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Investigation on Protonic Ionic Liquids immobilized in phosphoric acid-doped polybenzimidazole matrix enable Polymer Electrolyte Fuel Cell operation at 200 °C

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Abstract

Protonic ionic liquids (PILs) based on the anion bis(trifluoromethanesulfonyl)imide were confined in polybenzimidazole (PBI) matrices. Quasi-solidified ionic liquid membranes (QSILMs) were fabricated and examined for mechanical and thermal stability. After doping in phosphoric acid (PA), the QSILMs exhibited conductivities of 30-60 mS cm⁻¹ at 180 °C. Fluorescence microscopy was used to investigate the structure of the composite PBI membranes. Membrane-electrode assemblies, fabricated with PA doped QSILMs, were tested in a single fuel cell and exhibited a performance increase with increasing temperature up to 200 °C. The best performance was obtained for the membrane electrode assembly containing 50 mol% of diethyl-methyl-ammonium bis(trifluoromethylsulfonyl)imide confined in the phosphoric acid doped PBI matrix with closed porosity. It reached 0.32 W·cm⁻² at 200 °C and up to 900 mA·cm⁻². The catalyst layer of the gas diffusion electrode impregnated with protonic ionic liquid exhibited better long-term stability than the gas diffusion electrode impregnated with phosphoric acid within 100 h of operation at 200 °C and anhydrous conditions.

1. Introduction

Fuel cells with a polymer electrolyte membrane operated at higher temperatures (HT-PEMFC) have attracted much attention in the past years. Among their main benefits there is a higher tolerance of the catalyst to carbon monoxide compared to the low temperature fuel cells (LT-PEMFCs) [1,2]. It enables fueling HT-PEMFCs with hydrogen-rich reformates, which makes it attractive for engineers to couple methanol reforming units with the fuel cell and eliminate complex systems for CO removal [3,4].

It is known that the performance of LT-PEMFCs strongly depends on the hydration level of the membranes, which are conventionally based on perfluorosulfonic acid (PFSA) polymers such as Nafion® [5,6]. At elevated temperatures of around 160-200 °C, however, sufficient humidification becomes an issue as water can only be present in the gas phase of the system. Therefore, development of an alternative electrolyte, which does not involve water in the conductivity mechanism, has been an intensive field for more than two decades. Many attempts were made in order to find an alternative membrane among sulfonated hydrocarbon-based polymers including polystyrene sulfonic acid (PSSA), polyetheretherketone (PEEK),
polyethersulfone (PES), polyimide (PI), and polybenzimidazole (PBI), among others [7–9]. As they lack intrinsic conductivity, different fillers were investigated in these membranes ranging from acids and nanoparticles to ionic liquids (ILs) in order to achieve the required conductivity [10–18].

Poly[2,2-(m-phenylene)-5,5-benzimidazole] (PBI) has been extensively studied as an alternative polymer matrix in the past years due to its excellent chemical and thermal stability. Since the proton conductivity of PBI is very low, it requires incorporation of a secondary proton conducting phase in order to support ion conductivity [19]. Phosphoric acid (PA) is of particular interest in this connection due to its high intrinsic proton conductivity and low vapor pressure [20]. Phosphoric acid doped polybenzimidazole membranes (PBI-PA) have therefore been thoroughly studied [21–23]. The conductivity increases upon humidification of the feed gas (up to 5% relative humidity (RH) at 200°C).

Typical conductivities of the fully doped PBI-PA membranes with an acid content corresponding to about 5.6 mol H₃PO₄ per polymer repeat unit and a RH of 5.5% at 200 °C (68 mS·cm⁻¹) [21] are almost as high as those of fully humidified perfluorinated membranes at 80-90 °C and less dependent on the relative humidity [24]. The proton conductivity in this case mainly depends on the acid doping level (ADL), i.e., the number of PA molecules per repeat unit of PBI [22]. However, the specific adsorption of the PA electrolyte on platinum is known to inhibit the oxygen reduction reaction activity on the cathode side [25,26]. Despite of the low volatility of PA above 100 °C, it starts to condense at around 150 °C and forms dihydrogen phosphate, which also blocks electrochemically active centers for oxygen reduction on the platinum surface [10] and results in conductivity decay [27].

Immobilized protic ionic liquids (PILs) can be alternative electrolytes for HT-PEMFCs because of their negligible vapor pressure as well as good thermal stability at elevated temperatures [16]. PILs have dissociated protons and, therefore, can act as proton conductors. Conductivities of the membranes with incorporated PILs are in the order of 0.1 or 10 mS·cm⁻¹ at 160 °C [28–30]. Plasticizing effects of the PILs can lead to lower elastic modulus and poor mechanical stability, and a progressive release of the PIL component can lead to a decrease of the proton conductivity of the membrane with time [31].

There are three main approaches of immobilization of PILs inside polymer matrices: 1) intercalation of inorganic fillers modified with ILs [32], 2) quasi-solidified ionic liquid membranes (QSILM) which are produced via solution casting of a mixture of the polymer solution and IL (closed porosity of the matrix), and 3) supported ionic liquid membranes (SILM) produced by posterior impregnation of the IL into a polymer support with open porosity [33]. QSILMs structures are the most attractive structures for immobilizing relatively high volumes of ionic liquids with simple procedure and low consumption of toxic organic solvents. However, recent electrochemical studies of Smith and Walsh revealed that pure PILs cannot support proton shuttling between the electrodes of fuel cells and require inclusion of either acidic or basic proton shuttles in order to achieve the desired performance [34].

Here we report about QSILM-type immobilization of self-synthesized PILs based on bis(trifluoromethanesulfonylimide ([NTf₂]), Scheme 1) within PBI matrices followed by post-treatment with PA. The morphologies and the physico-chemical properties of the QSILMs were investigated and the influence of acid doping on their conductivities was studied. Membrane
Electrode Assemblies (MEA) were manufactured and the fuel cell performance was evaluated by means of single fuel cell tests.

![Scheme 1 – Ionic liquids used in this work](image)

2. Experimental

2.1. Chemicals

Polybenzimidazole ($M_w$ 45000 g mol$^{-1}$) was purchased from Danish Power Systems (Denmark). Methylimidazole, polyvinylpyrrolidone (PVP) with a $M_w$ of 40 kDa (type K30), $M_w$ of 360 kDa (type K90), N-methyl-2-pyrrolidone (99%), and lithium chloride were purchased from Sigma Aldrich GmbH (Germany). Phosphoric acid (85-87%) was purchased from J.T. Baker. Ethylimidazole (>98%) and bis(trifluoromethylsulfonyl)imide (acid form) aqueous solution (80 wt.%) were purchased from IoLiTec (Germany). $N,N$-Diethylmethylanime (>98%) was purchased from TCI (Germany) and 1,1,3,3-tetramethylguanidine (99%) was purchased from Alfa Aesar (USA). Ethanol (99.9%) was purchased from Carl Roth (Germany). All materials were used as received. Ultrapure water was made by a Puranity 15 UV VWR water purification system, equipped with 0.22 mm filter from VWR. GDL type H23C2 with microporous layer and without hydrophobic treatment was purchased from Freudenberg. The gas diffusion electrodes (GDE) with Pt loading of 1.3 mgPt cm$^{-2}$ were purchased from Danish Power Systems (Denmark).

2.2 Synthesis of ionic liquids

For the synthesis of the ionic liquids, listed in scheme 1, the corresponding base (1.00 eq.) was dissolved in pure water (20 mL per 1 mL of base). To the resulting homogenous solution bis(trifluoromethanesulfonyl)imide (80% aqueous solution, 1.05 eq.) was added dropwise under ice cooling for about 30 min to form a second, hydrophobic phase. After additional stirring for 2 h, the aqueous phase was removed and the organic residue was dissolved in dichloromethane (15 mL per 1 mL of initial base) and extracted 4 times with water. The organic solvent was removed by rotary evaporation and the residue dried in oil-pump vacuum at 50 °C for two days. The identity and purity of the resulting ionic liquids was confirmed by NMR
spectroscopy (Figs. S1-S6). The conductivities of the ILs have been measured in the temperature range \(25^\circ C \leq T \leq 125^\circ C\), fitted with the Vogel-Fulcher-Taman law and extrapolated up to 200°C. The extrapolated conductivities at 200°C amount to 80 and 100 mS cm\(^{-1}\), respectively. Details can be found in the supporting information (Fig. S7).

2.3 Preparation of quasi-solidified ionic liquid membranes

**Membrane casting:** Quasi-solidified ionic liquid membranes (QSILMs) were produced through direct blending. The commercial powder of PBI was dissolved in DMAc at 160°C under vigorous stirring for 24 h to obtain a 7 wt.% solution. After cooling to ambient temperature, the solution was filtered (0.45 µm PTFE filter) to remove undissolved matter. The ILs were thereafter added to the polymer solution in molar ratios of IL/PBI = 1 and 2, and kept with stirring for 24 h. After obtaining homogenous mixtures, composite membranes were cast on a glass plate with a Doctor’s blade and left in an oven at 80°C for 24 h to evaporate the solvent. After drying, all membranes were peeled off from the glass plate in water. The QSILMs are hereafter referred to as “\(X.Y\)”, where \(X\) is related to the number of IL (see scheme 1) and \(Y\) is related to the IL/PBI ratio in a composite membrane.

**Post-doping of QSILM with phosphoric acid:** After overnight-drying in a vacuum oven at 120°C / 1 mbar and determination of the initial weight \((W_1)\) the samples (films of 12 × 18 mm\(^2\), thickness 50-70 µm) were covered with a thin layer of 85 wt.% PA on both sides and placed between two objective glasses for 3 days to allow diffusion of PA into the membranes. The excess PA was thereafter wiped off with blotting paper. Alternatively, all the samples were immersed into bulk 85 wt.% PA for 4 h. Remaining water was evaporated by drying at 120°C for 24 h, and the final weights \(W_2\) of the doped membranes were determined. The acid doping level (ADL) was calculated in the following way:

\[
ADL = \frac{(W_2-W_1):M_{PBI}}{M_{PA}:W_{PBI}} \tag{1}
\]

PBI membranes with zero IL content were doped with PA in the same way as bench-mark membranes.

2.4 Membrane characterization and fuel cell testing

Stress-strain curves were recorded by a Comtech machine Model QC-508E (Taiwan), equipped with a 50N load cell. Specimens of a size of 4×1 cm\(^2\) were fixed between two clamps. The samples were stretched at room temperature at a crosshead speed of 1 mm min\(^{-1}\) until 1% elongation to determine Young’s modulus and with 10 mm min\(^{-1}\) to determine tensile strength and elongation at break afterwards. At least five repetitions were done for each sample.

For the cross-sectional scanning electron microscopy (SEM) imaging of the PBI support and the QSILMs, the samples were fractured in liquid nitrogen with tweezers. The samples were gold coated using an Emitech K675X sputter equipment operating at 125 mA during 45 s in a
10 mbar argon atmosphere. SEM pictures were taken using a FEI scanning electron microscope (QuantaTM 250 FEG) operating at 5 kV. The same procedure was used for QSILMs.

Thermal analysis was carried out using a Netzsch TG 209F1 Iris analysis system. The samples were investigated in the temperature range from 30 to 800 °C at an heating rate of 10 K min⁻¹ under an air flow of 40 mL min⁻¹.

Fluorescence Microscopy was carried out using an Olympus IX71 coupled with the fluorescent lamp Olympus U-RFL-T to get pictures of fluorescence of the QSILMs structures. Extinction was applied in a blue range of spectra with λ=360-370 nm and emission was detected at λ>420 nm. Fourier Transform Infrared spectroscopy (FT-IR) was carried out using a Shimadzu IRSpirit (Japan) in the wavenumber range of 4000-400 cm⁻¹.

Conductivity measurements were performed in a self-made cell as shown in Fig. S8. The samples of 10×20 mm² were fixed between four wires; the outer and inner wires are located at opposite sides of the membrane to measure the resistance in the plane of the membrane avoiding measurements of the surface conductivity. The thickness of the samples was measured with a micrometer. The cell was connected to a Bio-Logic SP-150 potentiostat (Bio-Logic Science Instruments, France), to perform cyclic voltammetry in H₂ flow at high temperatures (80-180 °C) at a relative humidity of 5% for QSILMs. Resistance was taken as the I-V slope in a range of -0.3V < ΔE < 0.3V. The proton conductivities for all the membranes were calculated according to Equation 2, where σ is the conductivity in S cm⁻¹, L is the distance between the inner electrodes (L=0.425 cm), R is the measured resistance in Ohm, A is the cross-sectional area of the membrane in cm²:

\[
\sigma = \frac{L}{R \cdot A}
\]  

The membrane electrode assemblies (MEAs) with active area of 4 cm² were prepared by means of hot pressing using a Specac Atlas™ 15T Hydraulic Press coupled with Specac 4000 Series™ High Stability Temperature Controller. The composite membranes were pressed between gas diffusion electrodes (GDE) with Pt loadings of 1.3 mgPt cm⁻² (Danish Power Systems) at 150 °C and 100 kg cm⁻² for 10 min. The electrodes were doped with 1.7 mgPA cm⁻² for the better adhesion. The obtained MEAs were sandwiched with a clamping torque of 2 N m⁻¹ between two carbon plates with serpentine flow pattern and two end plates with metal rods for heating to high temperatures. The anode side was supplied with hydrogen at a flow rate of 60 mL min⁻¹ and cathode side was supplied with an air flow of 180 mL min⁻¹. Prior to obtaining the polarization curves the MEAs were preconditioned at 0.2 A cm⁻² until constant voltage was reached. Polarization curves were recorded in galvanostatic mode.
3. **Results**

3.1 **Membrane composition and morphology**

The pristine, i.e. undoped QSILMs (see photographs in Fig. 1) were fabricated with the compositions presented in the Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Immobilized IL</th>
<th>Content of PBI, mol%</th>
<th>Content of IL, mol%</th>
<th>IL/PBI ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>[DEMA][NTf₂]</td>
<td>50</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>[DEMA][NTf₂]</td>
<td>33</td>
<td>67</td>
<td>2</td>
</tr>
<tr>
<td>2.1</td>
<td>[HHTMG][NTf₂]</td>
<td>50</td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>2.2</td>
<td>[HHTMG][NTf₂]</td>
<td>33</td>
<td>67</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 1 – Composition of pristine quasi-solidified ionic liquid membranes

![Figure 1 – Photographs of pristine QSILMs](image)

The **morphologies** of QSILMS were investigated using SEM. Fig. 2 displays the cross-section images of the membranes. The images exhibit “sponge-like” structure of the membranes where ILs are confined in the 3D polymer network. The pores are 10 to 20 µm in diameter, with a pore wall thickness of about 0.5 µm. A thin layer of dense PBI is formed on the upper surface and the thickness of the layer as well as the pore size decrease with an increase of the IL content. Hence, we assume it is beneficial to increase the loading of IL in order to avoid formation of a nonconductive PBI layer from one side. Even though bulk [HHTMG][NTf₂] crystallizes at room temperature, here in the confinement no damage in structure can be observed during SEM analysis. For the blending procedure the aggregate state of the IL does not play a role since all the studied ILs are soluble in DMAc.
Fig. 3 displays FT-IR spectra of QSILMs. All the samples exhibit a characteristic peak of PBI at the wavenumber of ca. 800 cm\(^{-1}\). In addition, all samples have peaks at 1360-1335 cm\(^{-1}\) and 1170-1145 cm\(^{-1}\) representing antisymmetric and symmetric stretch vibrations of SO\(_2\) groups in sulfonamides and therefore indicating the presence of ILs in the QSILMs.
In order to investigate the distribution of the phases in the pristine QSILMs, samples were observed by means of fluorescence microscopy. Fig. 4 shows an image from the microscope with fluorescent lamp in black and white field. The membranes exhibit a “quinoa-like structure” with segregated globules of the ILs within the polymer matrix. This indicates closed porosity.

Figure 3 – FT-IR spectra of pristine QSILMs

Figure 4 – Images of pristine QSILMs from fluorescence microscope
The mechanical properties of pristine QSILMs were measured and the main results are listed in Table 2.

Table 2 - Mechanical properties of pristine quasi-solidified ionic liquid membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-PBI [35]</td>
<td>72.3 ± 5.0</td>
<td>1124.2 ± 72.7</td>
<td>33 ± 20</td>
</tr>
<tr>
<td>1.1</td>
<td>28.2 ± 4.4</td>
<td>504.8 ± 28.5</td>
<td>87 ± 5</td>
</tr>
<tr>
<td>1.2</td>
<td>11.3 ± 1.1</td>
<td>185.4 ± 5.8</td>
<td>67 ± 11</td>
</tr>
<tr>
<td>2.1</td>
<td>24.4 ± 2.3</td>
<td>578.5 ± 13.3</td>
<td>47 ± 9</td>
</tr>
<tr>
<td>2.2</td>
<td>11.2 ± 0.8</td>
<td>252.8 ± 6.1</td>
<td>57±11</td>
</tr>
</tbody>
</table>

It can be seen that ILs act as plasticizers making the membrane more flexible. The tensile strengths for QSILMs containing one portion of IL and double portion of IL are similar or slightly lower than those of phosphoric acid doped PBI membranes at room temperature, which amount to ADLs of 5-7, respectively.

3.2 Electrochemical membrane characterization

Table 3 shows a comparison between the conductivities of our neat ionic liquids and published values for PA-doped PBI.

Table 3 - Conductivities of ionic liquids and PA-doped PBI

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductivity mS cm⁻¹</th>
<th>Temperature °C</th>
<th>Relative humidity %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DEMA] [NTf₂]</td>
<td>95</td>
<td>200</td>
<td>0</td>
<td>Fig. S7</td>
</tr>
<tr>
<td>[HHTMG] [NTf₂]</td>
<td>77</td>
<td>200</td>
<td>0</td>
<td>Fig. S7</td>
</tr>
<tr>
<td>PBI - 5.6PA</td>
<td>68</td>
<td>200</td>
<td>5</td>
<td>[21]</td>
</tr>
<tr>
<td>PBI - 6.6PA</td>
<td>80</td>
<td>180</td>
<td>8</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>200</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>PBI - 11PA</td>
<td>150</td>
<td>180</td>
<td>0</td>
<td>[42]</td>
</tr>
</tbody>
</table>

The conductivities of our dry protic ionic liquids used in this work correspond approximately to the conductivities of PBI with ADL values of 6 to 7 and RH values around 5%.

Fig. 5a displays the temperature dependence of the conductivities of pristine QSILMs measured in the self-made cell in the range of 80-180 °C. For all the tested membranes, conductivities increased with increasing temperature. Membrane 2.2 exhibits the highest value of all pristine...
membranes and reaches 0.3 mS cm\(^{-1}\) at 180 °C which is two orders of magnitude lower than state-of-the-art PBI membranes doped with PA.

In order to increase this sluggish conductivity of our QSILMs, a post-doping with PA was performed and the influence of the doping level on the conductivity was studied. In order to reach ADL values of about 6 (see Eq. 1) QSILMs were doped in a thin film with a certain amount of PA. After doping, the conductivities increased by two orders of magnitude and reached maximum values of about 60 mS cm\(^{-1}\) for the QSILM with the [HHTMG]\(^+\) cation at 180 °C. Fig. 5b shows a comparative analysis of the conductivities of the different QSILMs with low ADL. Samples 2.1 and 2.2 (with the [HHTMG]\(^+\) cation) exhibit conductivity values twice as high as samples 1.1 and 1.2 (with the [DEMA]\(^+\) cation). Fig. 5c shows the conductivity of sample 2.1 at 180 °C as a function of absorbed PA which was obtained via two different routes of doping: left – in thin film, right – in concentrated solution. As expected, the immersion technique allows a higher ADL what, accordingly, results in higher conductivities. A maximum ADL of 9 was obtained after 4 h of treatment and yielded an in-plane conductivity of about 140 mS cm\(^{-1}\) at 180 °C which corresponds to the typical value of 140-150 mS cm\(^{-1}\) for PA-doped PBI at 180 °C with an ADL of 11 [43].

In pristine QSILMs the enclosed ILs have a comparatively high conductivity, but due to the closed porosity there is no conductivity percolation path. The conductivity path consists of repeat units of 10-20 µm (pore diameter) well-conducting IL and of about 0.5 µm badly conducting (undoped) PBI (pore wall). In PA-doped QSILMs the conductivity path consists of repeat units of 10-20 µm very well-conducting IL and about 0.5 µm well-conducting PA-doped PBI connecting the IL domains. Therefore the conductivity of PA-doped QSILMs is similar to that of bulk PA-doped PBI.

For the further analyses and fuel cell tests, QSILMs doped via immersion technique were used. Their compositions are listed in Table 4.

| Table 4 – Compositions of the doped QSILMs (* means doped in thin film) |
|-----------------|-------|-------|-------|-------|-------|
| Sample          | PBI, %mol. | IL, %mol. | H\(_3\)PO\(_4\), %mol. | ADL | Thickness, µm |
| Thin film doping |       |       |       |       |       |
| PBId*           | 34.5  | 0     | 65.5  | 1.9  | 27    |
| 1.1d*           | 14.5  | 14.5  | 71.0  | 4.9  | 28    |
| 1.2d*           | 13.2  | 26.3  | 60.5  | 4.6  | 48    |
| 2.1d*           | 14.1  | 14.1  | 71.8  | 5.1  | 46    |
| 2.2d*           | 14.1  | 28.2  | 57.7  | 4.1  | 40    |
| Bulk doping     |       |       |       |       |       |
| 1.1d            | 9.1   | 9.1   | 81.8  | 9.0  | 70    |
| 1.2d            | 7.8   | 15.6  | 76.6  | 9.8  | 80    |
| 2.1d            | 10.8  | 10.8  | 78.5  | 7.3  | 90    |
| 2.2d            | 8.6   | 17.2  | 74.1  | 8.6  | 100   |
Figure 5 – (a) Conductivities of pristine QSILMs and (b) QSILMs doped in thin film of 85 wt.% H₃PO₄; (c) Dependence of conductivity values on the doping level for the sample 2.1: grey – in thin film of PA, white – via immersion into PA solution
TGA in air was performed in order to evaluate the thermal stability of pristine and doped QSILMs at real operating conditions of HT-PEMFCs and the influence of acid post-doping. Fig. 6 shows the TGA curves of QSILMs at operating temperatures of HT-PEM-FC. Pristine membranes lose some water (1-4 wt.%) while heated up till 100 °C. Doped membranes exhibit higher loss of water (5-7 wt. %) which indicates they are more hygroscopic than pristine membranes due to the PA content. The second weight loss for doped membranes appears at 150 °C when thermal decomposition of PA takes place and reaches 4-5 wt.% loss at 200 °C, 6-9 wt.% at 220 °C and 8-13 wt.% at 240 °C. In case of both ILs, the membranes containing a lower amount of IL exhibit 0-4 wt.% less weight loss within 100-250 °C. It can be observed that the higher the content of IL immobilized in the matrix is, the higher is the weight loss within this temperature range. That confirms the difference in the loading of ILs. The results of analysis suggest that both pristine and doped QSILMs can be operated in HT-PEMFCs at temperatures up to 250 °C. The decomposition of PA at 150-250 °C occurs because of complete water loss. During HT-PEMFC operation, however, water is constantly produced on the cathode side. Hence, part of it may diffuse into the membrane and reduce the effect of thermal decomposition. Therefore doped QSILMs may safely be operated at temperatures of 200-220 °C.

Figure 6 – Comparative TGA curves of pristine QSILMs and QSILMs doped with phosphoric acid measured in air with 10 °C min⁻¹ heating rate till HT-PEMFC operating temperatures

3.3 Fuel cell performance and durability test

In order to evaluate the fuel cell performance of the QSILMs, MEAs were fabricated by means of hot pressing. Doped QSILMs were found to do not lose free PA from the matrix, in other words, we did not observe any leaching. This is in contrast to PA-doped PBI membranes. Lack of leaching causes poor adhesion between the membrane and the commercial GDEs (with Pt loading of 1.3 mgPt cm⁻²). Therefore, these GDE were impregnated with 1.7 mg·cm⁻² of PA in order to improve the three-phase boundary region. Fig. 7 shows the polarization curves of the MEAs tested at different temperatures and non-humidified conditions.
In all cases the performance increases gradually with increasing temperature and reaches a maximum at 200 °C. The highest power density of 0.32 W·cm⁻² was achieved for the membrane 1.1d while operated at 200 °C and 900 mA·cm⁻². At this current density the flow stoichiometries were: $\lambda_{\text{H}_2}=2.2$, $\lambda_{\text{Air}}=2.8$. The MEAs containing membranes 2.1 and 2.2 exhibit lower performances than those with 1.1 and 1.2, respectively, despite having higher conductivities. But PA leached out of the catalyst layer during the operation, loses water, and undergoes thermal decomposition at the temperatures above 150 °C. Therefore, alternatively, the GDE was self-prepared from commercial GDL by means of spraying a catalyst ink consisting of Pt/C 60 wt.% catalyst dispersed in absolute ethanol and a certain amount of the corresponding IL. This resulted in the catalyst loading of 1.3 mgPt cm⁻² and 0.4 mgIL₄ cm⁻². In this case we used ionomer-free GDE since Nafion does not work as electrolyte at these high temperatures under dry conditions [18]. Membrane 2.1 was chosen for this experiment due to its lowest doping level. The MEA was prepared like described in the Experimental Section. Figs. 8a, b show the comparison of the performances of MEAs with membrane 2.1 as electrolyte and GDEs impregnated with IL2 and PA, respectively.

In order to estimate the long-term stability, durability tests were performed at 200 °C for both MEAs. Fig. 8c shows the voltage response at a constant current density of 200 mA cm⁻² within 100 h of operation.

Figure 7 - Polarization curves of doped QSILMs in dependence on temperature: black - 120°C; red - 140°C; green - 160°C; blue - 180°C; orange - 200°C; purple - 220°C
Figure 8 - Polarization curves of MEA_2.1d with the following GDL doping:

- a - [HHTMG][NTf₂]; b – PA: black - 120°C; red - 140°C; green - 160°C; blue - 180°C; orange - 200°C; purple - 220°C.

(c) comparative durability tests at 200 °C and 0.2 A cm⁻² for 2.1d QSILM and electrodes treated with phosphoric acid (above) and IL2 (below).

After 10 h of operation the MEA with IL2 in the catalyst layer reached a kind of stationary state and subsequently exhibited a lower degradation rate than the MEA with PA in the catalyst layer. Hence, usage of IL in the catalytic layer can be beneficial for the long-term stability.
4. Discussion

It is known that PBI exhibits fluorescence in a broad wavelength range and several research groups used this property to study the agglomeration of PBI [37,38]. To the best of our knowledge, fluorescence of PBI never was used as a tool to analyze the morphology of PBI films. In this work we used florescence microscopy in order to observe the phase separation in QSILMs structures and the IL distribution within the PBI matrix. The images from florescence microscopy show that there are hardly any interconnected IL channels, in accordance with cross-section SEM images, but rather closed pores insulated by non-conductive polymer walls. This continuous percolating polymer film blocks proton transport between conductive globules, hence the membranes act as insulators. The hypothesis of segregated globules can also be supported by the image from confocal microscopy (Fig. S9).

In order to support continuous transport of protons across the membranes, the PBI network has to gain conductivity via protonation or grafting of the functional groups. Therefore, all pristine QSILMs were doped in thin film of PA, and the conductivities of the resulting doped QSILMs exhibited values three orders of magnitude higher than the pristine ones and higher than PBI with ADL 1.9 which was obtained during the same procedure. The fact of boost in conductivity after doping with the acid supports the observation of phase separation within QSILMs assumed from fluorescence pictures. After doping of the polymer backbone, protons are provided with continuous pathways between phases of the polymer network and segregated globules of ILs, and therefore QSILMs achieve good conductive properties. Different conductivity values of composite membranes are reported in the literature due to various experimental conditions [34]. Thus, Wang and Hsu reported conductivities for the QSILM-based aprotic ionic liquid PBI / 2[C₆H₄C₆H₄][OTf] at anhydrous conditions of about 10 mS cm⁻¹ at 240 °C whereas only 5 mS cm⁻¹ was achieved at 160 °C [10]. These authors demonstrated as well that the increase in IL content improves the conductivity.

Previously a few research groups have already made an effort of combining ILs and PA as mixed electrolyte [39–41]. For example, Ye et al. proposed a gel-type PBI membrane containing 1-methyl-3-propyl-methylimidazolium dihydrogen phosphate ([C₆H₄C₆H₄][H₂PO₄]) as ionic liquid and additional PA [39]. The maximum reported conductivity for a PA/ [C₆H₄C₆H₄][H₂PO₄] / PBI membrane (2/4/1) reached 2 mS cm⁻¹ at 150 °C under anhydrous conditions. In this work we could obtain conductivity values one order of magnitude higher under similar conditions for doped QSILMs. Rewar et al. fabricated the blended PBI membrane containing polymeric IL poly(diallyldimethylammonium) trifluoromethanesulphonate P[DADMA][OTf] and doped with PA [40]. They reported through-plane conductivities up to 7 mS cm⁻¹ at 150 °C for PBI with 45 wt.% of [DADMA][OTf] and a doping level of 23 mol PA per repeat unit. This doping level is twice higher than the doping level we used in our work for QSILMs which can lead to leaching of free PA into GDE. As it was mentioned before, in our experiments no leaching was observed for doped QSILMs at room temperature.

Membranes containing [HHTMG]⁺ cations exhibited lower performances in fuel cell tests than those with [DEMA]⁺ cations despite having higher conductivities. However, it should be stressed that the membrane 1.1d was 70 μm thick, whereas the membrane 2.2d was 100 μm thick. Rewar et al. [40] observed a maximum performance for the composite PBI membrane containing 25 wt.% of [DADMA][OTf] and 107.3 wt.% PA uptake and reached 0.5 W cm⁻² at
160 °C in H₂/O₂ fuel cell. No data on the tests under higher temperatures and air flow on the cathode side were provided. These authors reported the utilization of Nafion solution during the catalyst ink preparation which is not favorable for operation at the temperatures above 100 °C as was discussed before. Therefore fuel cell test remain the main tool to evaluate the performance of the membrane.

We suppose that QSILMs structures with acid post-doping are beneficial for immobilization of ILs inside a polymer matrix due to its closed pore structures preventing them from leaching out during the operation in a fuel cell. Moreover we assume that acid post-doping has a tremendous effect on the conductive properties of the studied QSILMs not only due to the protonating PBI backbone back also due to diffusion of free PA in the closed pores filled with ILs providing non-stoichiometry to the electrolyte.

Thus, Smith and Walsh [34] thoroughly studied [DEMA][TfO] as electrolyte for non-humidified fuel cells by means of comprehensive electrochemical analysis. In their work they concluded that protic ILs cannot support proton shuffling between the electrodes of fuel cells due to their (tentative) vehicle mechanism of proton transport; protic ILs seem to require inclusion of dissolved acidic or basic proton shuttles in order to be utilized as electrolyte [34]. According to the mechanism that was proposed in their work, we assume the following mechanism for our IL.

For the protic ILs [DEMA][NTf2] and [HHTMG][NTf2], the ionization (protonation-deprotonation) occurs by proton exchange between the proton donor and acceptor:

\[
\begin{align*}
\text{a) } & \quad \text{DEMamine} + \text{Tf}_2\text{NH} \rightarrow \text{DEMA}^+ + \text{NTf}_2^- \\
\text{b) } & \quad \text{HTMG} + \text{Tf}_2\text{NH} \rightarrow \text{HHTMG}^+ + \text{NTf}_2^-
\end{align*}
\]

The driving forces are

\[
\begin{align*}
\text{a) } & \quad \Delta pK_a^{\text{DEMA-NTf2}} = pK_a^{[\text{DEMA}]^+} - pK_a^{[\text{NTf}2^-]} = 10.5 \text{ (10)} = 20.5 \quad [44] \\
\text{b) } & \quad \Delta pK_a^{\text{HHTMG-NTf2}} = pK_a^{[\text{HHTMG}]^+} - pK_a^{[\text{NTf}2^-]} = 13.9 \text{ (10)} = 23.9 \quad [45]
\end{align*}
\]

The Gibbs free energy for the ionization is then given by:

\[
\begin{align*}
\text{a) } & \quad \Delta G^o = -2.303 \, RT \, \Delta pK_a = -117.0 \text{ kJ/mol} \\
\text{b) } & \quad \Delta G^o = -2.303 \, RT \, \Delta pK_a = -136.4 \text{ kJ/mol}
\end{align*}
\]

When these ILs are solely consisting of [HHTMG]+ cations and NTf₂⁻ anions, i.e. in the absolute absence of excess HTMG, the only proton acceptor is NTf₂⁻ and similarly in the absolute absence of Tf₂NH, the only proton donor is [HHTMG]+.

In fuel cells the hydrogen oxidation at the anode needs a proton acceptor to carry the produced protons away. It has always been assumed that bases function as proton acceptors and the anode half-reactions are hence:

\[H_2 + 2 \text{HTMG} \rightarrow 2 [\text{HHTMG}]^+ + 2e^-\]

And then the [HHTMG]^+ ions as the proton carriers travel through the PIL electrolytes and deliver the proton to the cathode for the oxygen reduction reaction:
\[ \frac{1}{2} \text{O}_2 + 2 \text{[HHTMG]}^+ + 2e^- \rightarrow 2 \text{HTMG} + \text{H}_2\text{O} \]

Thus the overall reaction is simply:

\[ \frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \]

This, however, can never be the case because there is hardly any molecular any HTMG in the pure PILs. At the anode the only proton acceptor is [NTf₂]⁻, not the bases. The anode half-reaction should therefore be:

\[ \text{H}_2 + 2 \text{[NTf}_2]\text{]}^{-} \rightarrow 2 \text{NTf}_2\text{NH} + 2e^- \]

And the formed NTf₂NH, if possible at all, is not the charge carrier that is transporting protons through the electrolyte from the anode to the cathode. At the cathode the only proton donor, which is involved in the oxygen reduction reaction, is the protonated [HHTMG]⁺. This means that the only possible cathode half-reaction is:

\[ \frac{1}{2} \text{O}_2 + 2 \text{[HHTMG]}^+ + 2e^- \rightarrow 2 \text{HTMG} + \text{H}_2\text{O} \]

As a result the overall reaction will be

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 + 2 \text{[NTf}_2]\text{]}^{-} + 2 \text{[HHTMG]}^+ \rightarrow 2 \text{HTMG} + 2 \text{NTf}_2\text{NH} + \text{H}_2\text{O} \]

This is the sum of the two reactions:

\[ \frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \quad \Delta G^0 = -237 \text{ kJ/mol}[34] \]

\[ 2 \text{[NTf}_2]\text{]}^{-} + 2 \text{[HHTMG]}^+ \rightarrow 2 \text{[HTMG]} + 2 \text{[NTf}_2]\text{]}^{-} \quad \Delta G^0 = 136.4 \text{ kJ/mol} \]

Therefore, the free reaction enthalpy for the total reaction can be estimated to be in the range of \( \Delta G^0 = -237 \text{ kJ/mol} + 2 \cdot 136.4 \text{ kJ/mol} = 35.8 \text{ kJ/mol} \), which makes the reaction impossible to occur or at least energetically unfavorable (including temperature effects etc. in the calculation).

This phenomenon supports the idea of synergy effect of protic ILs and PA post-doping proposed in this work, in accordance with considerations in a recent paper by Watanabe et al. [46].

The potential drawback of the post-doping would be the leaching of PA into the catalyst layer of a GDE. Since PA loses water and undergoes thermal decomposition at temperatures above 150 °C, it seems important to find alternative electrolytes/binders for the catalyst layer which could demonstrate good durability at temperatures above 200 °C in order to increase the performance of a fuel cell and integrate the system with a reforming unit without heat losses. Traditionally PBI was used as a binder for HT-PEMFCs which required impregnation with acid in order to be protonated. In this work we fabricated PBI-free GDE by means of spraying followed by impregnation with the corresponding IL. We observed that the MEA carrying IL in the catalytic layer exhibits a performance twice lower than the one with PA in GDE whereas it provides better stability revealed during the long-term durability test operated at non-humidified conditions and 200 °C.

5. Conclusions
Quasi-solidified ionic liquid membranes containing [DEMA][NTf₂] and [HHTMG][NTf₂] were fabricated with different contents of ILs by means of blending into the polymer solution and solution casting. To the best of our knowledge for the first time the performances of PBI based QSILMs membranes in H₂/air HT-PEMFC were tested. MEAs fabricated with PA doped QSILMs and PA doped GDEs showed performances comparable to state-of-the-art PA doped PBI membranes. The maximum power density was obtained for MEA_1.1d at 200 °C and reached 0.32 W·cm⁻² at 900 mA·cm⁻². It was found that the performance depends on several factors apart from conductivity, such as MEA elaboration, membrane thickness and catalyst treatment, and cannot always be predicted. According to Smith and Walsh [34] IL supported by an open-porous PBI cannot be employed in a fuel cell. Theoretically the poor performance could be also related to leaching leading to a serious disruption of the conductive path; therefore, the closed porosity of QSILMs has a high importance. However, ILs immobilized in closed PBI pores do not show high conductivity because of the very high resistance of pure PBI matrix. Doping with PA not only strongly reduces the resistance of PBI pore walls, connecting the IL domains, but also allows to draw a direct protonic current through the IL, possibly by doping the IL with PA, as an additional proton source, hydrogen bond donor and acceptor. So only the combination of encapsulation and acid post-doping enables the employment of immobilized ILs in HT fuel cell membranes.

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