



Using neutron methods SANS and PGAA to study evolution of structure and composition of alkali-doped polybenzimidazole membranes

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ABSTRACT

Potassium hydroxide (KOH) doped polybenzimidazole (PBI) membranes are investigated as compelling candidates for water electrolysis applications, drastically reducing the ohmic losses in contrast to thick ZrO₂ based diaphragms. Using small angle neutron scattering (SANS) we have found that the structure of the (KOH doped) PBI changes with doping time on a minute time scale, and that the development of the structure is highly dependent on the KOH concentration. This data is correlated with macroscopic measurements of membrane swelling resulting from the doping process which also occurs on a minute time scale. Then, using prompt gamma activation analysis (PGAA) to follow the changes in time of the chemical composition, we have found that the K concentration of these samples only increases slightly with doping times after a very rapid initial uptake, reaching a saturation value that is relatively independent of KOH concentration for long doping times of up to 24 h. However measurements of similarly doped samples show increases in ion-conductivity of nearly 3 fold, and resistivity reductions of over 2 fold on the same time scales. These measurements prove that PGAA is a sensitive method to follow changes in the chemical compositions during doping, while SANS can give information on the sub-micro structural changes of polymer electrolyte membranes. Since these methods can be correlated with *ex-situ* measurements of composition, resistance, ion-conductivity and macro-structure, the combined use of PGAA and SANS provides a promising means for *in-operando* study in order to elucidate changes in membrane performance due to electrochemical cycling, as well as to help characterize and optimize doping parameters through *in-situ* doping measurements, by enabling real-time study of such membrane systems.

1. Introduction

One of the substantial challenges for our society is the conversion of electrical energy to chemical energy, especially for example where the excess energy coming from wind turbines and photovoltaics needs to be converted into an energy vector such as H₂ [1–3]. The re-electrification of H₂ will also play an important role for transportation purposes such as fuel cells. This task can be achieved by polymer electrolyte membrane (PEM) based electrochemical energy conversion devices, where the ion conducting membrane is a key component of the

electrochemical cell [4]. Polybenzimidazole (PBI) membranes, that can be doped with phosphoric acid have been routinely used in high temperature polymer electrolyte membrane fuel cells (HT-PEMFCs) [5,6]. For electrolysis on the other hand, alkaline electrochemical cells are promising candidates. Here KOH is the electrolyte inside the PBI membrane which transports OH⁻ species from the cathode to the anode [7]. There are only a few recent articles in the literature dealing with PBI doped with KOH [4,8–12], therefore the understanding of the doping mechanism of PBI with KOH and how this is affecting the ion conductivity as well as the lifetime and aging of these membranes is of

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imminent importance.

Indeed, the doping of PBI membranes with KOH is not yet fully understood. For other electrochemical membranes, such as Nafion, it is known that nano-scale channels play an important role in the electrochemical function, i.e. the efficient transfer of ions from the anode to cathode in the electrochemical cell [13,14]. Therefore information on the nano-scale structures of PBI membranes, and how they evolve during the doping process and change during charge-discharge cycles, is important for understanding these systems [15].

For hydrogen-atom containing materials, neutron imaging and scattering provide powerful analytical tools, due to the high sensitivity of neutrons to scattering from hydrogen [16,17]. For example small angle neutron scattering (SANS) can be used for the non-destructive study of polymeric membranes, providing structural information in size scales from over 1 μm to around 1 nm. [18] This size range is ideally suited for the size of the channels known to be important for ion conduction in electrochemical membrane systems [14]. Furthermore, in addition to interpreting the nano-structural arrangement by SANS, one would like to be able to non-destructively monitor changes in the nano-structure while doping with KOH and also the evolution of chemical composition resulting from the doping process and/or the electrochemical cycling of the membranes. This complementary information on the chemical composition can be provided by Prompt Gamma Activation Analysis (PGAA) [19].

In this work, we will show data from PGAA (chemical composition) and SANS (structure) for two series of samples. In the first series 5 different types of polybenzimidazole membranes (crosslinked and non-crosslinked) are explored as a survey. For the second series we analyse non-crosslinked meta-polybenzimidazole in more detail, with the focus on the doping concentration and time dependence. In addition, the obtained data will be compared with a conventional composition analysis based on titration, which will be correlated to the macroscopic structure via measurements of swelling, and to resistance and ion-conductivity measurements.

The demonstrations in this work will show that SANS and PGAA are powerful tools for studying the properties of PBI membranes.

2. Experimental details

Neutron experiments were performed at the MLZ in Garching: PGAA measurements on the PGAA instrument operated by the Technische Universität München [19] and SANS measurements on the KWS2 instrument operated by the Jülich Centre for Neutron Science [20]. Electrochemical measurements, swelling measurements and characterization of the composition by titration were conducted at the Korea Institute of Science and Technology (KIST).

2.1. Materials

PBI and crosslinked PBI membranes were prepared from meta-PBI provided by Danish Power Systems (Dapozol powder, MW 52,000 g/mol), following the procedure of Li et al. [23]. After dissolving 5.387 g in 32.6 ml DMAc, 0.2693 g and 0.5387 g dibromoxylene were added and dissolved to prepare PBI crosslinked with 5 wt% and 10 wt% crosslinker, respectively. The solutions were cast on a glass plate using a doctor blade with a 500 μm gap width, and the solvent was evaporated at 60 °C in vacuum, after which the temperature was raised to 80 °C for 24 h to complete the crosslinking. After cooling to room temperature, the membranes were delaminated from the glass plate by wetting them with water. The non-crosslinked PBI membrane was prepared in the same way, but without addition of dibromoxylene as a crosslinking agent. Additionally, two commercially available membranes were used, Dapozol [21] from Danish power systems and FAAM-55 from Fumatech [22].

All membrane samples for neutron measurements were doped with potassium hydroxide in a similar manner. The concentrations of the

KOH-D₂O solutions are given in weight percent (wt%) after correcting for the mass of water absorbed from humidity in the KOH salt. Here, deuterated water was used for the doping solution in order to lower the incoherent background contribution caused by hydrogen in neutron measurements and to increase the contrast. The prepared KOH solutions ranging from 5 wt% to 50 wt% were divided into vials and pre-heated to 80 °C, since this is also the relevant temperature during operation of an electrochemical cell [8].

The PBI samples used for the electrochemical characterization, composition and swelling determination were prepared as above, but at room temperature and using standard deionized (DI) water instead of D₂O. Standard solutions of hydrochloric acid (HCl) (Daejung Chemicals and Metals Co., Ltd, 0.05 M) and phenolphthalein (p/p) mixture (Sigma Aldrich, 0.5 wt% in ethanol and water 1:1) were used for acid-base titration.

2.2. Neutron measurements of structure and composition

For a survey of membranes we used all five membranes described above, non-crosslinked PBI, 5% crosslinked PBI, 10% crosslinked PBI, and the commercial membranes Dapozol and FAAM-55.

The membranes were cut with a punching tool into 14 mm diameter discs and immersed in the preheated KOH solutions for the desired amount of time, ranging from one minute to 24 h for the 50 wt% KOH solution while maintaining the temperature constant at 80 °C in an oven. For the 5 wt% and 25 wt% KOH the doping was only performed for 24 h and also at 80 °C. The vials were closed for the doping times over 10 min to prevent evaporation. After doping for the desired amount of time, the membrane discs were removed from the solution and the excess KOH was removed (by blotting) at room temperature. The weight of all samples was measured before and after the doping as a first indication of K uptake. The samples were held at room temperature in closed vials until the SANS measurements which were performed within 24 h of sample preparation.

For the SANS measurements, a Peltier-heated sample holder was used to hold the membrane samples at a temperature of 80 °C during the entire course of the experiment, which took around 24 h. Stacks of 3 membrane disks were used to increase the scattered signal intensity. The accessed momentum transfer, i.e. Q -range from 7.5×10^{-3} to 0.43 \AA^{-1} , was obtained with two detector distances of 2 m and 8 m and the data was calibrated to a scattering standard. The 2 m data was acquired for 5 min and the 8 m data for 1 h. Absolute scattered intensity units for the data were problematic to obtain due to thickness variations of the membranes and also different thickness swelling due to the doping. As a result, for clarity of the presented curves we scaled the data to match the incoherent background at high Q values of the sample doped at 25 wt% for 24 h. Further study would be required to extract numerical information concerning the absolute volume or density of structures in the doped samples, but for the analysis presented here this rescaling does not affect the data or the drawn general conclusions.

After performing the SANS measurements, the samples were sealed in Teflon bags and stored for the PGAA measurements which were done at a later time, after a few weeks, due to the scheduling availability of measurement time. For the PGAA measurement, since the method measures the global elemental composition, long term stability of the sample is not a concern, as the K will be contained in the sealed bag.

The PGAA measurements were conducted on the samples under vacuum with an evacuated neutron flight path to eliminate background from air. Each PGAA sample spectra is carefully corrected for the detector efficiency and the no-sample background. Stacks of 3 membrane disks as previously used for the SANS measurements were used to increase the sample volume and resulting signal intensity. Each sample was measured from 2 to 15 min to obtain very high statistics. The background was measured for 6 h to obtain the needed statistical accuracy.

PGAA, as indicated by the name, measures the unique prompt

gamma-ray spectrum of a sample caused by the absorption of an intense neutron beam. Each element has a very well-known gamma-ray spectrum of which the absolute cross sections of the emission lines have been determined to high precision [24]. While absolute elemental determination would require a calibration of neutron intensity and absolute illuminated sample volume, determination of relative concentrations in a sample is simply obtained by comparing the gamma-ray intensities of any two strong emission lines from different elements and scaling by the cross-section after correcting for the detector's energy dependence which is also very well calibrated.

Therefore, in order to observe the K content in a membrane, we must compare its signal to that of a fixed atom reference in the polymer chain backbone. Each of the membranes used here have nitrogen atoms in the backbone, and since nitrogen (N) gives a convenient PGAA signal we chose to measure the K content relative to the N contents. Since PGAA measurements are performed in vacuum, no corrections for gamma emission from N in the air are needed.

The PGAA measurements for the K uptake in the membranes are themselves insensitive to the hydration state of the membrane as we compare the ratio of K to N in the membrane backbone and are therefore not prone to the difficulties in determining absolute K uptake from comparing pre-doping mass to post-doping mass which would require control of hydration and residual solvent levels. Here possible residual solvent concentrations of the dimethylacetamide (DMAc), which is used to prepare the membranes, could give systematic contributions to the PGAA data. Residual DMAc, since it contains N, if present in the prepared membranes would leach out slowly during the KOH doping procedure, giving an extra N contribution in the PGAA signal that would decrease over KOH doping time and as a function of doping conditions. However, measurements of residual DMAc [25] show that we can estimate that the maximum amount of additional N signal in the PGAA spectra arising from DMAc would be below a few percent of the membrane signal and insignificant compared to the trends observed and conclusions of this paper. To check the validity of this assertion, we remeasured the PGAA spectra after the samples were allowed to dry in the vacuum for one day. In this case the intensity of the N signals remained unchanged within errors. As an additional check, the K concentration was also analyzed as a function of the H concentration of the fully desiccated samples, thus using instead the H atoms of the polymer to provide the fixed reference. These data trends using H gave results proportional to the data that used N as a reference. Further the ratio of 3 H atoms per N atom observed with PGAA corresponded to the expected value for PBI typically within 4%, again supporting the assertion that the possible DMAc (ratio of 9H per N) is below a few percent.

The SANS measurements of the initial samples showed structure peaks in the data for the non-cross linked PBI samples, thus we focused on this membrane for a further study of the structure development with respect to doping conditions. These PBI membranes were prepared in the same way as described above, however this time we focused around the area of maximum K uptake, doping the PBI at concentrations of 15 wt%, 20 wt%, 25 wt%, 30 wt%, and 35 wt% each for 24 h at 80 °C. Additionally, we did a time dependence study of the membranes doped with 25 wt% KOH by measuring at the doping times of 1, 5, 10, 30, 60 min and 24 h. These samples were then measured with PGAA and SANS in the same way as described previously in this section.

2.3. Swelling measurements and composition via titration

For obtaining the swelling, S , during doping a membrane, a sample of 4 cm x 1 cm dimension was washed in DI water for two days with several water refreshments and dried for one day under atmospheric conditions (21 °C, 40–45%RH) before doping. The length and thickness were recorded before doping as the dry dimensions, d_{dry} , and during the doping at 1, 5, 10, 30, 60 min and 24 h respectively giving the wet dimensions, d_{wet} in order to determine the swelling given as

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

Measurement of the length values were done using transparent millimeter paper and a scanner to determine the dimensional changes in-situ with a high resolution and thickness values were measured with a thickness gauge. This swelling data is presented later in Fig. 6.

Finally, the membrane KOH content was determined for 1 min, 1 h and 24 h doping time by acid-base titration (p/p indicator) for an estimation of KOH amount n_{KOH} in the membrane. Wet weight of the samples was noted before KOH was leached out of the membrane and dry weight was written down after it. Solution containing KOH was titrated with 0.05 M HCl until color change from vibrant pink to colorless was observed where n_{KOH} is simply $C_{HCl}V_{HCl}$.

2.4. Resistance and ion conductivity

Through-plane ion conductivity of doped membranes was measured by impedance spectroscopy (ZAHNER-elektrik GmbH & Co. KG). The membranes were fixed between two chambers with an active electrode area of 1.767 cm². The distance between the electrodes (gold coated copper discs at the end of the chambers) was 1.59 mm. The experiment was started by filling both chambers simultaneously with 25 wt% KOH 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 for 1, 5, 10, 30, 60 min and 24 h, respectively. Then the conductivity σ_m was calculated as according to Eq. (2) with membrane thickness values, t , obtained from the dimensional change measurement where A is the area of the electrode.

$$\sigma_m = \frac{t}{R_m \cdot A} \quad (2)$$

3. Results and discussion

3.1. Composition determined with PGAA

The first set of neutron experiments we present used PGAA to explore the dependence of the K content in the doped membrane on the KOH concentration of the doping solution, using solutions of 5, 25 and 50 wt% KOH. For comparison, also an undoped membrane was analyzed. The results of PGAA measurements in Fig. 1 show the variation in relative K content for the series of 5 different membranes. All of the membranes shown here resulted in a maximum K uptake of about 0.4–0.5 K atoms per N in the polymer chain. Interestingly the initial uptake within the first minutes leads to an almost saturated level of K concentration except for FAAM-55 which had somewhat slower uptake kinetics. The uptake of the 25 wt% KOH solution for 24 h leads to similar doping levels for PBI and 5 wt% crosslinked PBI, and even slightly higher K content when compared to the same membranes doped with the 50 wt% KOH solution for 24 h. This might be due to osmotic pressure effects and a stronger water swelling for the 25 wt% KOH solution. Incidentally, these values are consistent with other work which showed an optimal uptake at around 25–35 wt% KOH concentration [8].

For the second set of samples the time dependence of the KOH doping for the non-cross-linked PBI membrane doped at 25 wt% KOH was explored by varying the doping time from 1 min to 24 h, and the KOH doping concentration was varied from 15 wt% to 30 wt% in 5 wt% steps for a fixed doping time of 24 h. The results of the PGAA measurements on this series of samples are shown in Fig. 2A and B. As shown in Fig. 2B, the relative K content reaches a maximum at 20–25 wt% KOH doping concentration as in the prior measurement, and Fig. 2A shows the K content has reached ca. 90% of the 24 h uptake value after only 1 min and is thus nearly independent of the time it was doped.

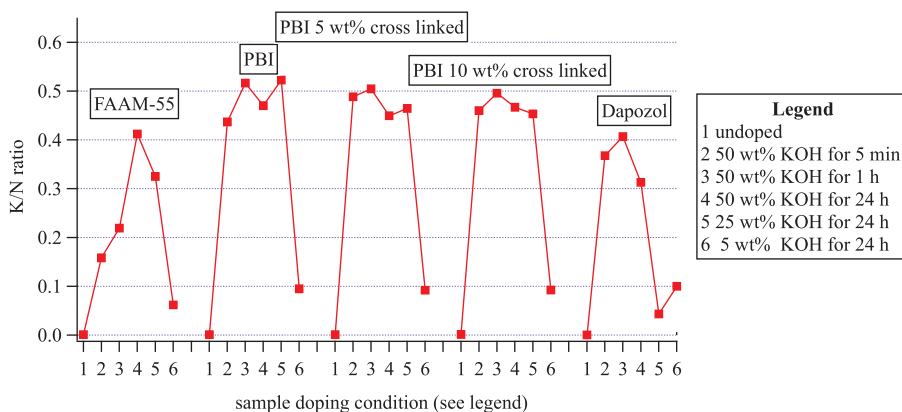


Fig. 1. PGAA measurements for different membranes at doping concentrations of 5 wt%, 25 wt%, and 50 wt% for 24 h, and doping at 50 wt% KOH concentration for 5 min, 1 h and 24 h. The data show that for the PBI membrane K uptake is reduced for the longest times at 50 wt% KOH doping, and that the 25 wt% KOH concentration doping gave the highest K uptake after 24 h. The lines are to guide the eye for each membrane type.

3.2. Structure determined with SANS

The SANS measurements are shown in Fig. 3A-B, and the obtained structural information is summarized in Fig. 4A-B. The data in Fig. 3A seem to show that despite the relatively quick uptake of K, the nano-structure of the membranes continues to evolve in the membrane on minute to hour time scales. Further, the data in Fig. 3B shows that the structure formation after 24 h is highly dependent on the KOH doping concentration. This dynamic structure formation gives us a complementary picture to the relatively static K uptake from the PGAA data.

To elucidate the structural changes, we fit the measured intensity data, $I(Q)$, to the Teubner-Strey bicontinuous model. Alkylated-PBI membranes have shown to give local lamellar structure with SAXS measurements [31] however this scattering occurs at larger Q-values, i.e. from smaller size scale structures, than the peaks observed in our data. Assuming a similar local lamellar structure in the KOH doped PBI here, the scattering by larger size scale structures suggest we are observing inter-domain channels that are being formed during the doping process. In this case of a two component structure presumably consisting of disordered domains of locally lamellar polymers and inter domain channel like structures containing the KOH solution. For such systems without a well defined particle shape, the Teubner-Strey is an often used model that can describe the relevant features of our data [26,27]. The functional form of this model plus a Porod-law and flat a background is used to fit the data. This model can be written as,

$$I(Q) = B + \frac{A}{Q^n} + \frac{C}{Q^4 - 2(Q_0 - \xi^{-2})Q^2 + (Q_0^2 + \xi^{-2})^2} \quad (3)$$

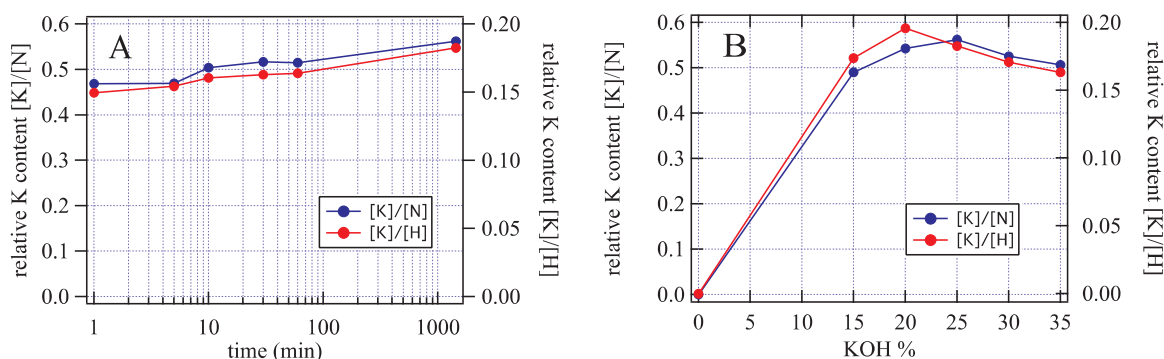


Fig. 2. Graphs showing the uptake of K in the PBI membrane as measured with PGAA relative to the N atoms in the polymer backbone (left axis open blue markers) or the H content in the desiccated sample (right axis closed red markers) (color available online). **Graph A** shows the increase in K uptake vs. time for 25 wt% KOH, **Graph B** shows the K uptake as a function of the KOH doping concentration for a 24 h doping time. The lines are to guide the eye, and the statistical errors are smaller than the marker size. Also presented are the K uptake data relative to the H concentration of the desiccated sample (red) which showed a typical -4% deviation from the N referenced data, the 20 wt% data point gave a maximum deviation of 8%. The SANS data for the samples shown in graphs A and B are given in Fig. 3A and B, respectively.

with the Teubner-Strey portion as deduced in Ref. [28]. Here A and C are scale parameters, n is the Porod exponent, B is the background, Q_0 is the correlation peak center which is related to the domain repeat distance or d-spacing by $d = 2\pi/Q_0$ and ξ is the correlation length which is a measure of the dispersion in d^{28} . In our fits n was about -4 and the background was held to a common value of $0.285 \text{ (cm}^{-1}\text{)}$. The data was fit to an intermediate range spanning the Porod-like low Q-range to past the correlation peak.

The fits for the SANS data in Fig. 3A exploring the structure variation as a function of doping time for 25 wt% KOH doping solution are summarized in Fig. 4A and B. Fig. 4A shows that nano-structures with a repeat distance of $d = 19.9 \pm 0.2 \text{ nm}$ have formed by 1 min, visible as a peak at $Q \sim 0.31 \text{ nm}^{-1}$ that decreases at longer time scales where the peak is nearly disappearing for doping times of 1 h and 24 h. The correlation length, initially $5.6 \pm 0.2 \text{ nm}$ at 1 min, appears to slightly increase up until 10–30 min after which it decays, as further evidenced by the data in Fig. 4B below. This implies a more ordered inter domain structure observable after initial doping decaying into a more amorphous structure as the doping progresses.

Fig. 5A and B show the fit parameters for the SANS data from Fig. 3B studying the KOH concentration dependence with 24 h doping time. Here we don't yet see a correlation peak at the lowest KOH concentration of 15 wt%, while a peak with d-spacing corresponding to a domain repeat distance of $17 \pm 5 \text{ nm}$ becomes visible at 20 wt% KOH and the d-spacing decreases with increasing KOH concentration down to $10.2 \pm 0.5 \text{ nm}$ at 35 wt% KOH. While in this data series the higher concentration maintained a significant structure peak for 24 h doping time, the d-spacing was about half the values of those for the 25 wt% doping series at low doping times, and the correlation lengths for all the

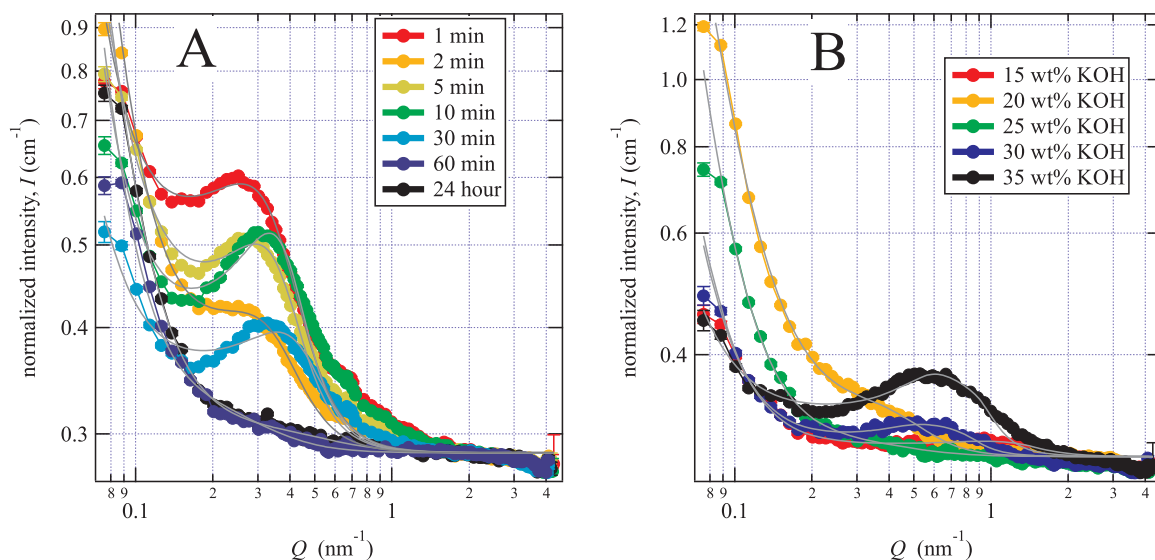


Fig. 3. SANS scattering data for the PBI membrane, the colored lines are to guide the eye, and the grey lines are the fits to the data using Eq. (2) (color available online). **Graph A.** SANS data as a function of doping time using a 25 wt% KOH doping solution. The diffraction peak in the 30 min data corresponds to 16 nm structures and the peak for 1 min corresponds to 20 nm structures. The PGAA data for the samples shown in this graph are given in Fig. 2 A. **Graph B.** SANS data as a function of KOH doping solution concentration (doping time: 24 h). The strong correlation peak in the 30 wt% and 35 wt% occurs for a nano-structure size of about 11 nm. The 25 wt% and 20 wt% KOH doped samples show an increased forward scattering presumably due to the formation of larger domains with increased D₂O uptake/swelling. The PGAA data for the samples shown in this graph are given in Fig. 2B.

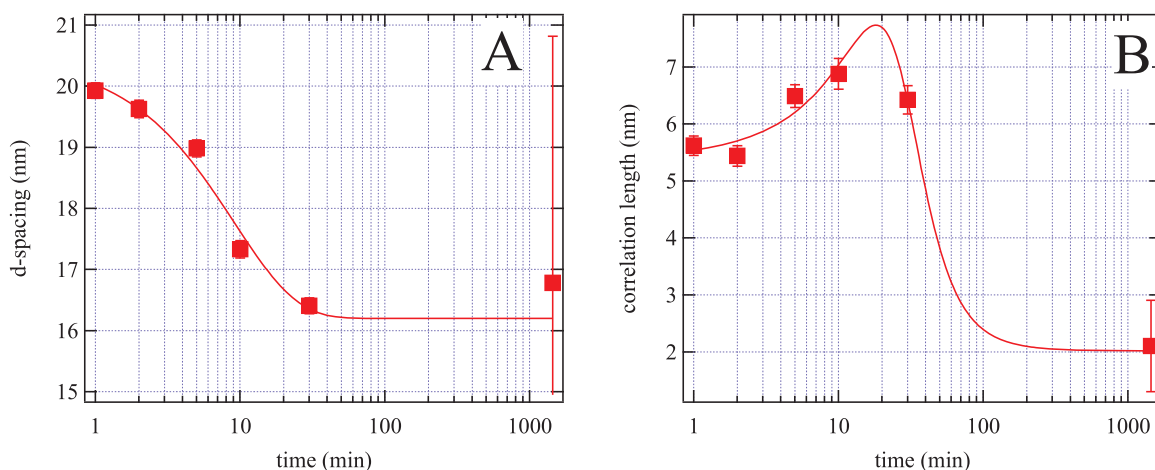


Fig. 4. Results of the fits using eq. 4 for the SANS data shown in Fig. 3A of the structure vs. time for PBI doped with 25 wt% KOH. **Graph A** shows the d-spacing of the structures in the membranes with an exponential fit line to guide the eye, the 24 h (1440 min) data point has a 40% error due to the low amplitude of the observed peak. **Graph B** shows the correlation length of the structures formed with a Lorentzian fit line only to guide the eye. Both plots are as a function of time during doping in 25 wt% KOH.

24 h doped samples were also approximately half that of the samples doped for short times (< 1 h). Again supporting the premise that the KOH initially forms ordered structures, with the KOH entering between domains in the PBI that are being broken up in time and with higher KOH concentration.

Given the variations in the SANS curves and resulting fit parameters in Figs. 4 and 5, we assume there are more variables in the process to control and a further and more detailed study could help better understand these trends. In the future we would aim to understand the variations in the relative correlation peak size to understand why the 30–35 wt% at 24 h doping time sample produced large peaks as opposed to the nearly absent peak for the 25 wt% 24 h doped samples, which for now we assume was due to variations in the samples or sample preparation. The peaking nature of the ξ -values in Fig. 4B may be fortuitous, the fit-line in the plot is only added to guide the eye, and more data points in this region would be required for conclusive

information. However, due to the limited availability of neutron beam-time such additional study was not yet performed.

Extended studies covering a broader Q-range either via neutrons and/or X-rays, could be used to gain understanding of the interplay between this possible inter-domain structures discussed here and possible local lamellar structure discussed in the following section, but this was beyond the scope of the current work.

Since the time scales of both the SANS and PGAA measurements are on the order of minutes for such membranes, one can envision eventual in-situ doping studies to further elucidate the processes involved. A main conclusion of this work is that this combination of PGAA and SANS could also be useful for *in-operando* studies of functioning fuel cells and electrolysis cells as a function of conditions and cycling because of its sensitivity to changes in composition and structure.

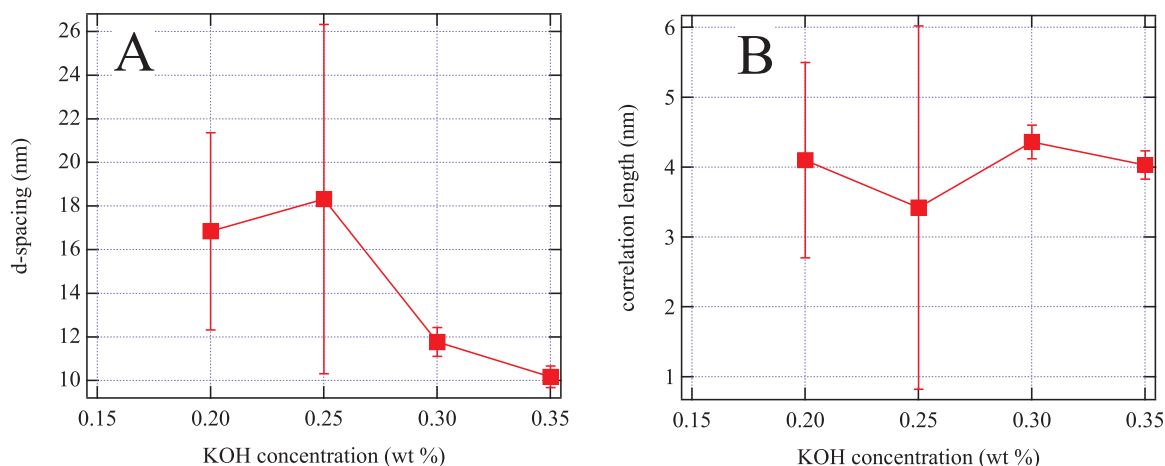


Fig. 5. Results of the fits using eq. 4 for the SANS data shown in Fig. 3B of the structure vs. KOH concentration for a 24 h doping time. **Graph A** shows the d-spacing of the structures in the membranes and **Graph B** shows the correlation length of the structures after a doping time of 24 h for varying concentrations of KOH. The 15 wt% SANS curve did not produce reliable fit parameters.

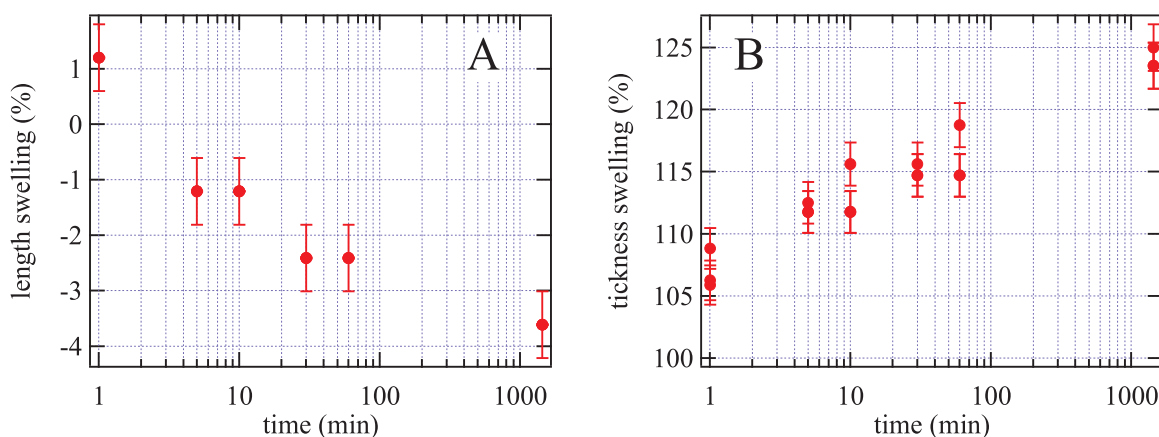


Fig. 6. Length swelling (A) and thickness swelling (B) of the membrane during 25 wt% KOH doping.

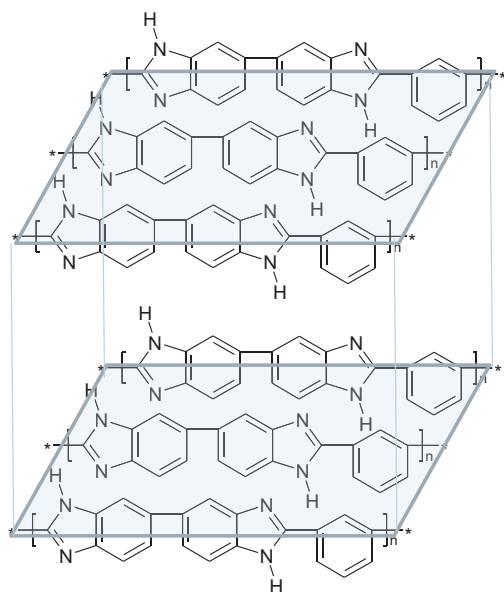


Fig. 7. An assumed lamellar structure of PBI which could explain the observed anisotropic swelling during doping.

Table 1

Composition of PBI membranes after different immersion times in 25 wt% KOH solution at room temperature.

Time	KOH uptake wt %	Water uptake wt %	Total uptake wt %	K/N ratio
1 min	39.6 ± 1.5	109.7 ± 0.2	149 ± 2	0.544 ± 0.020
1 h	39.7 ± 1.1	105.3 ± 3.9	145 ± 5	0.546 ± 0.015
1 day	39.9 ± 0.2	104.0 ± 5.3	144 ± 6	0.548 ± 0.003

3.3. Swelling and composition via titration results

When the membranes are immersed in 25 wt% KOH solution, they swell immediately in all directions, with a very strong preference towards swelling in thickness, or the z direction. After a few minutes, the membranes shrink in length, i.e. the in-plane dimension x or y, while the z direction still increases. Because the z-direction swells much stronger than the x or y direction, the volume swelling follows the same trend as the thickness swelling, and continuously increases after contact with KOH solution. We paid special attention to the measurements of the in-plane, i.e. x or y, dimension swelling to insure it is isotropic in these dimensions leading one to support a local lamellar structure in these membranes as opposed to a kind of nematic structure, in which all polymer chains are oriented along the casting direction.

Fig. 6A and B show this swelling in the length and thickness, respectively. Anisotropic swelling of PBI membranes is known for

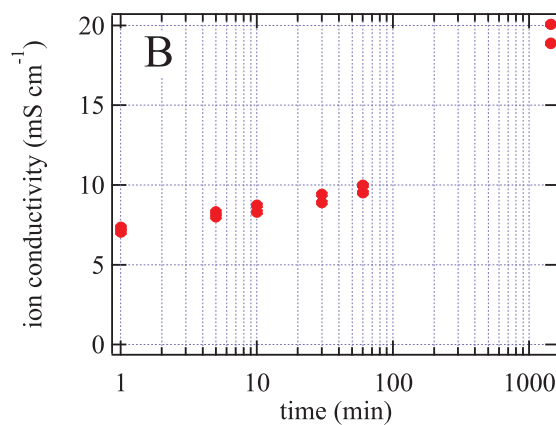
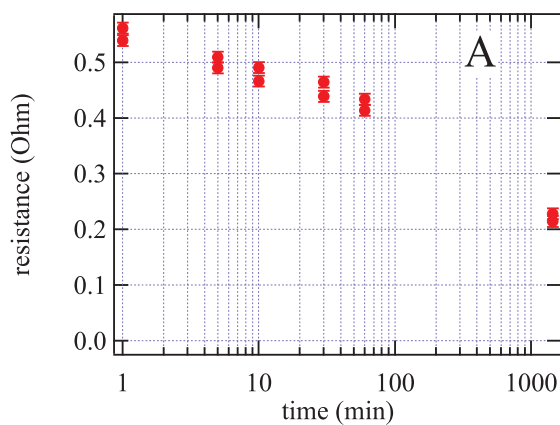


Fig. 8. Online-checked resistance of the membrane plotted against doping time (A) and the resulting membrane conductivity, based on ex-situ measured thickness data (B); the first data point was obtained after 1 min.

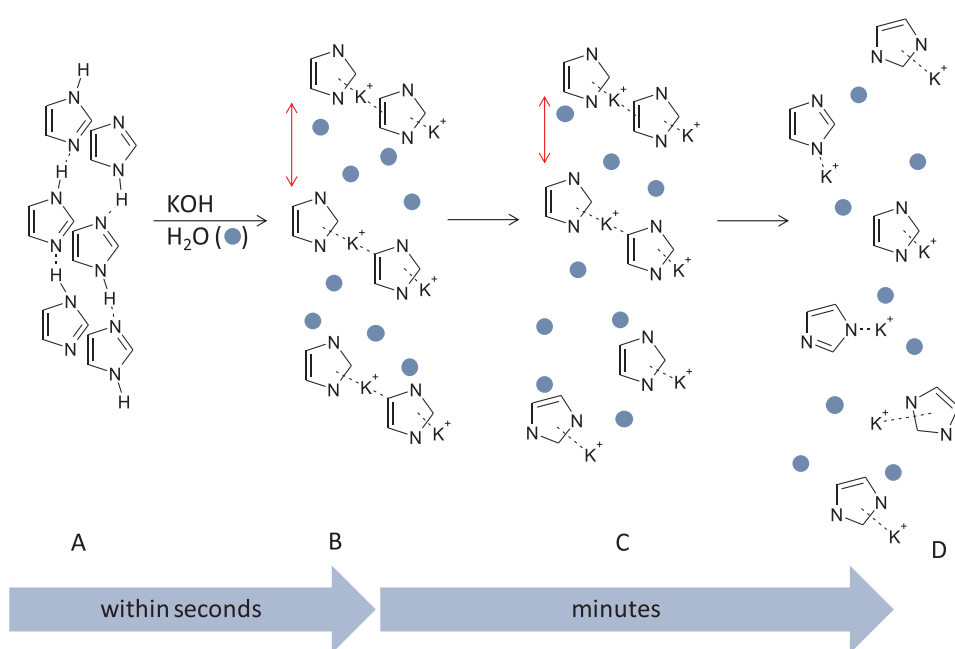


Fig. 9. Schematic representation of the suggested swelling process, the imidazole units represent units within individual polymer chains. A: Dense, hydrogen bonded structure; B: within seconds, KOH and water break up the hydrogen bonded structure, leading to a local lamellar structure, distance between the domains is in the range of 20 nm, as indicated by the red arrow; C: polymer chains start to reorganize, some areas get more amorphous, water is redistributed into the amorphous areas, reducing the size of the local layered domains and reducing their number within 30 min; D: after hours the scattering elements (domains) become more disordered, indicating an amorphous structure. General comment: In imidazole ions, the negative charge is delocalized over N1, C2 and N3. Therefore, K ions could interact with one negatively charged nitrogen atom (in plane with imidazole) or with the negatively charged group of atoms (on top or below the imidazole plane); in the latter case, interaction with two imidazole rings may be possible.

phosphoric acid doped membranes, although to a much lesser degree. Usually, the thickness swells 1.2–1.5 more than the x direction [29]. The reason for this anisotropic swelling behavior seems to be the arrangement of the polymer chains. WAXS data indicates two forms of interactions between the chains, parallel ring stacking (d spacing of 0.35 nm, typically observed in solution casted membranes), and staggered side-to-side packing (d spacing of 0.46 nm, typically observed for membranes prepared in the sol-gel-process) [30].

For an alkylated PBI, a phase separation into a lamellar structure was proven by SAXS [31]. Hence, at least partially, PBI chains may be packed in a similar way as described in Fig. 7. Since such local lamellar structures would be expected to be parallel to the x,y direction (parallel to the glass plate and casting direction), the observed initial swelling in the thickness direction when membranes are immersed in 25 wt% KOH solution suggests that the space between PBI local lamellar structures is filled rapidly with KOH solution. Then, on a slower time scale, the densely packed chains re-arrange. Movement in all directions leads to shrinking in the x and y direction.

As shown in Table 1, the weight gain was monitored for membranes doped for 1 min, 1 h and 24 h. Interestingly, while the volume swelling increased continuously, weight gain was constant within errors. This indicates a changed density, e.g. by less tight packing of polymer

chains, supporting the suggested morphological changes during doping. The K/N ratio is practically constant, except for a very slight increase over time, in line with the data obtained by PGAA.

3.4. Resistance and ion conductivity results

The conductivity of pure PBI was reported to be in the range of about 10^{-9} mS/cm [32], whereas doping with acids or bases increases the conductivity into the range of $10^1 - 10^2$ mS/cm. Since the composition of the membranes practically immediately reaches a K/N ratio of 0.5, a steep increase in conductivity is expected to occur within the first few seconds. After that, the increase should be minimal. However as shown in Fig. 8, the membrane through-plane resistance continuously increases over the observed time of 24 h. This supports the assumed lamellar structure (Fig. 2). Obviously, the presence of charge carriers will lead to a high conductivity, which will be further increased when the polymer chains rearrange into all directions, opening passages for ions migrating between the two membrane surfaces.

4. Conclusions and future steps

Fig. 9 proposes a conceptual understanding of the mechanisms

involved given our observations from the swelling data which suggests a local lamellar structure, and the SANS data that would then be interpreted as an evolution of inter-domain structures followed by their dissolution into a disordered phase while maintaining a nearly constant proportion of K to N atoms as measured by PGAA and titration.

Indeed in the combination of the data sets from PGAA and SANS shown here there is not a one-to-one correlation between K uptake and the nanostructure of the membrane. While related, there are additional parameters that may prove to be important for obtaining high performance (provided by a high OH⁻ conductivity) and reasonable durability profiles (backbone integrity against KOH attack) of such membranes. Since the SANS data presented suggests structural decomposition resulting from prolonged KOH doping and high KOH concentration, the neutron methods could provide information needed to better understand and thus optimize this durability. A very fast initial uptake of KOH could be observed on the time scale of minutes almost to saturation concentration, while structural properties were still evolving over longer time scales (several hours) in the same sample. The evolution of these structures leads eventually to higher OH⁻ conductivities (larger or more connected channels), but perhaps also towards a higher degradation rate in the case where the structure keeps changing over time.

To follow up on these results we plan to explore the doping process in-situ with SANS in order to obtain more complete information on the structure evolution during doping in real time in order to help maximize the conductivity and durability of KOH doped polybenzimidazole membranes. Additionally these neutron methods may also enable *in-operando* study of the evolution of the compositional, structural and electrochemical properties of these membranes over time during electrochemical cycling in water electrolysis systems. Further, these neutron methods could also help characterize and optimize doping parameters through the possibility of in-situ doping measurements. We have already explored in-situ measurements of nafion membranes in a humidity chamber to show that such *in-operando* and in-situ measurements would indeed be feasible for both PGAA and SANS given a suitable neutron-adapted cell, which will be presented in other publications.

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