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## Fabrication of proton exchange membrane for non-humidified fuel cells based on polyimide Matrimid<sup>®</sup> and hydrophobic protic ionic liquid

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New proton exchange membrane based on polyimide Matrimid<sup>®</sup> (PI) and hydrophobic protic ionic liquid, 1-methylimidazolium bis(trifluoromethylsulfonyl)imide (MIM-TFSI), has been prepared by casting from methylene chloride/dimethylformamide solution. Infrared analysis revealed physicochemical interactions between 1-methylimidazolium cations and imide groups of PI. The results of mechanical testing indicate significantly reduced tensile strength of PI/MIM-TFSI composite membrane compared to neat polymer. Moreover, the dynamical mechanical analysis results revealed sharp drop in storage modulus ( $E'$ ) of the polymer film above 60 °C.

To improve the elastic properties of the membrane, PI was successively cross-linked with polyetheramine Jeffamine<sup>®</sup> D-2000 (10 mol. %) in methylene chloride/dimethylformamide solution, as well as in solid film at 100 °C. This approach allowed to prepare PI/Jeffamine/MIM-TFSI (70 wt. %) composite film which has an acceptable  $E'$  value of 210 MPa at 140 °C. According to thermal gravimetric analysis data, PI/Jeffamine/MIM-TFSI composite has a thermal degradation point (i.e. 5 % weight loss) of 286 °C. The ionic conductivity of PI/Jeffamine/MIM-TFSI composite membrane is around  $10^{-4}$  S/cm at room temperature and reaches the minimal level of  $10^{-3}$  S/cm, required for fuel cell applications, above 100 °C. Overall, the results of this study indicate that the cross-linking of polyimide Matrimid with flexible polyetheramine Jeffamine is an efficient approach for preparing dense composite membrane with high content of the protic ionic liquid. Such polymer-electrolyte membrane has the reasonable combination of good stiffness, thermal stability, and ionic conductivity and therefore is a promising candidate for use in fuel cells operating at elevated temperatures in water-free conditions.

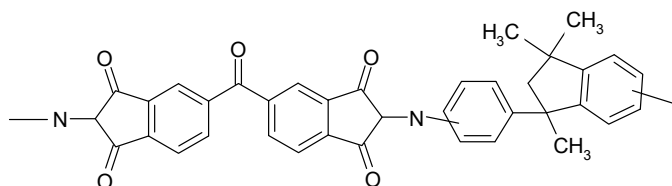
**Keywords:** polyimide, protic ionic liquid, proton exchange membrane, cross-linking, ionic conductivity

### Introduction

Polyimide Matrimid<sup>®</sup> (PI) (Fig. 1) has very unusual and desirable properties combining high thermal stability (above 450 °C), high glass transition temperature (above 330 °C), and good solubility in common organic solvents which make it suitable as a matrix resin for specific technical applications. Thus, Matrimid<sup>®</sup> is originally developed for use in the microelectronics industry, as well as in the gas separation industry [1]. Recently, PI has become a popular material for the design of polymer-electrolyte membranes (PEMs) for high temperature fuel cell applications [2-4]. For such purposes, PEM should combine high stiffness and ionic conductivity of at least  $10^{-3}$  S/cm in the temperature range 120-200 °C [5].

Protic ionic liquids (PILs), which are low temperature molten salts of Brønsted acids and Brønsted bases, has proved to be extremely promising proton conducting electrolytes [6, 7]. PILs have numerous advantages such as high thermal stability, low volatility, non-flammability, electrochemical stability, and high ionic conductivity in a wide temperature range. However, taking into account the dielectric nature of PI matrix, composite PI/PIL membranes must contain at least 60-70 wt. % of ionic liquid in order to reach the level of conductivity required for fuel cells [2-4, 8]. Thus, the microporous support

based on PI Matrimid<sup>®</sup> was impregnated with hydrophilic PIL, triethylammonium trifluoromethanesulfonate (TFSu-TEA), to prepare composite PEM with ionic liquid content up to 76 wt. % [2]. At 130 °C, the membrane exhibits proton conductivity of 20 mS/cm that is very close to that of the pure PIL. At the same time, PI/TFSu-TEA membrane retains a relatively high storage modulus ( $E' = 202$  MPa) up to 160 °C [2]. In another study, the composite PI/PILs membranes were prepared by immobilization of hydrophobic PILs, namely 1-alkylimidazolium bis(trifluoromethylsulfonyl)imide salts, in the porous PI [3]. Water immiscible PILs are considered especially promising due to their potential resistance to leaching during fuel cell operation. The composite membranes contained 63-72 wt. % of PILs and showed the minimal required level of ionic conductivity of  $10^{-3}$  S/cm at 160 °C [3].



**Fig. 1.** Chemical structure of polyimide Matrimid<sup>®</sup> 5218

From a practical point of view, the use of dense PI as a matrix for composite PEM seems more economical and convenient compared to porous polymer. However, the main problem of this approach is to prepare PEM with high ionic liquid content while keeping satisfactory mechanical properties at elevated temperatures. Thus, a dense composite membrane based on PI Matrimid<sup>®</sup> containing 50 wt. % of the hydrophobic PIL, 2-butylaminoimidazolium bis(trifluoromethylsulfonyl)imide (BAIM-TFSI), showed significant decrease of storage modulus from 1780 to 75 MPa upon heating to 120 °C [4]. The cross-linking of the PI with polyetheramine Jeffamine<sup>®</sup> D-400 allowed to prepare PI/Jeffamine/BAIM-TFSI (50 %) membrane with  $E'$  value of 300 MPa at 130 °C. The ionic conductivity of this cross-linked composite membrane reached the level of  $10^{-2}$  S/cm at 130 °C suggesting therefore its potential use in medium temperature fuel cells operating in water-free conditions [4]. However, a significant reduction in  $E'$  value of PI/Jeffamine/BAIM-TFSI composite occurred at higher temperatures.

In this study, new PEM based on polyimide Matrimid<sup>®</sup> and hydrophobic PIL, namely 1-methylimidazolium bis(trifluoromethylsulfonyl)imide (MIM-TFSI), has been obtained. To improve the tensile properties of the composite membrane at elevated temperatures, combined chemical modification of PI was realized both in the solution and in the solid state by using polyetheramine Jeffamine<sup>®</sup> D-2000 as the cross-linking agent. The prepared PI/Jeffamine/MIM-TFSI membrane was characterized in terms of mechanical properties, thermal stability, and proton conductivity in a wide range of temperatures.

### **Experimental**

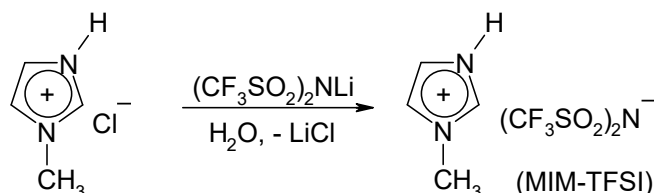
Following chemicals were used for the synthesis of ionic liquid and for the elaboration of PI-based composites: 1-methylimidazole (for synthesis, Sigma-Aldrich), lithium bis(trifluoromethylsulfonyl)imide (97 %, Acros), N,N-dimethylformamide, hydrochloric acid (37 %), methylene chloride (Uoslab, Ukraine). Polyimide Matrimid<sup>®</sup> 5218 powder and polyetheramine Jeffamine<sup>®</sup> D-2000 were kindly supplied by Huntsman (Switzerland).

The ionic liquid MIM-TFSI was synthesized according to the following procedure (Scheme 1). 1-methylimidazole (5 g, 0.06 mol) was dissolved in 30 ml of water and the solution was neutralized with

hydrochloric acid (10 ml). To the stirred solution of 1-methylimidazolium chloride was added lithium bis(trifluoromethylsulfonyl)imide (17.2 g, 0.06 mol) dissolved in 60 ml of water. The formed water immiscible layer was separated and dried at 120 °C for 24 h. MIM-TFSI was obtained as an amorphous solid of white color having melting point 49-50 °C.

$^1\text{H}$  NMR (400 MHz, DMSO- $\text{D}_6$ ):  $\delta$  = 3.86 (s, 3H,  $\text{CH}_3$ ), 7.65 (t,  $J$  = 1.7 Hz, 1H, C<sub>4</sub>-H), 7.67 (t,  $J$  = 1.7 Hz, 1H, C<sub>5</sub>-H), 9.03 (t,  $J$  = 1.1 Hz, 1H, C<sub>2</sub>-H).

$^{19}\text{F}$  NMR (188 MHz, DMSO- $\text{D}_6$ ):  $\delta$  = -75.2 (s, 6F).



### Scheme 1. Synthesis of protic ionic liquid MIM-TFSI

PI solution in methylene chloride (1 g/20 ml) was prepared. To this solution was added MIM-TFSI (2.4 g) dissolved in dimethylformamide (5 ml), and the mixture was stirred for 2 h. The solution was poured onto glass support and the solvent evaporated at room temperature for 24 h until a solid film was formed. Residual solvents were removed in vacuum 1 mbar at 60 °C for 12 h. Thus, composite membrane PI/MIM-TFSI containing 70 wt. % of PIL was prepared.

Following method was used to prepare composite membrane based on cross-linked PI. 1 g (0.0018 mol) of PI was dissolved in 20 mL of methylene chloride followed by the addition of 10 molar percent of Jeffamine<sup>®</sup> D-2000 with respect to PI. The solution was stirred for 24 h at room temperature after that the solution of MIM-TFSI (2.4 g) in dimethylformamide (5 ml) was added, and the mixture was further stirred for 2 h. The solution was poured onto glass support and the solvent evaporated at room temperature for 24 h until a solid film was formed. It was then kept for 12 h at 40 °C and 12 h at 100 °C. Residual solvents were removed in vacuum 1 mbar at 60 °C for 12 h. Thus, composite membrane PI/Jeffamine/MIM-TFSI containing 70 wt. % of PIL was prepared. Control samples of cross-linked PI were prepared without the addition of ionic liquid.

The vibrational properties of MIM-TFSI and its composites with PI were studied using a Vertex-70 Bruker (Germany) Fourier Transform Infrared (FT-IR) spectrometer equipped with a DTGS detector. The spectrum of pure ionic liquid was obtained from a tablet with KBr. PI-based composite films were placed into contact with the single reflection diamond ATR (Attenuated Total Reflection) crystal and the spectra were collected at room temperature over the range 400-4000  $\text{cm}^{-1}$  at a resolution of 1  $\text{cm}^{-1}$ .

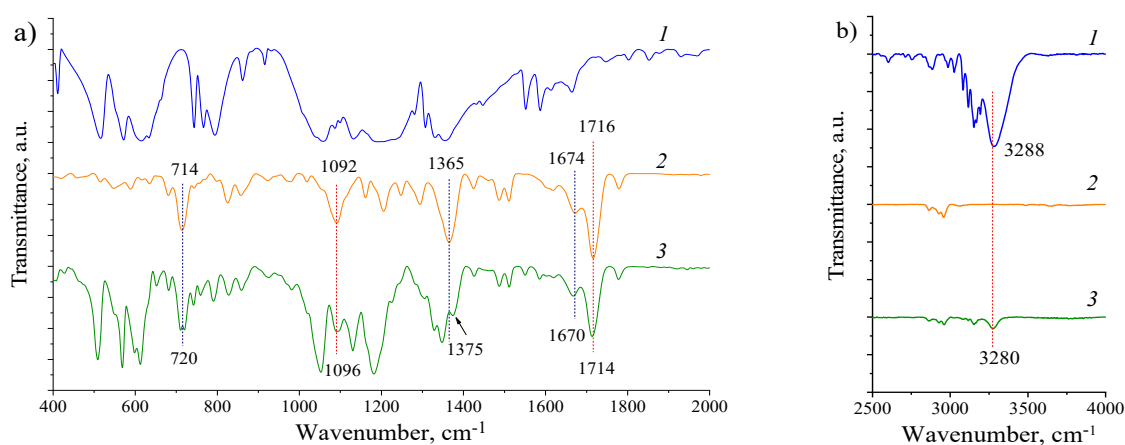
The mechanical testing of the polymer membranes was performed using P-50 universal tensile testing machine (Milaform, Russia) at a deformation rate of 10 mm/min. Polymer films were cut into specimens with the size of 50×10×0.2 mm. An average tensile strength value was calculated from the tensile strength of 3 individual samples. Dynamic mechanical analysis (DMA) investigations were carried out on a dynamic mechanical analyzer Q 800 (TA Instruments) in the tension mode at a frequency of 10 Hz and a heating rate of 2.0 °C/min. The samples for DMA study had a size of 12×4×0.2 mm. The storage modulus ( $E'$ ) was recorded as a function of temperature.

Thermal gravimetric analysis was made using a Q-1500D thermal analyzer. About 100 mg of the sample was heated from 30 °C to 900 °C with a heating rate of 10 °C/min in air.

The ionic conductivity of ionic liquid and PI/Jeffamine/MIM-TFSI composite membrane was measured with the help of impedance spectrometer Solartron SI 1260 in the temperature range from 25 to 160 °C.

### Results and Discussion

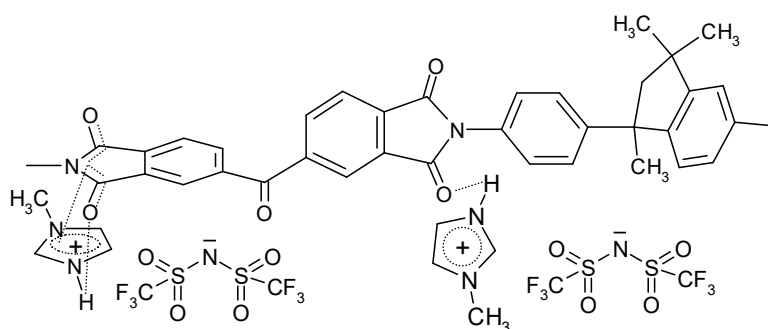
FTIR-ATR spectra of PI Matrimid, MIM-TFSI, and their composite are presented in Fig. 2. For the ionic liquid, the main cation characteristic bands are the N-H stretching mode at 3288  $\text{cm}^{-1}$ , the ring C<sub>4,5</sub>-H stretching mode at 3168  $\text{cm}^{-1}$ , and the ring C<sub>2</sub>-H stretching mode at 3116 and 3083  $\text{cm}^{-1}$ . The band at 2986  $\text{cm}^{-1}$  is assigned to the symmetric stretching vibrations of CH<sub>3</sub> group. The band at 1587  $\text{cm}^{-1}$  corresponds to the stretching mode of CH<sub>3</sub>N group, and the stretching bands of CH<sub>3</sub>NCN groups are observed at 1281 and 1330  $\text{cm}^{-1}$  [9]. The bands at 1447 and 1430  $\text{cm}^{-1}$  are assigned to asymmetric and symmetric bending vibrations of CH<sub>3</sub> groups, respectively. In the region 1170-400  $\text{cm}^{-1}$ , the IR spectrum is dominated by contributions from TFSI anion. The strong bands at 1226, 1240, and 1307  $\text{cm}^{-1}$  are attributed to CF<sub>3</sub> symmetric stretching vibrations, whereas the bands at 1200 and 1178  $\text{cm}^{-1}$  correspond to CF<sub>3</sub> asymmetric stretching mode [9, 10]. Two SO<sub>2</sub> asymmetric stretching modes are observed at 1330 and 1355  $\text{cm}^{-1}$ , and the band at 1333  $\text{cm}^{-1}$  is assigned to SO<sub>2</sub> symmetric stretching mode [10]. Further strong band is SNS asymmetric stretching, C-C stretching, and NCH<sub>3</sub> twisting at 1059  $\text{cm}^{-1}$ . The band at 658  $\text{cm}^{-1}$  corresponds to SNS bending vibrations. In the region between 500 and 750  $\text{cm}^{-1}$  a few strong bending modes are observed which are assigned to CF<sub>3</sub> asymmetric bending at 571  $\text{cm}^{-1}$ , SO<sub>2</sub> asymmetric bending at 600 and 616  $\text{cm}^{-1}$ , and CF<sub>3</sub> symmetric bending at 743  $\text{cm}^{-1}$  [9, 10].



**Fig. 2.** IR spectra: 1 - MIM-TFSI, 2 - PI Matrimid, 3 - PI/MIM-TFSI (70 %)

The spectrum of PI Matrimid contains characteristic bands at 1779  $\text{cm}^{-1}$  and 1716  $\text{cm}^{-1}$  assigned to asymmetric and symmetric stretching modes of imide C=O group, respectively, and a small intensity band at 1674  $\text{cm}^{-1}$  is attributed to the stretching vibrations of ketone C=O group [11]. The strong band at 1365 and 1092  $\text{cm}^{-1}$  are attributed to the C-N-C axial and *trans* stretching modes [12, 13], and the bands at 714 and 1424  $\text{cm}^{-1}$  are assigned to the out of plane bending vibrations of NCO and NCC bonds [11]. The small intensity bands at 1487, 1511, and 1620  $\text{cm}^{-1}$  are assigned to C-C stretching vibrations of aromatic rings. The weak bands at 2868, 2927, and 2959  $\text{cm}^{-1}$  are attributed to aliphatic C-H stretching vibrations of the five-membered cycle of PI. The bands at 859 and 1162  $\text{cm}^{-1}$  corresponds to out of plane and in plane bending mode of aromatic CCH groups, respectively [11].

For PI/MIM-TFSI composite films, the peak position of the bands corresponding to vibrations of both imide and ketone C=O groups slightly shifted to lower frequencies, from 1716 to 1714  $\text{cm}^{-1}$  and from 1674 to 1670  $\text{cm}^{-1}$ , respectively (Fig. 2 a). The peak of N-H stretching mode of MIM-TFSI has also shifted from 3288 to 3280  $\text{cm}^{-1}$  (Fig. 2 b). This may indicate the hydrogen bonding between N-H groups of 1-methylimidazolium cation and C=O groups of PI (Scheme 2). Moreover, with the introduction of MIM-TFSI, the C-N-C vibrational modes of the imide cycle shifted to higher frequencies: from 1365 to 1375  $\text{cm}^{-1}$ , from 1092 to 1096  $\text{cm}^{-1}$ , and from 714 to 720  $\text{cm}^{-1}$  (Fig. 2 a). According to these results, it can be suggested that  $\pi$ - $\pi$  interaction between 1-methylimidazolium cation and imide cycle of PI occurs (Scheme 2). Such physicochemical interactions probably cause good compatibility of MIM-TFSI with the polymer matrix.



**Scheme 2.** Possible physicochemical interactions between PI and MIM-TFSI

The results of mechanical testing of PI-based composite membranes are summarized in Table 1. The high content of the ionic liquid in PI/MIM-TFSI membrane leads to dramatically reduced tensile strength (by approximately 86 %) compared with neat polymer. However, cross-linking of PI with 10 mol. % of polyetheramine Jeffamine<sup>®</sup> D-2000 significantly improved its mechanical properties. Thus, PI/Jeffamine/MIM-TFSI composite film has a tensile strength which is almost 58 % of that of a neat PI. At the same time, low elongation at break indicates a high rigidity of the polymer membrane.

**Table 1.** Mechanical properties of composite membranes

Sample	Tensile strength, MPa	Elongation at break, %
PI Matrimid (control)	38±2	7±1
PI/MIM-TFSI (70 %)	5.5±1	15±2
PI/Jeffamine (10 mol. %)	48±2	9±1
PI/Jeffamine/MIM-TFSI (70 %)	22±2	6.5±1

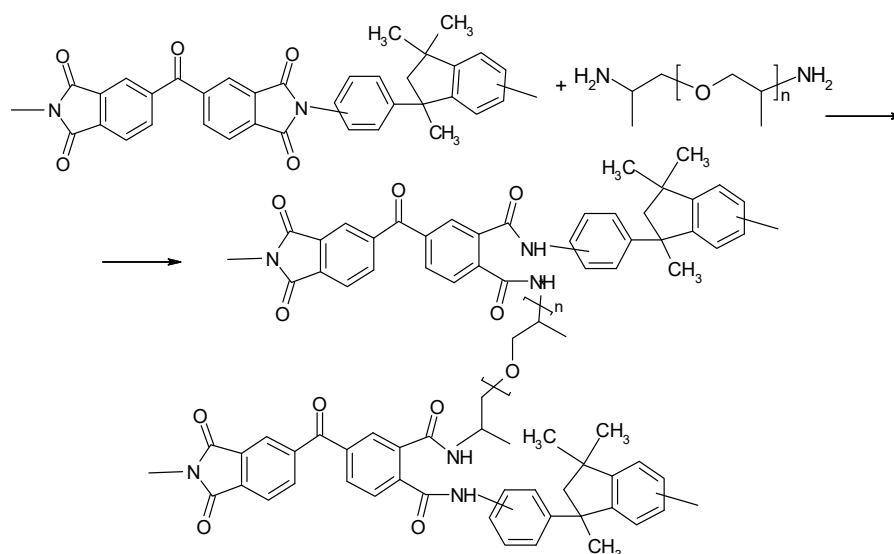
DMA study was further performed to assess the mechanical response of PI/MIM-TFSI membranes to higher temperatures. Polyimide Matrimid has a high storage modulus ( $E' = 1340$ - $1200$  MPa) in the temperature range 20-200 °C (Fig. 3, curve 1), indicating its excellent elastic properties as a polymer matrix for PEM. PI/MIM-TFSI composite film has a significantly narrowed the temperature range of mechanical stiffness from 20 to 60 °C (Fig. 3, curve 2, Table 2). The sharp reduction of  $E'$  value is probably caused by the plasticizing effect of ionic liquid on PI leading to soft material.

Recent studies have shown that polyimide Matrimid easily reacts with aliphatic diamines to form cross-linked structures [4, 14] (Scheme 3). As one can see from Fig. 3 and Table 2, cross-linking of PI with 10 mol. % of polyetheramine Jeffamine<sup>®</sup> D-2000 significantly improved its viscoelastic properties. Thus, PI/Jeffamine/MIM-TFSI membrane demonstrated good stiffness similar to common Nafion-based PEMs [15, 16] up to 140 °C (Fig. 3, curve 3). The obtained results agreed with previously reported ones

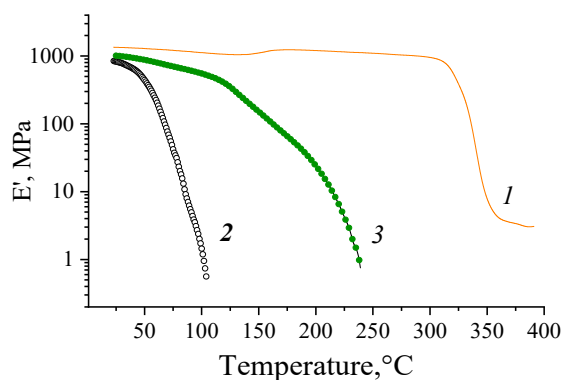
and indicate that the intermolecular cross-linking increases the resistance of PI/PIL composite membranes to deformation [4].

**Table 2.** Viscoelastic characteristics of PI/MIM-TFSI membranes

Sample	$E'_{T=25\text{ }^\circ\text{C}}$ , MPa	$E'_{T=60\text{ }^\circ\text{C}}$ , MPa	$E'_{T=120\text{ }^\circ\text{C}}$ , MPa	$E'_{T=130\text{ }^\circ\text{C}}$ , MPa	$E'_{T=140\text{ }^\circ\text{C}}$ , MPa
PI	1342	1259	1061	1045	1053
PI/MIM-TFSI (70 %)	828	224	-	-	-
PI/Jeffamine (10 %)/ MIM-TFSI (70 %)	1012	805	400	296	210



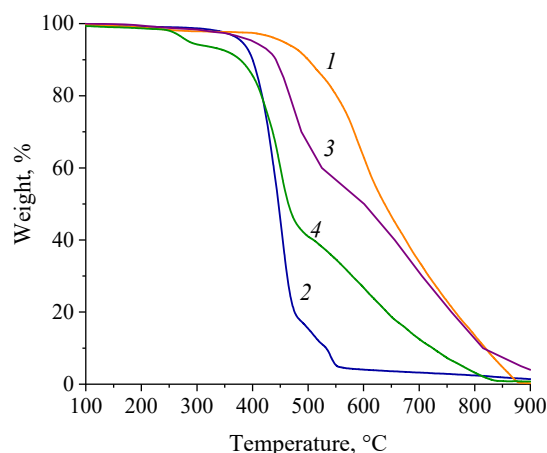
**Scheme 3.** Cross-linking of polyimide Matrimid with polyetheramine Jeffamine



**Fig. 3.** DMA curves of  $E'$ : 1 - polyimide Matrimid, 2 - PI/MIM-TFSI (70 %), 3 - PI/Jeffamine/MIM-TFSI (70 %)

The results of TGA data for PI, MIM-TFSI, and their composites are summarized in Fig. 4 and Table 3. Ionic liquid has a thermal degradation point (i.e. 5 % weight loss) of 381 °C with a maximum rate at 456 °C (Fig. 4, curve 2) that indicates sufficient thermal stability for high temperature fuel cell applications. Polyimide Matrimid has outstanding thermal properties being stable to at least 456 °C with a maximum degradation rate at 595 °C (Fig. 4, curve 1). PI/MIM-TFSI composite also showed excellent thermal stability (Fig. 4, curve 3) with a thermal degradation point at 397 °C. Cross-linking of PI with Jeffamine significantly reduced the thermal degradation point of the polymer, as well as PI/MIM-TFSI

composite (Fig. 3, curve 4, Table 3). This is probably due to the opening of PI rings, as well as the presence of flexible aliphatic chains in the polymer structure (Scheme 3).

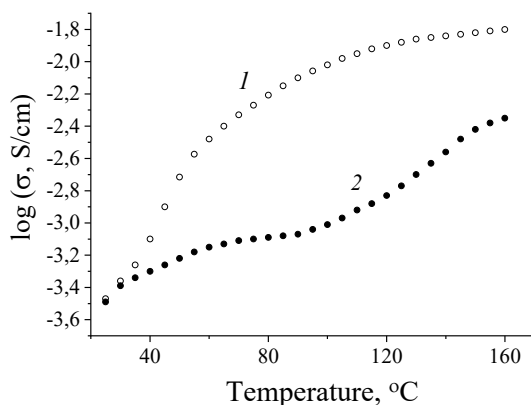


**Fig. 4.** TGA curves: 1 - PI, 2 - MIM-TFSI, 3 - PI/MIM-TFSI (70 %), 4 - PI/Jeffamine/MIM-TFSI (70 %)

**Table 3.** TGA data for composite PI membrane

Sample	$T_{\Delta m=5\%}, ^\circ\text{C}$	$T_{\Delta m=10\%}, ^\circ\text{C}$	$T_{\Delta m=20\%}, ^\circ\text{C}$	$T_{\Delta m=50\%}, ^\circ\text{C}$
PI	456	500	551	638
MIM-TFSI	381	400	417	447
PI/MIM-TFSI (70 %)	397	440	471	601
PI/Jeffamine	316	344	373	600
PI/Jeffamine/MIM-TFSI (70%)	286	377	416	464

The ionic conductivity of MIM-TFSI ionic liquid is  $1.9 \cdot 10^{-3}$  S/cm at its melting point. This value increases by almost one order of magnitude above  $100^\circ\text{C}$  (Fig. 5, Table 4). PI/Jeffamine/MIM-TFSI composite membrane has poor conductivity of  $3.3 \cdot 10^{-4}$ - $8.7 \cdot 10^{-4}$  S/cm in the temperature range from  $25$  to  $80^\circ\text{C}$ . This is probably caused by low free volume of the system which creates barriers for efficient proton transfer in the dielectric PI matrix. With a further increase in temperature, the conductivity of the membrane significantly increases reaching the minimal level of  $10^{-3}$  S/cm required for PEM above  $100^\circ\text{C}$  (Fig. 5, Table 4). This can be explained by enhanced free ionic mobility of MIM-TFSI in the polymer membrane [4, 8]. It is worth noting that the similar results were obtained for PEM based on microporous polyimide Matrimid impregnated with MIM-TFSI [3].



**Fig. 5.** Ionic conductivity as a function of temperature for MIM-TFSI ionic liquid - 1 and PI/Jeffamine/MIM-TFSI membrane - 2 at 1 kHz

**Table 4.** Electrical conductivities of PI/Jeffamine/MIM-TFSI composite membranes as a function of temperature

Sample	$\sigma$ , S/cm				
	25 °C	80 °C	120 °C	140 °C	160 °C
MIM-TFSI	$3.5 \cdot 10^{-4}$	$6 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$
PI/Jeffamine/ MIM-TFSI (70%)	$3.3 \cdot 10^{-4}$	$8.7 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$

### Conclusions

In this study, dense polymer-electrolyte membrane (PEM) based on polyimide Matrimid® (PI) and hydrophobic protic ionic liquid 1-methylimidazolium bis(trifluoromethylsulfonyl)imide (MIM-TFSI) has been prepared by casting from methylene chloride/dimethylformamide solution. IR analysis revealed hydrogen bonding between 1-methylimidazolium cations of the ionic liquid and carbonyl groups of PI, as well as  $\pi$ - $\pi$  interaction between 1-methylimidazolium cations and imide heterocycles. Such physicochemical interactions probably cause good compatibility of PI with MIM-TFSI. The results of mechanical testing indicated significantly reduced tensile strength (by approximately 86 %) of PI/MIM-TFSI (70 wt. %) composite film compared to neat polymer. Moreover, DMA analysis revealed a narrow temperature range of mechanical stiffness of this composite from 20 to 60 °C. It can be explained by the plasticizing effect of ionic liquid on PI at elevated temperatures.

To improve the elastic properties of the PI/MIM-TFSI membrane, PI was cross-linked with polyetheramine Jeffamine® D-2000 (10 mol. %) in two successive stages: in methylene chloride/dimethylformamide solution at room temperature, as well as in solid film at 100 °C. The prepared PI/Jeffamine/MIM-TFSI (70 %) composite membrane demonstrated an acceptable storage modulus  $E'$  (400-210 MPa) in the temperature range 120-140 °C. According to TGA results, cross-linking of PI significantly reduces the thermal stability of the polymer. However, PI/Jeffamine/MIM-TFSI composite has a thermal decomposition point of 286 °C which allows its use in high temperature fuel cells. The results of electrochemical impedance spectroscopy suggested that PI/Jeffamine/MIM-TFSI membrane has poor ionic conductivity (of the order of  $10^{-4}$  S/cm) in the temperature range from 25 to 100 °C. Above 100 °C, the conductivity of the membrane reaches the minimal level of  $10^{-3}$  S/cm required for fuel cell applications. Thus, the cross-linking of polyimide Matrimid with flexible polyetheramine Jeffamine allows to prepare a dense composite membrane with high content of the protic ionic liquid. The new PEM demonstrated acceptable mechanical stiffness up to 140 °C, as well as good thermal stability and ionic conductivity that indicates its availability for use in fuel cells operating at elevated temperatures under anhydrous conditions.

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## Одержання протонобмінної мембрани для безводних паливних елементів на основі полііміду Matrimid® та гідрофобної протонної іонної рідини

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Одержано нову протонобмінну мембрану на основі полііміду Matrimid® (ПІ) і гідрофобної протонної іонної рідини біс(трифторметилсульфоніл)іміду 1-метилімідазолію (МІМ-ТФСІ) поливом з розчину в суміші метиленхлорид/диметилформамід. Аналіз методом інфрачервоної спектроскопії свідчить про фізико-хімічну взаємодію між катіонами 1-метилімідазолію та імідними групами ПІ. Згідно з результатами механічних досліджень, композитна плівка ПІ/МІМ-ТФСІ має суттєво знижену міцність на розрив (на 86 %) у порівнянні з чистим полімером. Крім того, методом динамічного механічного аналізу встановлено різке зменшення модуля пружності ( $E'$ ) полімерної мембрани за температури вище 60 °С.

Для покращення віскоеластичних властивостей протонобмінної мембрани проведено хімічне зшивання ПІ за допомогою поліетераміну Jeffamine® D-2000 в суміші метиленхлорид/диметилформамід, а також у твердій фазі за температури 100 °С. Застосування такого методу дало можливість отримати композитну плівку ПІ/Jeffamine/МІМ-ТФСІ із вмістом іонної рідини 70 масових відсотків, яка має задовільну величину  $E'$  (210 МПа) за температури 140 °С. Згідно з результатами термогравіметричного аналізу, композит має температуру початку деструкції 286 °С. Іонна провідність композитної мембрани ПІ/Jeffamine/МІМ-ТФСІ має порядок  $10^{-4}$  См/см за кімнатної температури і досягає мінімального рівня  $10^{-3}$  См/см, необхідного для застосування в паливних елементах, за температури вище 100 °С. Таким чином, результати цієї роботи свідчать, що зшивання полііміду Matrimid гнучким поліетером Jeffamine є ефективним методом одержання суцільної композитної мембрани з високим вмістом протонної іонної рідини. Така мембрана має оптимальне поєднання механічної жорсткості, термічної стійкості та іонної провідності і є перспективною для застосування в паливних елементах, які функціонують за підвищеної температури і за відсутності зволоження.

**Ключові слова:** поліілід, протонна іонна рідина, протонобмінна мембрана, зшивання, іонна провідність