solution, the absorbed electrolyte in PF-51 has a calculated concentration of 55%, which is at the solubility limit. In summary, the ideal membrane should absorb large amounts of electrolyte of a concentration of about 20-30%.

Figure 6: Conductivity values of the obtained membranes at temperatures between 20 and 25 °C; (a) plotted against the KOH concentration in the doping bath; (b) plotted against the PBI contents; (c) plotted against the weight gain during doping; (d) plotted against the weight ratio of KOH and polymer. Data is also listed in the supporting information (**Table S3-6**).

3.4 Alkaline Stability

Alkaline stability was assessed by doping membranes with KOH, and then immersing them in 25% KOH solution at 85 °C. While FAA3i already disintegrated during the doping step, all other membranes could be handled for testing. As shown by Aili et al. [27], mPBI does not show large changes in the IR and NMR spectra, but some small changes indicate that hydrolysis of the imidazole groups occurs, resulting in chain scission. The tensile strength was reported to decrease from 94 MPa to 8.9 MPa after 26 days of testing in 6 mol L⁻¹ (ca. 27 wt%) KOH at 85 °C.[27] This value is very similar to our data (**Figure 7**). The tensile strength, Young's modulus and proportional limit stress degrade rapidly within the first days, and then stabilize, with

practically no changes between the 2nd and 4th week. The deterioration rate of the tensile strength of the blend membranes was lower than that of pure mPBI. After 4 weeks in hot, strong alkaline solution, PF-41 shows similar tensile strength as mPBI before aging. Also the weight loss of blend membranes is lower than that of mPBI. This is counterintuitive, since the degradation rate of the pure blend component FAA3i was very high. One possible explanation is that the quaternary ammonium groups of FAA3i ionically interact with PBI's imidazolidine groups, and that these interactions are maintained also by the oligomers which stem from FAA3i-degradation.

Figure 7: Alkaline stability at 85 °C in 25wt% KOH solution; (a) tensile strength, (b) Young's modulus, (c) proportional limit stress of doped, aged membranes; (d) weight loss (pristine vs. aged, dedoped membrane).

The degradation is expected to also affect the conductivity of the membranes. For this purpose, the through-plane conductivity of membranes immersed in 25 wt% KOH solution at room temperature was tested. All membranes showed decreased conductivity after aging (**Figure 8**). While the conductivity of mPBI decreased rather linearly over time, the blend membranes'

conductivity decreased strongly within the first 2 weeks, and then slowly until the 4th week of the test. A comparison of the IR spectra did not indicate degradation, e.g. no new signals which would suggest hydrolysis of the imidazole rings (**Figure S5**) were observed. Also the composition of the PF-41 membrane seems to be unchanged, apparently no FAA3i leached out.

Figure 8: Conductivity of membranes aged in 25 wt% KOH at 85 °C.

Taken all the above into account, it can be assumed that the properties change mainly because of changes in the composition. This is supported by the visual observation that membranes were transparent during the aging test, but turned opaque when taken out from the cooled down aging solution. This could indicate loss of KOH, resulting in the formation of pores, which scatter the light when the membranes lose water. SEM analysis of an aged, dedoped membrane showed the formation of pores (**Figure S6**), and analysis of the membrane composition for membranes aged for 2.5 weeks showed indeed that mPBI, PF-51, PF-41, PF-31 and PF-21 lost 37, 78, 85, 80 and 92% of the initially absorbed KOH, respectively. For mPBI, this relates to a decrease in KOH uptake from the initial 41% (after 16 hours) to 25% after 2.5 weeks. This is in good agreement with the literature, which reports KOH uptake values of 47% (2.6 KOH/repeat unit) after 16 hours at 90 °C[20] and 22% (1.2 KOH/repeat unit) after several days at 85 °C[25]. In order to test if the KOH loss is reversible, membranes were aged for 6 weeks, washed free of KOH by immersion in water for 6 days, and re-doped. In comparison to the values measured after 4 weeks aging, the conductivity only increased marginally (**Figure 8**).

Another observation was that a PF-41 sample aged for 6 weeks was still relatively flexible, but became too brittle to handle when the remaining KOH was leached out by immersion in DI water.

In summary, membranes apparently rapidly absorb KOH within the first hours, and then slowly lose again KOH over the following days. Since no significant degradation was observed, the reason could be changes in the polymer morphology, like crystallization, or in the case of blends membranes, formation of polymeric salts, by the interaction of ammonium and imidazolid ions.

3.5 Application in an electrolysis cell

Membranes of mPBI, PF-41 and PF-31 were evaluated in an alkaline electrolyzer cell at KOH concentrations of 10, 15 and 20 wt%. The initial polarization behavior of the PF-41 membrane at different KOH concentrations is shown in **Figure 9a**, and the time evolution in polarization curves for the PF-41 membrane operated at 20 wt% KOH are shown in **Figure 9b**. Similar plots for PF-31 and pure mPBI membranes are available in **Figure S7a** and **S7c**. It is evident that the polarization performances increase with increasing KOH concentration for all membranes. This is expected considering the membrane conductivity presented in **Figure 6** and the general conductivity behavior of the bulk KOH electrolyte. Surprisingly, compared to the almost negligible measured conductivity for 10 wt% KOH doped membranes, the cells with 10 wt% KOH are able to draw a significant current. Differences in ex-situ measurements (purely AC) and in-situ cell behavior (DC bias), or differences with regards to doping may explain this observed difference. Significant discrepancy between conductivity and cell measurements have been observed also for mes-PBI, although the trend was opposite with good ex-situ conductivity but negligible electrolysis performance at 5 wt% KOH [26]. The time evolution displayed in **Figure 9b** for PF-41 matches well with the measured behavior for changes to the through-plane conductivity over time, as there seems to be a change in slope, particularly between the first and the second polarization curve. The effect appears more pronounced for mPBI and PF-31, **Figure S7b** and **S7d**. Likely as a result of an actual effect, but also because the change for PF-41 is somewhat masked behind a slight activation of the electrodes between the first and second polarization curves. Note that for this type of nickel foam-nickel foam cells, quite a substantial contribution to the cell resistance arises from the liquid electrolyte and not only from the membrane employed. Consequently, while the changes in slope seem almost negligible compared to the observed development in conductivity, it is not necessarily a large discrepancy as the supporting liquid electrolytes contribute substantially to the overall cell resistance.

Figure 9: Polarization behavior of cells based on the PF-41 membrane at 60°C. (a) Variations in polarization with different supporting electrolyte concentration. (b) Development in polarization over 4 days of operation at 200 mA cm⁻² for the PF-41 membrane operated at 20 wt% KOH.

The area specific series resistance of the cells were estimated from EIS data by fitting a L-R-RQ-RQ equivalent circuit model to the EIS data (L is an inductance, R is a resistance, and RQ represents a parallel resistance and constant phase element). Values for the area specific series resistance obtained from EIS recorded at 20 mA cm⁻² are shown in **Figure 10a**. Unlike what is suggested by looking at the full polarization curves and by the conductivity data presented in **Figure 8** these results are somewhat inconclusive, and rather point the opposite direction. A general trend towards decreasing cell resistance in time is observed across most data sets. **Figure 10b** shows the time evolution of cells operated with 20 wt% KOH for each membrane evaluated in the electrolyzer. In general the membranes appeared intact without visible defects after 4 days of operation, however the cell with PF-31 operated at 15 wt% failed during the experiment. Some variation in the potential can be expected throughout the experiment, as the nickel electrodes can passivate or activate depending on the amount of impurities present. Secondly, although water was added manually on a daily basis based on the cumulative Faradaic charge passed through the cell, a net difference may still arise over several days.

Figure 10: (a) Fitted area specific resistances obtained from EIS at 20 mA cm⁻², missing data for PF-31 at 15 wt% KOH was due to cell failure. (b) Life time data recorded from the cells operated at 20 wt% KOH at 60 °C. Cells were operated at 200 mA cm⁻² between polarization curve measurements.

3.6 Water and KOH flux through membranes

For industrial hydrogen production, the gas streams need to be dried. To cut down the costs of drying, it could be attractive not to feed water to the cathode, but to rely on the water which permeates through the membrane. Furthermore, some of us found a 5.8 times improved cell

performance when the cathode feed of an AEM based system was changed from DI water to none.[35] As shown in **Figure S8**, the initial performance of such a system was very promising ($> 470 \text{ mA cm}^{-2}$ at 1.8V), but dropped rapidly to ca. 230 mA cm^{-2} . At that current density, the performance seemed to stabilize, but the cell had to be switched off because alkaline solution leaked through the cathode gas outlet. Since this was not observed at an anode feed concentration of 0.5 M KOH when operating cells with Tokuyama A201[35] or Fumatech's FAA3-PK-75 membrane, it seems to be important to measure the membranes' liquid/liquid electrolyte permeation. As expected, weight gain during doping (**Figure 3**) and permeation increase with the KOH concentration in the doping bath (**Figure 11**). With the single exemption of the data for PF-31 at 10% KOH (a repeat measurement gave a similar but even slightly higher value), the permeability decreases when the FAA3i content in the membranes increases. As shown in **Figure S1a**, the concentration of the KOH solution absorbed by the membranes during doping is usually above that of the doping solution. However, the concentration of the permeated KOH solution had a similar concentration as the doping solution, at least for the analyzed systems (PF-31 and mPBI with 20 % KOH, mPBI with 10%).

Figure 11: Permeation of KOH solution through membranes.

4. Conclusions

An investigation of the membranes' composition and properties showed that homogenous blends can be prepared. Upon doping in KOH solution, blend membranes swell more than mPBI, but increase less in weight, which may be related to different free volumes, e.g. a more tightly

packed structure in the blend membranes. This could also be the reason why blend membranes (especially PF-31 and PF-41) show higher tensile strength and Young's modulus.

Ex-situ measurements did not reveal an increased conductivity at low KOH concentrations, as was hoped for. However, at the high KOH concentration of 25 wt%, PF-51 showed 80% higher conductivity than mPBI, reaching 166 mS cm^{-1} .

An alkaline stability test at 85°C in 25 wt% KOH solution indicated that blend membranes are much more stable than mPBI, which had lower tensile strength and Young's modulus after 4 weeks and larger weight loss than PF-21, PF-31 and PF-41. However, the conductivity decreased for all membranes, and analysis of the composition suggested that the main reason for changes in the membrane properties may not be chemical degradation, but changes in the composition (polymer, water, KOH).

While the electrolysis test in a standard setup (20 wt% KOH feed solutions, 60°C) was successful, a test with a cell with an open cathode (no feed solution, the water needs to permeate from the anode through the membrane) failed rapidly, because permeated KOH solution flooded the cathode compartment. It was concluded that the permeation characteristics of membranes need to be evaluated. The permeation of 10 wt% KOH solution through ion-solvating membranes was in a similar range as the permeation of 0.5 M KOH solution through a FAA3 membrane. However, when the KOH concentration was varied between 10 wt% and 20 wt%, the permeation of KOH solution through the ion-solvating membranes increased by 2 orders of magnitude. Therefore, a strategy for future work on ion-solvating membranes could be to operate the system at low KOH concentrations and without cathode feed, to improve electrolyzer performance[35] and alkaline stability.

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