Ionic (Proton) Transport and Molecular Interaction of Ionic Liquid–PBI Blends for the use as Electrolyte Membranes

Jingjing Lin,a,b Sabine Willbold,c Tatiana Zinkevich,d Sylvio Indris,d and Carsten Korte,a,b\*

a Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research - Fuel Cells (IEK-14), 52425 Jülich, Germany

b RWTH Aachen University, 52062 Aachen, Germany

c Central Institute for Engineering, Electronics and Analytics, Analytics (ZEA-3), Jülich, Germany

d Institute for Applied Materials-Energy Storage Systems (IAM-ESS), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

KEYWORDS: protic ionic liquid, fuel cell, polymer electrolyte membrane, proton transport, molecular interaction

**ABSTRACT**

Protic ionic liquids (PILs) are discussed as new candidates for the use as non-aqueous electrolytes for fuel cells operating at temperatures above 80 °C. The molecular inter­actions in Diethylmethylammo­nium triflate ([Dema][TfO]) doped polybenzimidazole (PBI) blend membranes and the proton transport mechanism were investi­gated by means of TGA, IR and NMR. The mobility of the PIL ions is restricted to the PBI host polymer. The [Dema]+ cations and [TfO]− anions interact strongly via H bonds with the polar groups of the PBI chains. This will significantly confine the proton con­ductivity of the membrane to vehi­cular transport. The proton transport was investi­gated by comparing to an analogous liquid state model using the monomer benzimi­dazole (BIm) instead of the PBI polymer. During fuel cell operation, it is unavoidable that residual water is present in significant quantities. Resulting from 1H-NMR and PFG self-diffu­sion measure­ments, proton transport in the liquid state model takes place via a co­operative mecha­nism involving all of the species NH[Dema]+/NHBIm/H2O depending on the water fraction. Thus, it is suggested that conductivity in the PIL–PBI membrane be mainly provided by the cooperative transport of the protons. This study is intended to broaden understanding of the structure and proton transport mechanism, as well as to give possible ways to optimize PIL electrolyte doped polymer blend membranes for intermediate operating temperatures.

**1. INTRODUCTION**

Research on polymer electrolyte fuel cells (PEFCs), able to operate at tem­perature of 80–160 °C, has attracted much attention. An elevated operating temperature offers several advan­tages compared to fuel cells operated at lower temperatures (< 80 °C), such as: simplified water management (no feed gas humidification, respectively no water recyclation), more effec­tive cooling of the cell, reduced poisoning due to feed gas impurities, and improved activity of the Pt electrode catalyst leading to a reduced Pt catalyst loading of the electrodes.[[1](#_ENREF_1), [2](#_ENREF_2)] However, the development of this intermediate temperature PEFC is also facing challenges: at elevated tempera­tures (>80 °C), the water vapor pressure (relative humidity) is very low. The proton transport mechanism that only relies on the presence of water will not take place.[[3](#_ENREF_3)]

Currently, so-called high temperature (HT-)PEFCs are based on phosphoric acid (H3PO4)-doped polybenzimidazole (PBI) membranes and can be operated at 160–180 °C.[[4-9](#_ENREF_4)] Protonic charge carriers are formed due to a strong autoprotolysis (H4PO4+ + H2PO4−), which provides high proton conductivity also at very low water concen­trations.[[10](#_ENREF_10), [11](#_ENREF_11)] However, the presence of H3PO4 is causing a slow cathodic oxygen reduc­tion reaction (ORR) kinetics.[[12](#_ENREF_12)] This is primarily due to an inhibition (poisoning) effect by the specific adsorption of H3PO4 and its anionic species on active sites of the redox catalyst platinum but also due to an insufficient oxygen solubility and diffusivity.[[13](#_ENREF_13), [14](#_ENREF_14)] Meanwhile, these membranes are difficult to operate below 160 °C as the conductivity will drop to insufficient values. Thus, there is a necessity for alternative non-aqueous proton-conducting electrolytes opera­tional for the intermediate temperature range of 80-160 °C.[[15-19](#_ENREF_15)]

Protic ionic liquids (PILs) have received much attention for possible use as an electrolyte in PEFCs at temperatures above 80 °C. [[20-24](#_ENREF_20)] PILs with anions based on very strong acids, respectively super acids as trifluoromethanesulfonic acid or bis-trifluoro­methyl­sulfonimid, have a less inhibiting effect than H3PO4 because these anions, *e.g.* triflate CF3SO3− or triflimid (CF3SO2)2N−, are less strongly adsorbed on Pt than H3PO4 or H2PO4−.[[13](#_ENREF_13), [25](#_ENREF_25), [26](#_ENREF_26)]Diethylmethylammonium triflate ([Dema][TfO]), a commercially available PIL, has been widely investigated, due to its excellent properties in terms of a wide electro­chemical window, high thermal stability and sufficient oxygen solubility and diffusi­vity. [[27](#_ENREF_27)] Nakamoto et al. investigated almost 70 different PILs and noted the well-balanced bulk properties of [Dema][TfO] as a fuel cell electrolyte at medium tem­peratures. [[28](#_ENREF_28)] Meanwhile, Liu et al. tested the properties of [Dema][TfO] doped PBI membranes. A high ionic conductivity of up to 20.73 mS cm−1 at 160 °C was observed. [[29](#_ENREF_29)]

In a water-free PIL, protons can only be transported via the protonated cations by means of a vehicular mechanism, as has been observed in bulk [Dema][TfO].[[30](#_ENREF_30)] However, in a solid proton exchange membrane (PEM) electrolyte, the vehicular trans­port of the rela­tively large PIL cations (and anions) is sterically restricted due to the con­strained space and directed interactions. During fuel cell operation water will be produced on the cathode side. A water uptake depending on the equilibrium water vapor pressure of the PIL will unavoidably take place also above 100 °C.[[31](#_ENREF_31), [32](#_ENREF_32)] Thus, the investigation of the mole­cular interaction and proton transport mechanism[[33-36](#_ENREF_33)] would be essential to opti­mize the durability and conductivity of PEMs based on PIL electrolytes.

In this contribution, we present an experimental study of PEM electrolytes, con­sisting of the ionic liquid [Dema][TfO] and PBI as a host polymer with basic moieties. Membrane with a composition from 1 to 4 [Dema][TfO] molecules per PBI repeating unit were prepared, and are denoted as [Dema][TfO]-PBI, *λ*PIL = 1–4 (abbreviated to DP1–DP4). The interactions between the [Dema][TfO] cations and anions and the PBI chains were determined by means of TGA, IR, (MAS-) 1H-NMR and 19F-NMR. The thermal stability of the membranes under the operating con­dition was ensured and the capacity for water uptake was calculated. To maximize understan­ding of the interaction with water, as well as the proton transport mechanism, a liquid state model was used. The monomer benz­imidazole (BIm) features the same basic functional group as the polymer PBI. By mixing appropriate amounts of [Dema][TfO], BIm and H2O at various molar ratios, liquid state models with a composition varying from 2 : 1 : *n* (*n* = 0–4) were used. The cooperative proton transport mechanism was determined by means of 1H-NMR spectroscopy, respectively by applying the pulsed-field gradient tech­nique (PFG). Thereby, a model of proton transport processes in the [Dema][TfO]-PBI membrane during operating condition could be compiled.

**2. EXPERIMENTAL**

**2.1 Materials**

Diethylmethylammonium triflate [Dema][TfO] (CAS No.: 945715-39-9), with a nomi­nal purity of > 98 wt%, was purchased from IoLiTec GmbH (Germany). Poly-[(1-(4,4′-diphenyl­ether)-5-oxybenzimidazole)-benzimidazole] powder (PBI-OO) was obtained from FuMA-Tech GmbH (Germany). The PBI-OO is denoted as PBI hereinafter for the sake of simplicity. Dimethyl sulfoxide (DMSO) (≥99.9%) was purchased from VWR chemicals and Benzimidazole (BIm) (99%) from Alfa Aesar GmbH (Germany) and used without further purification.

**2.2 Preparation of PIL-PBI blend membranes**

PBI powder was dissolved in DMSO to obtain a 5 wt.% solution. An appropriate amount of the PIL [Dema][TfO] was added to the solution. The ratio *λ*PIL of the molar amount of the PIL to the molar amount of the repeat units of the PBI polymer is defined as follows:

(1)

Samples with a ratio *λ*PIL adjusted to a value of 1, 2, 3 and 4 were prepared. The homogeneous solution was stirred for 4 h at 70 °C. Then, the solution was cast onto a glass slide and dried at 80 °C for 48 h and subsequently at 150 °C for 8 h to remove the residual solvent (DMSO) and water. The content of the [Dema][TfO] in the PIL-PBI blend membrane was 36 – 70 wt. %, corresponding to *λ*PIL= 1 – 4. For the sake of simplicity, the casted [Dema][TfO]-PBI blend membranes with a *λ*PIL = 1, 2, 3 and 4 were denoted as DP1, DP2, DP3 and DP4, respectively.

**2.3 Characterization of the PIL-PBI blend membranes**

The thermal stability of the PIL-PBI blend membranes and as well of the pure PBI and the pure PILs, was examined using a TGA (Perkin Elmer STA 6000). The samples were heated up in air, starting at room temperature up to 800 °C with a rate of 5 °C min−1. The weight loss was measured and reported as a function of temperature. The baseline correction was performed with an empty crucible by using the identical measurement program. ATR-IR spectra of the PIL-PBI blend samples and of the neat PIL were measured in reflection mode in the range of 500–4000 cm-1 (Monolithic diamond GladiATR, PIKE Technolo­gies). The experiments were carried out at room temperature.

1H and 19F MAS NMR spectroscopy were performed using a Bruker Avance 500 MHz spectrometer at a magnetic field of 11.7 T, corresponding to resonance frequencies of 500.2 MHz and 470.6 MHz, respectively. Spinning was performed in 2.5mm rotors at 25 kHz. The spectra were acquired with a single-pulse sequence, a π/2 pulse length of 3.4 μs for 1H and 7.0 μs for 19F, and a recycle delay of 20 s for 1H and 30 s for 19F. Chemical shifts are referenced to tetramathylsilane for 1H and to CFCl3 for 19F.

1H and 19F PFG-NMR was performed at a magnetic field of 7.0 T and with pulsed field gradient of up to 10 T/m. A stimulated-echo pulse sequence with bipolar gradients was used to observe the echo damping as a function of gradient strength.

**2.4 The equilibrium water content of the PIL-PBI blend membranes**

The moisture sensitivity of the PIL-PBI blend membranes DP2 and DP4 was investiga­ted at a temperature of 80 °C and at 40% relative humidity (RH). The weight of the 2 cm × 4 cm rectangular test PIL-PBI blend membrane strips, was measured with a microbalance before equilibrating them in a climate chamber at 80 °C/40% RH for a certain time. The test strips were taken out and immediately weighed to measure the membrane’s weight in its hydrated state. After weighing, the membrane was placed back to the climate chamber to proceed with the treatment. The equilibration and weighting steps were repeated until a total equilibration time reached 45 h. The final weight in its hydrated state will be denoted as. The composition of the sample DP4 before and after the treatments was checked by TGA.

The original and final equilibrium water content in the membrane samples was measu­red by Cou­lometric Karl-Fischer titration (852 Titrando / Metrohm company) before and after the humidification. For each membrane sample, three pieces with a size of 1 cm × 1.5 cm were measured before and after the treatment to obtain the original water content, and the final water content,. The equilibrium number of water molecules *λ* in the membrane per repeating unit of the polymer before and after the humidification experiment is defined as in Eq. (2):

and (2)

where and are the molar amounts of H2O before and after the humidi­fica­tion and is the molar amount of the PBI repeating units in the membrane sample. According to Eq. (1), the number of PIL (ion pairs) in the membrane per repeating unit of the polymer after the humidification experiment is defined as follows:

(3)

where is the molar amounts of the PIL in the membrane sample after the humidi­fication experiment. Considering that the molar mount of the polymer, respecti­vely its mass , does not change during the humidification, the mass of the samples before and after the humidification as well as Eq. (2) and (3):

and , (4)

it can be derived: [[1]](#footnote-1)

(5)

Hereby, and are the mass fractions of water, respectively, and are the weights of the membrane sample before and after the humidification treatment. Eq. (2) and (5) yield the equilibrium number of water in the membrane before and after the humidification measurement *λ*:

and (6)

During the humidification measurements, the PIL in the blend membrane may leak out and thus the composition of the membrane after the humidification may diffe­r from the originally adjusted composition , see Eq. (1). The changed composi­tion of the membrane can be obtained:

(7)

In the case of the samples DP2 and DP4, the originally adjusted composition before the treatment is 2 and 4, respectively.

**2.5 Preparation of the liquid state PIL-BIm-H2O model system**

The liquid state model systems [Dema][TfO]-BIm were prepared to analyse the mole­cular/ionic interactions. As there are two imidazole groups per PBI repeating unit in PIL-OO, in the case of the DP2 and DP4 membrane samples the molar ratio of the PIL:imida­zole groups is 1:1 and 2:1 (*λ*=2 and 4), respectively. Thus, to obtain a liquid state model compound with a ratio PIL:imidazole groups that corresponds to the DP4 samples a molar ratio of PIL:BIm = 2:1 is required. The mixture of the ionic liquid [Dema][TfO] and BIm was prepared by slowly adding BIm powder into [Dema][TfO] while stirring at 60 °C. The mixture was stirred for 4 h at 60 °C until completely homogenisation.

To investigate the influence of water, an appropiate amount of water was added into the [Dema][TfO]-BIm mixture. The molar ratio of [Dema][TfO] : BIm : H2O was adjusted to 2 : 1 : *n* (*n* = 0–4). For the sake of simplicity, the samples are denoted hereinafter as DBH (*n* = 0–4).

**2.6 Spectroscopic investigations of the liquid state PIL-BIm-H2O model system**

The acquisition of the NMR data was performed by using a Bruker 600 MHz spec­tro­meter, equipped with a 5 mm cryoprobe. Capilla­ries filled with D2O were included in the sample tubes to be used as a field lock.

The self-diffusion coefficients were measured by using the PFG/DOSY technique. The values of the gradient duration δ, diffusion time Δ and gradient strength were opti­mized to give rise to at least 80 % signal attenuation at strongest gradient field.

**2.7 Proton conductivity**

The conductivities of the liquid state model compounds were measured in a four-probe conductivity cell by applying an AC voltage and using platinum electrodes. The cell con­stant as a function of the sample volume was determined by using a 0.1 M KCl solution for calibration. The intended H2O contents of the ternary [Dema][TfO] + BIm + H2O =2 : 1 : *n* (*n* = 0–4) mixtures were verified by Karl-Fischer titration at the beginning of each measurement. The total ohmic resistance σ of the [Dema][TfO] : BIm : H2O mix­tures as a function of temperature *T* was determined by means of impedance spectro­scopy. The temperature *T* was increased in increments of 10 °C from 60 to 100 °C and vice versa. The AC excitation amplitude was adjusted to 10 mV. The specific conduc­tivity σ is calculated by using the cell constant.

**3 RESULTS AND DISCUSSION**

**3.1 Molecular interaction of PIL-PBI blend membranes**

***IR-Spectroscopy***

The interaction between [Dema][TfO] and PBI can be monitored by IR-ATR spectro­scopy. The IR-ATR spectra of the PBI membrane, [Dema][TfO] and the DP4 membrane are depicted in Figure 1. In the case of the PBI, the spectral region comprising 1550 and 1650 cm−1 is characteristic for the benzimidazole moiety. The band at 1598 cm−1 is generally assigned to a resonance between the fused benzene and imidazole rings, whereas that at 1633 cm−1 is caused to a C=C/C=N stretching mode. [[37](#_ENREF_37), [38](#_ENREF_38)] In the [Dema][TfO]-PBI blend membrane DP4, *i.e.* with four equivalents [Dema][TfO] per repeat unit PBI, the bands at 1598 and 1633 cm−1 slightly shift up to 1600 and downwards to 1631 cm−1, respectively. This can be attributed to a weakened conjugation effect as a result of a partial proton transfer to a N atom which shifts electron density the imida­zole ring and thus a decreasing absorption frequency of the second mode. Correspon­dingly, the increasing electron density on the C=N bonds of the hetero cycle leads to a raising absorption frequencies of the first mode. [[39](#_ENREF_39)] These observations indicate a direct interaction between the [Dema][TfO] and the imino nitrogen atoms of the benzimidazole moieties in PBI chains. [[38](#_ENREF_38), [40](#_ENREF_40), [41](#_ENREF_41)]



**Figure 1.** IR-ATR spectra of neat PBI (blue), neat [Dema][TfO] (orange) and of the DP4 blend membrane (red).

***NMR-Spectroscopy***

Neat PBI and the DP2 and DP4 samples were investigated by solid-state MAS-NMR. The 1H and 19F NMR spectra of the membrane samples are depicted in Figure 2. In all membrane samples, the 1H signals of PBI polymer are extremely broad and thus difficult to discern. Only the protons of the CH3 and CH2 groups of the [Dema]+ cation, *i.e.* the signals **e**, **f** and **g** (as shown in the NMR spectra of the liquid state model systems in Figure 5) have an FWHM that allows a clear assignement by MAS-NMR. They can be observed at 3.3, 2.8 and 1.3 ppm, respectively. The signal of the F atoms in the [TfO]− anion can be found at −177.6 ppm in the case of the sample DP2, and slightly shift to −177.5 ppm for the sample DP4. The narrow 1H-signals of the [Dema]+ cation and as well narrow 19F-signal of the [TfO]− anion suggest a certain mobility of the [Dema][TfO] ions between the PBI chain which shortens the relaxation time, which may indicate the weak interaction between the cation, anion and PBI.



**Figure 2.** (a) 1H-MAS-NMR and (b) 19F-MAS-NMR spectra of the DP2 and DP4 membrane samples and neat PBI.

***Thermogravimetric analysis (TGA)***

In order to maintain stable PEFC operation in the intended temperature range of 80–160 °C at varying humidity, the electrolyte membranes should provide sufficient thermal and moisture stability. TGA measurements of the DP1, DP2, DP3 and DP4 membrane samples, as well as of neat PBI and [Dema][TfO] were performed to evaluate the ther­mal properties, as depicted in Figure 3 (*m*/*m*0 *vs.* *T*).

Various experimental studies on PBI doped with H3PO4 have been reported in the literature. It is shown that the benzimidazole moieties of the polymer are fully protona­ted by H3PO4 due to its high acidity. [[39](#_ENREF_39)] However, in the case of the [Dema][TfO]-PBI blend membranes, the acidity of [Dema][TfO] (of the Dema+ cation [[42](#_ENREF_42)]) is accor­ding to its pKA value of 10.55 and is not able to fully pro­tonate the benzimidazole moieties of PBI as the pKA of the conjugated acid, *i.e.* benzimidazolium+, has a value 5.6. Thus, the observed interaction between [Dema][TfO] and PBI may be different compared to high acidic electrolytes like H3PO4.



**Figure 3.** TGA curves of the DP1, DP2, DP3 and DP4 membrane samples in comparison to the curves of neat PBI and [Dema][TfO]. The relative weight m/m0 is plotted against the temperature *T*.

According to Figure 3, neat PBI shows an excellent thermal stability. The polymer begins to decompose above 480 °C. [[43](#_ENREF_43)] The weight loss below 200 °C might be attribu­ted to residual water and solvent. In the case of neat [Dema][TfO], the decomposition starts at about 290 °C. The [Dema][TfO]-PBI blend membranes exhibit a good thermal stability. At a temperature of 250 °C, 380 °C and 500 °C, three weight loss steps Δ*m*/*m*0 can be observed, marked with (s1), (s2) and (s3) respectively. The step (s3) at 500 °C can be safely attributed to the decomposition of the PBI polymer:

**s3:** PBI + x O2 = CO2 + N2 + volatile hydrocarbons + C-rich residuals (8)

Hereby, “PBI” represents one polymer repeating unit. In the case of the decomposition step (s2) at 250 °C, the increasing (relative) mass loss Δ*m*/*m*0 at 250 °C, *i.e.* from DP1 to DP4, is proportional to the in­creasing content of [Dema][TfO].

The first weight loss step (s1) found in the TGA curves of the DP membranes is lower than the decomposition temperature of neat [Dema][TfO], *i.e.* due to a proton transfer from [Dema]+ to [TfO]− and subsequent evaporation of diethylmethylamine and TfOH at 290 °C:

**s1:** (C2H5)2CH3NH+ ∙ CF3SO3− = (C2H5)2CH3N ↑ + CF3SO3H ↑ (9)

but higher than the boiling point of the diethylmethylamine at 66 °C. Thus, the [Dema]+ cation may be interacted with PBI by weak H-bonds. The decomposition by proton transfer from [Dema]+ to the benzimidazole moiety of the polymer and subsequent eva­poration of the neutral base does not start before 250 °C due to its significant lower acidity compared to the protonated benzimidazole moiety:

**s1’:** 2*x* (C2H5)2CH3NH+ ∙ CF3SO3− + *x* PBI =  
 *x* (C2H5)2CH3N ↑ + (PBI-H2+)*x* ∙ (CF3SO3−)2*x* (10)

In the case of a ratio of two equivalent PIL units per repeat unit of the polymer PBI, both imidazole groups of the repeat unit will be occupied by direct interactions with the acidic [Dema]+ cations, and with the [TfO]− anions, respectively. If more than two equivalents of the PIL are present, *i.e.,* in the cases of samples DP3 and DP4, no direct interaction between the excess [Dema][TfO] and imidazole moieties is (theoretically) pos­sible. Only weak H-bonds among the PIL ions can be expected. The first weight loss step (s1) may include both, a loss of diethyl­methyl­amine due to the decomposition of the excess [Dema][TfO] as given in Eq. (8) and a loss of diethylmethylamine due to a pro­ton transfer to the polymer as conveyed in Eq. (9). A “polymer salt” (PBI-H2+)*x* ∙ (CF3SO3−)2*x* is formed. The following weight loss step (s2) at about 380 °C indicates its decomposition temperature: [[44](#_ENREF_44)]

**s2:** (PBI-H2+)*x* ∙ (CF3SO3−)2*x* = *x* PBI + 2*x* CF3SO3H ↑ (11)

The assumptions above could be confirmed by calculating the compositions of the samp­les. The mass percentage of each steps in the TGA curves, assigned as *% in TGA*, and the theoretical mass percentages of each compositions in the prepared samples, assig­ned as *% in theo.*, are calculated for comparison. The results are as listed in Table 1. For all the samples, the theoretical calculated compositions in the membranes fit well to the TGA weight losses. Thus, when considering the extent of the steps in the TGA, the weight losses in the TGA curves at 250 °C, 380 °C and 500 °C can be attributed to (s1) the loss of excess (free) [Dema][TfO] and the diethylmethylamin due to the proto­na­tion of the PBI, forming (PBI-H2+)*x* ∙ (CF3SO3−)2*x* , (s2) the loss of TfOH due to the decom­po­sition of (PBI-H2+)*x* ∙ (CF3SO3−)2*x* and finally (s3) a complete decomposition of PBI, forming CO2, N2, hydrocarbons and C-rich residuals.

**Table 1.** Mass percentage of the compositions in the membranes and TGA curves.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | (s1) a : weak bonded [Dema][TfO] + bonded [Dema] | | (s2) a : bonded [TfO] | | (s3) a : PBI | |
| % in theo.b | % in TGAc | % in theo. | % in TGA | % in theo. | % in TGA |
| DP1 | 13.3 | 9.2 | 23.0 | 23.4 | 63.7 | 65.5 |
| DP2 | 19.5 | 17.0 | 33.7 | 30.2 | 47.0 | 51.0 |
| DP3 | 36.4 | 32.3 | 26.6 | 28.1 | 36.9 | 37.7 |
| DP4 | 47.5 | 42.8 | 22.0 | 25.3 | 30.0 | 30.5 |

a The decomposition steps in Figure 1.

b The theoretical mass percentage in the membrane samples according to the initial membrane preperation composition.

c The mass percentage obtained roughly by the TGA curves.

The molecular interaction in [Dema][TfO]-PBI blends was also investigated by R. Pant et al. by a MD simulation. [[45](#_ENREF_45)] Both the results of the computa­tional study and the experimental study suggest that the cation and the anion interact with the N atoms of the benzimidazole moiety via hydrogen bonds. The interaction of the [TfO]− anion is stronger compared to the [Dema]+ cation. [[45](#_ENREF_45)]

**3.2** **Impact of H2O on the molecular interaction and proton transport**

***Stability and equilibrated water/ PIL content of the PIL-PBI membranes***

During fuel cell operation, the presence of a significant amount of residual water is unavoidable even at elevated temperatures. In the temperature range of 80–160 °C, a dynamic change of water content will unavoidably take place depending on the electri­cal load. A water uptake may challenge the stability of the membrane regarding de­mixing phenomena. The moisture sensitivity of the [Dema][TfO]-PBI membranes are evaluated by treating the membranes under high humidity operating condition 80 °C/40% RH for 48 h. Compared to H3PO4 doped PBI membranes [[46](#_ENREF_46)] with a doping level of 11 H3PO4 molecules per PBI repeat unit which corresponds to weight fraction of 87 wt% H3PO4 in the membrane, the DP4 membrane sample with 70 wt% [Dema][TfO] is substantially more stable. Only < 5 wt% weight loss can be observed in both the DP2 and DP4 membranes. By comparing the TGA curves of the DP4 membrane before and after the 48 h moisture treatment, the composition of the weight loss is due to the trace leakage of the [Dema][TfO], as can be reckoned in Figure 4 (a). Thus, the interaction between the [Dema][TfO] and PBI is relatively stable during the operation condition.

It is well known that PBI is hydrophilic and has an affinity for moisture. It has been repor­ted that it is able to absorb about 15 wt% of water under an ambient atmosphere (40 RH%) at room temperature. This corresponds to about three water molecules per repeating unit, *i.e.* molar ratio H2O : PBI of 3 : 1. [[47](#_ENREF_47)] Figure 4 (b) shows the composition of the mem­brane, as well as the equilibrium water/ PIL content in DP2 and DP4 membrane samples before and after the 48 h moisture treatment. Prior to the treatment, the membranes were placed at ambient condition for more than 5 days. This yielded an initial value of the mem­brane water capacity. After the 48 h moisture treatment, a molar ratio H2O : [Dema][TfO] : PBI of 1.8 : 1.8 : 1 could be measured in the DP2 membrane sample and of 2.8 : 3.8 : 1 in the DP4 membrane sample (per PBI repeat unit).

The neat [Dema][TfO] has a rela­tively low hygroscopicity. [[42](#_ENREF_42)] The equilibrium water content of the neat [Dema][TfO] at 80 °C / 40 RH% was 4.4 wt%, *i.e.* a molar ratio H2O : [Dema][TfO] of 0.63 : 1. Considering the [Dema][TfO]-PBI blend membranes, the introduction of [Dema][TfO] occupies the N and N-H functional groups of the PBI polymer. This may suppress a direct H-bond formation between H2O and the polymer.





**Figure 4.** (a) Weight change of the DP2 and DP4 membrane samples and as a reference of H3PO4 doped PBI (87 wt% H3PO4) as a function of time at 80 °C/40% RH, (inset) TGA curves of a DP4 membrane sample before and after the moisture treatment. (b) Equilibrium water/ PIL content per PBI repeat unit in DP2 and DP4 membrane samples before and after the 48 h moisture treatment.

***Molecular interaction in the DBH model system***

Ionic conductivity is an essential parameter that governs the overall performance of a PEM. The conductivity of PIL-PBI blend membrane is highly depended on both, the temperature and the relative humidity, as shown in Figure S1 in supplementary infor­ma­tion section. The proton transport mechanism can be investigated by NMR measure­ments. However, using the NMR technique on solid materials is usually limited due to anisotropic dipole-dipole and quadrupole inter­actions, respectively long relaxation times, leading to very broad and complex signals. Thus, a liquid state model system is prepared for proton transport investigation using the pulsed field gradient (PFG) tech­nique. In order to obtain a liquid state model that maintains the functional groups of the ionic liquid and the PBI polymer, the polymer is replaced by its monomer with the characteristic moieties, *i.e.* a liquid state model system consisting of [Dema][TfO] and benzimidazole (BIm) is prepared. In the liquid state model system, a ratio [Dema][TfO] : BIm of 2 : 1 is adjusted, corresponding to the ratio PIL : basic moieties in the [Dema][TfO]-PBI blend membrane samples DP4. In addition, the water content in the liquid state model systems were varied in the range of 0 to 4 molar equivalents per BIm functional group to obtain conditions comparable to the (humidified) DP4 membrane samples. Thus, the molar ratio of [Dema][TfO] : BIm : H2O is adjusted to 2 : 1 : *n* (*n* = 0–4). The samples are denoted as DBH (*n* = 0–4).



**Figure 5.** 1H-NMR spectra of (a) the DBH (n = 0–4) samples and (b) a mixture of neat [Dema][TfO] and H2O with a molar ration of 1 : 1.

The 1H-NMR spectra of the DBH (*n* = 0–4) samples and a mixture of neat [Dema][TfO] and H2O with a molar ration of 1 : 1 are depicted in Figure 5. The measure­ments were performed at room temperature. The five spectra of DBH (*n* = 0–4) for different water contents in Figure 5. (a) are superimposed with a common baseline in order to facilitate the detection of signal shifts. The spectra are plotted in different colour according to the water content *n*. In the case of sample with a composition [Dema][TfO] : H2O of 1 : 1 in Figure 5. (b), the CH3 protons of the methyl group **f** can be found at 2.8 ppm and the signals of the CH2 and CH3 protons of the ethyl group, **e** and **g**, are at 3.2/3.3 and 1.3 ppm, respectively. A singlet is expected in the case of signal **f**, a quartet for signal **e** and a triplet for signal **f**. Actually, a two multiplets are observed for the CH2 protons. This is also described by Mori et al. and can most likely be attributed to a hindered rotational motion around the C-N bonds (at room temperature), resulting in unisochronous CH2 protons.[[48](#_ENREF_48), [49](#_ENREF_49)] The rotational hindrance is caused by the protonation on the amine N, as in case of the free base the CH2 protons appear (as expected) as a quartet. The signal at 8.3 ppm can be assigned to the N-H proton **d**. The signal of the H2O protons can be identified at 4.0 ppm. The signals of the H2O and N-H protons are clearly detectable and discernible. The detected chemical shifts suggest that no comparatively fast exchange process take place. [[31](#_ENREF_31), [48](#_ENREF_48)] The rate constant for the proton transfer from the [Dema]+ cation to H2O is obviously only very small due to the significant acidity difference between the [Dema]+ (pKA = 10.55) and the hydroxonium cation (pKA = 0) of about ten orders of magnitude. [[42](#_ENREF_42), [50](#_ENREF_50)] Thus, in the system [Dema][TfO] + H2O, the proton resides largely on the amine-N during the NMR sampling process. No averaged signal of H2O and the [Dema]+ cation can be detected due to an extremely slow proton exchange rate between cation and H2O.[[31](#_ENREF_31)]

In the liquid state model system DBH ([Dema][TfO]-BIm-H2O), for the protons situated at the benzene ring of the BIm only two signals **b, c** can be identified at 7.8 and 7.4 ppm, respectively. This indicates a fast exchange of the N-H proton, resulting in isochronous protons in the ortho- and para-position of the benzene ring. At a water content *n* of 0, the C-H proton **a** of the imidazole moiety of BIm is found at about 8.4 ppm. The signal of **a** slightly shift (+0.2 ppm) towards higher magnetic field when *n* increases from 0 to 4. A slight shift (+0.1 ppm) is also observed in the case of the protons **e** and **f** signals from the [Dema]+ cation. The CH3 protons of the ethyl group are not influenced by H2O content and can be found at 1.3 ppm. This is the same for the binary system [Dema][TfO] + H2O. The slight shift of the protons **e, f** and **a** may due to the changing of the local electron density of the N-H moieties in [Dema]+ cation and also in the BIm monomer.

In contrast to the binary system [Dema][TfO] + H2O, in the ternary liquid state model system DBH the signal of the H2O protons does not show up for all investigated H2O contents. There is only one broadened signal **d** thah shifts to a higher field and increa­ses its integral area when increasing the water content *n*, which indicates a fast proton exchange between N-H groups of the [Dema]+ cations and of BIm as well as with water. Thus, only an averaged (and broadened) signal **d** can be detected in the spectrum. This indicates an interaction between [Dema][TfO], BIm and the H2O molecules. The inter­action of the [Dema][TfO] with both the BIm and the H2O molecules is also comfirmed by the shift of the N+-H band with IR in Figure S2 and the 1H-NOESY spectra in Figure S3 in the supplymentary information section.

***Protolysis equilibria***

The p*K*A values of [Dema]+ and H3O+ differ significantly by 10 orders of magnitude. Thus, considering the protolysis equilibrium with H2O the proton resides most of the time on the [Dema]+ cation, because *k*1 should be 10 orders of magnitude smaller than *k*2, *i.e.* the equilibrium constant :

*k*1

CH3(CH3CH2)2NH+ + H2O ⇄ CH3(CH3CH2)2N + H3O+ (12)

*k*2

The p*K*A of HBIm+ has a value of 5.6 and is therefore in the middle between the values of [Dema]+ and H3O+. The acidity differences between [Dema]+ and HBIm+, as well as between HBIm+ and H3O+, are much smaller compared to [Dema]+ and H3O+. Due to the presence of BIm, the protolysis equilibrium in Eq. (12) will be split up in a sequence of two protolysis equilibria involving [Dema]+, BIm/HBIm+ and H2O/H3O+ as follows:

CH3(CH3CH2)2NH+ + C6H4N(NH)CH ⇄ CH3(CH3CH2)2N + [C6H4(NH)2CH]+ (13)

*k*4

*k*3

[C6H4(NH)2CH]+ + H2O ⇄ C6H4N(NH)CH + H3O+ (14)

*k*6

*k*5

The equilibrium constant of the reaction in Eq. (14) is given by the p*K*A value of HBIm+, *i.e.,* . The equilibrium constant of the reaction in Eq. (13) is the quotient *K*A([Dema]+) / *K*A(HBIm+) = *k*3 / *k*4 = (*k*1 *k*6) / (*k*2 *k*5) = 10−4.95. Thus, rate constants *k*3 and *k*5 are about 5 orders of magnutude smaller than *k*4 and *k*6. However, the rate constants *k*3 and *k*5 are still fast compared to the difference in NMR frequencies of the species. The active protons of the species [Dema]+, BIm/HBIm+ and H3O+/H2O, involved in the equilibria in Eq. (12) to (14), cannot be separated by 1H-NMR, if the proton exchange rates are fast compared with the spacings (in Hz) of the corresponding peaks in case of no interaction, leading to a signal at an averaged ppm value, assigned as **d** in Figure 5. The averaging is weighed by the molar fractions of the species in the equilibrium. Despite the deshieding effects of the H-bonds, this may explain why the (averaged) signal shifts towards a lower ppm value, when the water con­tent is increased. When the water fraction *n* is 0, *i.e.* in the (quasi-) anhydrous [Dema][TfO]-BIm samples, only the fast proton exchange reaction according Eq. (13) will occur.





**Figure 6.** (a) Self-diffusion coefficients of the active protons, respectively of different proton carrying species and the TfO− anion of the liquid state [Dema][TfO] : BIm : H2O = 2 : 1 : *n* model system vs. the H2O content n at a temperature of 25 °C. (b) (Total) conductivity of the liquid state [Dema][TfO] : BIm : H2O = 2 : 1 : *n* model system vs. the H2O content *n.*

*Diffusion coefficients and conductivities*

These observations were confirmed by 1H-PFG-NMR measurements of the self-diffusion coefficients. The results for the liquid state model system [Dema][TfO]-BIm-H2O *vs.* the H2O content *n* are shown in Figure 6 (a). For all of the investigated water contents *n*, the diffusion coefficients of the non-active/non-acidic CH protons of BIm and [Dema]+ and thus the self-diffusion coefficients *D*BIm and *D*[Dema]+ are nearly equal. A coupled move­ment due to an interaction by *e.g.* an H bond can be inferred. The self-diffusion coeffi­cients *D*BIm and *D*[Dema]+ should be identical to the diffusion coefficient *D*H*+,*vehicle of the protonic charge carriers due to a vehicular mechanism. With the increasing water content *n*, the slight increase of *D*BIm and *D*[Dema]+ are most likely caused by a decrease of the viscosity.

The self-diffusion coefficient of the active N-H and O-H protons of [Dema]+, BIm/HBIm+ and H3O+/H2O is significantly higher than the values of *D*BIm and *D*[Dema]+ measured for the entire BIm and [Dema]+ cation molecules. The diffusion coefficients of individual protons of the DBH (n =4) model systems measured by DOSY spectroscopy are shown in Fig. S4 in the supplementary information section. The measured value also demonstrates a strong dependence on the water fraction *n* and a linear increase can be obser­ved. Considering the strong shift of the averaged signal of the [Dema]+, BIm/HBIm+ and H3O+/H2O protons **d** in Figure 5 as a function of the water content *n*, the increased mobility is most probably due to fast proton exchange processes between these species, see equilibria in Eq. (12) to (14). Thus, the total self-diffusion coefficient of all mobile protonic charge carriers, *i.e.* of the active NH and OH protons of [Dema]+, BIm/HBIm+ and H3O+/H2O can be identified as a sum of the self-diffusion ceoefficent *D*H+,coop for cooperative transport and of *D*H+,vehicle for vehicular transport of the protonic charge carriers. [[31](#_ENREF_31)]

*D*H+ = *D*H+,coop + *D*H+,vehicle (15)

The linear increase may indicate an increased probability/frequency of proton exchange processes due to an increasing water content.

The (total) conductivity σ of the liquid state DBH (*n* = 0–4) model systems *vs.* the H2O fraction *n* is depicted in Figure 6 (b). The measurements were performed in the tem­perature range of 60 to 100 °C. Consistent with a diffusion coefficient *D*H+ of all mobile protonic charge carriers, the (total) conduc­tivity, , increases as a func­tion of the water fraction *n*, indicating an (quasi-)linear behavior. The conductivity should be provided by the vehicular motion of the [Dema]+ cation, [TfO]− anion and the cooperative transport among the positive charge ions [Dema]+, BIm+ and H3O+. The diffusion coef­ficient *D*H+of all mobile protonic charge carriers can be connected by the Nernst-Ein­stein equation to the (partial) proton conductivity σH+:

(16)

The concentration of mobile protonic charge carriers cannot exceed the concentra­tion of [Dema][TfO]. Using this value with Eq. (16), the obtained partial conductivity is higher than the measured (total) conductivity in Figure 6 (b), indicating a significant fraction of oppositely charged ions moving together in the time scale of diffusive motion (ion pairs). [[51](#_ENREF_51), [52](#_ENREF_52)] It can be expected that due to the coupled movement of the [Dema]+ cation, the [TfO]− anion and BIm molecules, the motion of these neutral, short-lived ion clusters [Dema][TfO]-BIm-[Dema][TfO] only contributes to a (local) vehicular self-diffusion but not to the (long distance) charge transport. The estimation is sup­ported by the identical self-diffusion coefficients of the [Dema]+ cation, [TfO]− anion and BIm molecular. Thus, the conductivity is mainly provided by the proton exchange between the active N-H and O-H protons of [Dema]+, BIm/HBIm+ and H3O+/H2O. Considering the dynamic protolysis equilibrium, the positive charges may partially par­ticipate in the fast exchange process and be detected as *D*H+,coop. The fraction of [Dema][TfO], *i.e.* of the positive charge ions, that participate in fast exchange process can be estimated in accordance with experimental macroscopic conductivity. In the case of the liquid model system DBH with a water fraction of 1.4, at 60 °C, the *D*H+,coop calculated by Eq. (15) yields to 2.1 · 10−6 cm2 s−1. To achieve a conductivity of 17 mS cm−1, as depicted in Figure 6 (b), about 40% of the positive charge carriers should participate to the cooperative transport. At 80 °C, the fraction totals about 22%. When also considering the contribution of the negative charge carriers to the total conductivity, the fraction will further decrease. However, compared to the fraction of the cooperative transport of the positive charge carriers, no more than halved reduction should be caused by the vehicular motion of the [TfO]− anion.

Thus, in the [Dema][TfO]-BIm model system, the active protons are migrating via cooperative mechanism, while the molecules by vehicular mechanism. The presence of water protons also has a role in the proton exchange processes, which benefits the cooperative transport and so the conductivity.

**3.3** **Proton transport in the PIL-PBI membrane**

As noted above, the equilibrium water fraction in the DP4 membrane at 80 °C/40% RH amounts to 2.8 per PBI repeat unit. However, the conductivity of the DP4 membrane at 80 °C/40% RH amounts to 0.1 mS cm-1(see FigureS1 in the supplementary information section), which is two orders of magni­tude lower compared to the liquid-state DBH (*n*=1.4) model system, which is due to the higher steric hindrance of the long PBI chains and the possible inhomogeneous distribution of the PIL/H2O molecules in the solid membrane. Drawing on the solid-state PFG-1H-NMR at 30–70 °C, the diffusion coefficients of the DP2 and DP4 membrane samples are shown in Figure 7. Only the diffusional motion of the [Dema]+ cation and [TfO]− anion are available here. The diffusion coefficients are 2-3 orders of magnitude lower compared to the bulk [Dema][TfO]. [[31](#_ENREF_31)]



**Figure 7.** The normalized 1H-NMR signal intensities of the DP2 and DP4 membranes at 30–70 °C are plotted vs. the gradient strength. The diffusion coefficients of the ions are obtained by fitting the exponential decay of the signal.

It is worth noticing that, the *Di* of both 1H and 19F barely change in the temperature range of 30–70 °C, especially in DP2 membrane. The effect of temperature is potentially subdued and exhibits an insignificantly influence on the diffusion motion of the molecules. In light of the above discussion, it can be assumed that the PIL ions may be spatially restricted by the molecular interaction between the PIL and the PBI. The H-bonds may lead to a (quasi-) localized motion of the [Dema]+ cation and [TfO]− anion. A non-monotonically slight increase is observed in the case of 1H diffusion of DP4. Compared to the DP2, the higher *Di* may due to the weaker H-bonding interaction of the “excess” PIL, thus enhanced mobility. The possible restriction of the molecular motion leads to a limited vehicular proton transport. Thus, the share of cooperative proton transport in the membrane is increasing compared to vehicular transport of protonic charge carriers. This conclusion corresponds to the findings of Liu et al., who calculated the activation energy *Ea* of the proton conductivity of [Dema][TfO] doped PBI membranes. *Ea* is in a range that is common for a cooperative mechanisms, [[29](#_ENREF_29)] whereas in neat [Dema][TfO] it fits to a vehicular mechanism. [[30](#_ENREF_30)]



**Figure 8.** Proton transport in the DP4 membrane during an operation condition.

In accordance with the discussion above, a schematic of the proton transport processes in the [Dema][TfO]-PBI membrane during the operation condition is depicted in Figure 8, *i.e.* considering the presence of water molecules. The composition of the DP4 blend membranes is used as an example. At 80 °C and 40% RH, the number of water mole­cules totals about 3 per PBI repeating unit. [Dema][TfO] is interacting with the imidazole group, as can be inferred through the unified decomposition temperature in TGA curve in Figure 2. However, the proton transfers from the [Dema]+ cation back to the [TfO]− anion are highly improbable, due to the large difference in acidity between the conjugated acid and anion. With the presence of water, fast proton exchange between the NH[Dema]+ / NHBIm / H2O protons is observed by PFG-1H-NMR in the liquid state model system. This should also be the case in the solid membrane, assuming that no further interactions with the ether group and benzene ring on the PBI (PBI-OO) chain occur. The fast proton exchange in the range of the PBI chain would provide dynamic pathways for proton transport. Thus, it is expected that the presence of cooperative proton transport may improve the conductivity in ionic liquid based PBI blend membranes suitable for the application in a future medium temperature fuel cell.

**4. CONCLUSION**

In this study, the molecular interaction and proton transport mechanism of a diethyl­methylammo­nium triflate ([Dema][TfO]) doped polybenzimidazole (PBI) membrane was investigated by means of various experimental methods. It was found that in solid [Dema][TfO]-PBI blend membranes, the [Dema]+ cation and [TfO]− anion are evidently interacting with the imidazole moieties of the PBI. The mobility of the ions is restricted, which leads to a limited degree of vehicular transport. The proton transport mechanism was investigated by using liquid state model system using the benzimidazole (BIm) monomer instead of PBI polymer. A fast proton exchange process of the NH[Dema]+ / NHBIm protons occurred as a result of the interactions between the [Dema]+ cation and BIm. The presence of resi­dual water during the fuel cell operation is able to elevate the rapid cooperative transport in the electrolyte. By varying the water fraction in model compounds, proton conduc­tion takes place via a cooperative mechanism that involves all of the species of NH[Dema]+ / NHBIm / H2O, that result from 1H-NMR and PFG self-diffusion measurements. Thus, it is suggested that the conductivity in the PIL-PBI membrane is primarily provided by the cooperative transport of these protons. There­fore, this work establishes a pathway to understanding the structure and proton transport mecha­nism, as well the optimization of the inter­mediate temperature polymer electrolyte membranes.

Author Contributions

J.L. designed and performed the most experiments and drafted the manuscript. S.W. performed liquid-state NMR measurements. T.Z. and S.I performed solid-state NMR measurements. All authors contributed to the results and discussion and revised the final manuscript. C.K. had a great impact on the revision of the manuscript.

Acknowledgment

This work is partially supported by the China Scholarship Council (Grant No.: 201706060187). We are thankful to C. Wood for proofreading the manuscript.

References

[1] E. Quartarone, P.J.E. Mustarelli, E. Science, Polymer fuel cells based on polybenzimidazole/H 3 PO 4, 5 (2012) 6436-6444.

[2] D.J. Jones, J.J.J.o.M.S. Rozière, Recent advances in the functionalisation of polybenzimidazole and polyetherketone for fuel cell applications, 185 (2001) 41-58.

[3] K.-D. Kreuer, Proton conductivity: materials and applications, Chemistry of materials, 8 (1996) 610-641.

[4] Q. Li, J.O. Jensen, R.F. Savinell, N.J.J.P.i.p.s. Bjerrum, High temperature proton exchange membranes based on polybenzimidazoles for fuel cells, 34 (2009) 449-477.

[5] J.A. Asensio, E.M. Sánchez, P. Gómez-Romero, Proton-conducting membranes based on benzimidazole polymers for high-temperature PEM fuel cells. A chemical quest, Chemical Society Reviews, 39 (2010) 3210-3239.

[6] L. Vilčiauskas, M.E. Tuckerman, G. Bester, S.J. Paddison, K.-D. Kreuer, The mechanism of proton conduction in phosphoric acid, Nature chemistry, 4 (2012) 461.

[7] G. Qian, D.W. Smith Jr, B.C. Benicewicz, Synthesis and characterization of high molecular weight perfluorocyclobutyl-containing polybenzimidazoles (PFCB–PBI) for high temperature polymer electrolyte membrane fuel cells, Polymer, 50 (2009) 3911-3916.

[8] J. Wainright, J.T. Wang, D. Weng, R. Savinell, M. Litt, Acid‐doped polybenzimidazoles: a new polymer electrolyte, Journal of the Electrochemical Society, 142 (1995) L121.

[9] M.E. Tuckerman, G. Bester, S.J. Paddison, K.-D. Kreuer, The mechanism of proton conduction in phosphoric acid, Nature Chemistry, 4 (2012).

[10] C. Korte, F. Conti, J. Wackerl, P. Dams, A. Majerus, W. Lehnert, Uptake of protic electrolytes by polybenzimidazole-type polymers: absorption isotherms and electrolyte/polymer interactions, Journal of Applied Electrochemistry, 45 (2015) 857-871.

[11] F.A. de Bruijn, R.C. Makkus, R.K. Mallant, G.J. Janssen, Materials for state-of-the-art PEM fuel cells, and their suitability for operation above 100° C, Advances in fuel cells, 1 (2007) 235-336.

[12] K. Wippermann, J. Wackerl, W. Lehnert, B. Huber, C. Korte, 2-Sulfoethylammonium Trifluoromethanesulfonate as an Ionic Liquid for High Temperature PEM Fuel Cells, Journal of The Electrochemical Society, 163 (2015) F25-F37.

[13] K. Hsueh, E. Gonzalez, S. Srinivasan, Electrolyte effects on oxygen reduction kinetics at platinum: a rotating ring-disc electrode analysis, Electrochimica Acta, 28 (1983) 691-697.

[14] K.L. Hsueh, E. Gonzalez, S. Srinivasan, D.T. Chin, Effects of phosphoric acid concentration on oxygen reduction kinetics at platinum, Journal of the Electrochemical Society, 131 (1984) 823-828.

[15] A. Sacca, I. Gatto, A. Carbone, R. Pedicini, E. Passalacqua, ZrO2–Nafion composite membranes for polymer electrolyte fuel cells (PEFCs) at intermediate temperature, Journal of power sources, 163 (2006) 47-51.

[16] C.M. Branco, S. Sharma, M.M. de Camargo Forte, R. Steinberger-Wilckens, New approaches towards novel composite and multilayer membranes for intermediate temperature-polymer electrolyte fuel cells and direct methanol fuel cells, Journal of Power Sources, 316 (2016) 139-159.

[17] H. Hou, H.M. Schütz, J.r. Giffin, K. Wippermann, X. Gao, A. Mariani, S. Passerini, C. Korte, Acidic Ionic Liquids Enabling Intermediate Temperature Operation Fuel Cells, ACS Applied Materials & Interfaces, (2021).

[18] A. Chandan, N.V. Rees, R. Steinberger-Wilckens, V. Self, J. Richmond, Improving the design of gas diffusion layers for intermediate temperature polymer electrolyte fuel cells using a sensitivity analysis: A multiphysics approach, international journal of hydrogen energy, 40 (2015) 16745-16759.

[19] A. Ibrahim, O. Hossain, J. Chaggar, R. Steinberger-Wilckens, A. El-Kharouf, GO-nafion composite membrane development for enabling intermediate temperature operation of polymer electrolyte fuel cell, International Journal of Hydrogen Energy, 45 (2020) 5526-5534.

[20] M.A.B.H. Susan, T. Kaneko, A. Noda, M. Watanabe, Ion gels prepared by in situ radical polymerization of vinyl monomers in an ionic liquid and their characterization as polymer electrolytes, Journal of the American Chemical Society, 127 (2005) 4976-4983.

[21] M.M. Mannarino, D.S. Liu, P.T. Hammond, G.C. Rutledge, Mechanical and transport properties of layer-by-layer electrospun composite proton exchange membranes for fuel cell applications, ACS applied materials & interfaces, 5 (2013) 8155-8164.

[22] D.E. Smith, D.A. Walsh, The Nature of Proton Shuttling in Protic Ionic Liquid Fuel Cells, Advanced Energy Materials, 9 (2019).

[23] L. Koók, B. Kaufer, P. Bakonyi, T. Rózsenberszki, I. Rivera, G. Buitrón, K. Bélafi-Bakó, N.J.J.o.m.s. Nemestóthy, Supported ionic liquid membrane based on [bmim][PF6] can be a promising separator to replace Nafion in microbial fuel cells and improve energy recovery: A comparative process evaluation, 570 (2019) 215-225.

[24] J. Escorihuela, A. Garcia-Bernabe, A. Montero, O. Sahuquillo, E. Gimenez, V. Compan, Ionic Liquid Composite Polybenzimidazol Membranes for High Temperature PEMFC Applications, Polymers (Basel), 11 (2019).

[25] P. Zelenay, B. Scharifker, J.M. Bockris, D. Gervasio, A Comparison of the Properties of CF 3 SO 3 H and H 3 PO 4 in Relation to Fuel Cells, Journal of the Electrochemical Society, 133 (1986) 2262-2267.

[26] V.S. Murthi, R.C. Urian, S. Mukerjee, Oxygen reduction kinetics in low and medium temperature acid environment: correlation of water activation and surface properties in supported Pt and Pt alloy electrocatalysts, The Journal of Physical Chemistry B, 108 (2004) 11011-11023.

[27] M.G. Nair, S.R. Mohapatra, Perchloric acid functionalized nano-silica and protic ionic liquid based non-aqueous proton conductive polymer electrolytes, Materials Letters, 251 (2019) 148-151.

[28] H. Nakamoto, M. Watanabe, Bronsted acid-base ionic liquids for fuel cell electrolytes, Chem Commun (Camb), (2007) 2539-2541.

[29] S. Liu, L. Zhou, P. Wang, F. Zhang, S. Yu, Z. Shao, B. Yi, Ionic-liquid-based proton conducting membranes for anhydrous H2/Cl2 fuel-cell applications, ACS Appl Mater Interfaces, 6 (2014) 3195-3200.

[30] S.-Y. Lee, A. Ogawa, M. Kanno, H. Nakamoto, T. Yasuda, M. Watanabe, Nonhumidified intermediate temperature fuel cells using protic ionic liquids, Journal of the American Chemical Society, 132 (2010) 9764-9773.

[31] J. Lin, L. Wang, T. Zinkevich, S. Indris, Y. Suo, C. Korte, Influence of residual water and cation acidity on the ionic transport mechanism in proton-conducting ionic liquids, Physical Chemistry Chemical Physics, (2020).

[32] J. Lin, C. Korte, Influence of the acid–base stoichiometry and residual water on the transport mechanism in a highly-Brønsted-acidic proton-conducting ionic liquid, RSC Advances, 10 (2020) 42596-42604.

[33] K.D. Kreuer, A. Rabenau, W. Weppner, Vehicle mechanism, a new model for the interpretation of the conductivity of fast proton conductors, Angewandte Chemie International Edition in English, 21 (1982) 208-209.

[34] Z. Wojnarowska, Y. Wang, J. Pionteck, K. Grzybowska, A. Sokolov, M. Paluch, High pressure as a key factor to identify the conductivity mechanism in protic ionic liquids, Physical review letters, 111 (2013) 225703.

[35] T. Dippel, K. Kreuer, J. Lassegues, D. Rodriguez, Proton conductivity in fused phosphoric acid; A 1H/31P PFG-NMR and QNS study, Solid State Ionics, 61 (1993) 41-46.

[36] P. Griffin, A.L. Agapov, A. Kisliuk, X.-G. Sun, S. Dai, V.N. Novikov, A.P. Sokolov, Decoupling charge transport from the structural dynamics in room temperature ionic liquids, The Journal of chemical physics, 135 (2011) 114509.

[37] J. Peron, E. Ruiz, D.J. Jones, J. Rozière, Solution sulfonation of a novel polybenzimidazole, Journal of Membrane Science, 314 (2008) 247-256.

[38] J. Hu, J. Luo, P. Wagner, O. Conrad, C. Agert, Anhydrous proton conducting membranes based on electron-deficient nanoparticles/PBI-OO/PFSA composites for high-temperature PEMFC, Electrochemistry Communications, 11 (2009) 2324-2327.

[39] R. Foglizzo, A.J.J.d.C.P. Novak, Spectres de vibration de quelques halogénures de pyridinium, 66 (1969) 1539-1550.

[40] R. Bouchet, E. Siebert, Proton conduction in acid doped polybenzimidazole, Solid state ionics, 118 (1999) 287-299.

[41] Y.-N. Chang, J.-Y. Lai, Y.-L. Liu, Polybenzimidazole (PBI)-functionalized silica nanoparticles modified PBI nanocomposite membranes for proton exchange membranes fuel cells, Journal of membrane science, 403 (2012) 1-7.

[42] K. Wippermann, J. Giffin, C. Korte, In Situ Determination of the Water Content of Ionic Liquids, Journal of The Electrochemical Society, 165 (2018) H263-H270.

[43] N.N. Krishnan, S. Lee, R.V. Ghorpade, A. Konovalova, J.H. Jang, H.-J. Kim, J. Han, D. Henkensmeier, H. Han, Polybenzimidazole (PBI-OO) based composite membranes using sulfophenylated TiO2 as both filler and crosslinker, and their use in the HT-PEM fuel cell, Journal of Membrane Science, 560 (2018) 11-20.

[44] J. Lin, C. Korte, PBI‐type Polymers and Acidic Proton Conducting Ionic Liquids–Conductivity and Molecular Interactions, Fuel Cells, (2019).

[45] R. Pant, S. Sengupta, A.V. Lyulin, A. Venkatnathan, Computational investigation of a protic ionic liquid doped poly-benzimidazole fuel cell electrolyte, Journal of Molecular Liquids, 314 (2020) 113686.

[46] K.-S. Lee, J.S. Spendelow, Y.-K. Choe, C. Fujimoto, Y.S. Kim, An operationally flexible fuel cell based on quaternary ammonium-biphosphate ion pairs, Nature energy, 1 (2016) 16120.

[47] T.-S. Chung, A critical review of polybenzimidazoles: historical development and future R&D, Journal of Macromolecular Science, Part C: Polymer Reviews, 37 (1997) 277-301.

[48] K. Mori, T. Kobayashi, K. Sakakibara, K. Ueda, Experimental and theoretical investigation of proton exchange reaction between protic ionic liquid diethylmethylammonium trifluoromethanesulfonate and H2O, Chemical Physics Letters, 552 (2012) 58-63.

[49] K. Mori, S. Hashimoto, T. Yuzuri, K. Sakakibara, Structural and Spectroscopic Characteristics of a Proton-Conductive Ionic Liquid Diethylmethylammonium Trifluoromethanesulfonate [dema][TfOH], Bulletin of the Chemical Society of Japan, 83 (2010) 328-334.

[50] E.C. Meister, M. Willeke, W. Angst, A. Togni, P.J.H.C.A. Walde, Confusing Quantitative Descriptions of Brønsted Lowry Acid Base Equilibria in Chemistry Textbooks–A Critical Review and Clarifications for Chemical Educators, 97 (2014) 1-31.

[51] C. Rey-Castro, L.F. Vega, Transport properties of the ionic liquid 1-ethyl-3-methylimidazolium chloride from equilibrium molecular dynamics simulation. The effect of temperature, The Journal of Physical Chemistry B, 110 (2006) 14426-14435.

[52] M.J. Monteiro, F.F. Bazito, L.J. Siqueira, M.C. Ribeiro, R.M. Torresi, Transport coefficients, Raman spectroscopy, and computer simulation of lithium salt solutions in an ionic liquid, The Journal of Physical Chemistry B, 112 (2008) 2102-2109.

1. Taking also the molar weights into account:

   , and [↑](#footnote-ref-1)