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New promising proton conducting electrolyte for high-temperature fuel cells based on hydrophobic guanidine salt

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Guanidine salts are promising proton conductors due to the high content of exchangeable protons in guanidinium cation that ensure an efficient proton transfer along hydrogen-bonded network formed by proton donor and proton acceptor sites. However, the high melting point of most guanidine salts is a serious drawback for their application as proton conducting electrolytes for fuel cells. Reducing the symmetry of guanidinium cations by the substitution of hydrogen atoms on alkyl radicals reduces the melting points but also leads to decreased proton conductivity. In this study, monosubstituted guanidine salt, N-butylguanidinium bis(trifluoromethylsulfonyl)imide (BG-TFSI), has been synthesized by a simple two-step method. It is water immiscible room temperature protic ionic liquid. The structure of BG-TFSI was confirmed by nuclear magnetic resonance spectroscopy, as well as infrared spectroscopy. According to thermal gravimetric analysis data, the ionic liquid has the thermal degradation point (5% weight loss) of 348 °C which indicates its excellent thermal stability for use in high-temperature fuel cells. The ionic conductivity of BG-TFSI determined by the electrochemical impedance method was found to be $9\cdot10^{-4}$ S/cm at room temperature. This value increased by almost one order of magnitude at temperatures above 100 °C thus reaching an acceptable level for use in fuel cells. The activation energy E_a of ionic conductivity calculated from the Arrhenius plot for BG-TFSI is 16.4 kJ/mol which is close to E_a values reported for other guanidine salts. Based on the obtained results one can assume that the proton transport in BG-TFSI is dominated by Grotthus-type (hopping) mechanism. The results of this study indicated that BG-TFSI is a promising proton conducting electrolyte for fuel cells operating at elevated temperatures in water-free conditions. The hydrophobicity of the ionic liquid is an important advantage since it can prevent its leaching from the polymer electrolyte membrane during fuel cell operation.

Keywords: guanidine salt, protic ionic liquid, ionic conductivity, proton conducting electrolyte

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Introduction

Nowadays, protic ionic liquids (PILs), which are low temperature molten salts of Brønsted acids and Brønsted bases, are considered extremely promising proton conducting electrolytes for fuel cell applications [1]. A wide variety of organic amines, both aliphatic and heterocyclic, can be used as Brønsted bases to prepare neutral salts with strong inorganic and organic acids such as trifluoromethanesulfonic acid, bis(trifluoromethylsulfonyl)imide, p-toluenesulfonic acid, dialkyl phosphate [2-6]. PILs have important advantages such as negligible vapor pressure, thermal stability which often exceeds 300 °C, as well as high ionic conductivity within the range from 10^{-3} to 10^{-1} S/cm at elevated temperatures under anhydrous conditions [1]. These compounds are being actively studied as potential proton conducting electrolytes for fuel cells operating above 100 °C without external humidification [1-3, 5-7]. Hydrophobicity is a desirable characteristic for proton conducting electrolytes, as it prevents them from being washed out by the water formed during fuel cell operation. Therefore, water-immiscible PILs comprising TFSI anion are of great interest.

Due to their polar structure, PILs have excellent compatibility with thermally stable polymers such as polybenzimidazole (PBI) and polyimide (PI) which are commonly used for the fabrication of polymer-electrolyte membranes for fuel cells [8-10]. Thus, dense composite membranes containing more than 50 wt% of PIL were prepared, namely PBI/diethylmethylammonium trifluoromethanesulfonate (dema/ TfO) [8], PI/1-butylimidazolium bis(trifluoromethylsulfonyl) imide (BIM-TFSI) [9], and PI/2-butylamino-imidazolinium bis(trifluoromethylsulfonyl)imide (BAIM-TFSI) [10].

The most commonly used PILs contain one or two mobile protons bound to the cation [2, 3, 7, 8]. At the same time, the high content of dissociable protons in the PIL structure is desirable since this can facilitate proton transfer along the hydrogen-bonded network. Moreover, in such a case a stronger physicochemical interaction between the ionic liquid and the polymer matrix can be expected [10]. From this point of view, guanidinium-based PILs seem very promising proton conductors due to the presence of six exchangeable protons in the cation [11, 12]. On the other hand, the high melting point of most guanidine salts is a serious drawback for their application as proton conducting electrolytes. Reducing symmetry of cations can reduce the melting points, and a series of room temperature PILs comprising both common and cyclic guanidinium cations and TFSI anion have been synthesized [13]. However, the substitution of hydrogen atoms on alkyl radicals in the cation led to decreased proton conductivity [14-16].

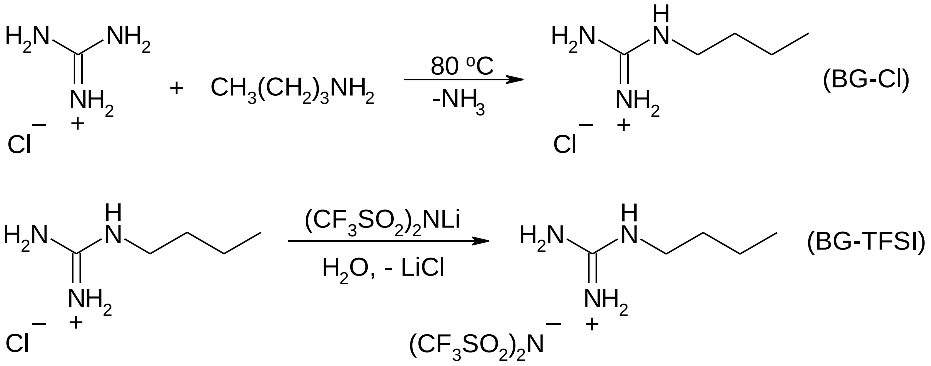
This research aimed to synthesize hydrophobic guanidine salt which is liquid at room temperature. Thus, water immiscible room temperature PIL based on monoalkylguanidine salt has been synthesized and studied in terms of thermal stability (TGA) and ionic conductivity by using electrochemical impedance.

Materials and methods

Following chemicals were used for the synthesis of ionic liquid: guanidine hydrochloride (98%), butylamine (for synthesis) (Sigma-Aldrich), lithium bis(trifluoromethylsulfonyl)imide (Acros), methylene chloride (Uoslab, Ukraine).

Hydrophobic ionic liquid N-butylguanidinium bis (trifluoromethylsulfonyl)imide (BG-TFSI) was synthesized according to Scheme 1. Water soluble precursor, N-butylguanidine hydrochloride (BG-Cl) was synthesized using the method described in [17]. The mixture of guanidine hydrochloride (20 g, 0.2 mol) and butylamine (29 g, 0.4 mol) was put into a round-bottomed flask equipped with a mechanical stirrer and reflux condenser. The mixture was heated to 80°C and stirred for 24 h. The residual butylamine was removed by distillation and further in vacuum 10 mbar at 80°C. The obtained product (BG-Cl) is viscous hazel liquid, highly soluble in water.

7.6 g (0.05 mol) of BG-Cl were dissolved in water (50 mL) under stirring and the solution of lithium bis(trifluoromethylsulfonyl)imide (14.5 g, 0.05 mol) in 50 mL of water was added. The formed bottom layer of the ionic liquid BG-TFSI was extracted with methylene chloride (2 × 50 mL), washed with water (100 mL) and dried under sodium sulfate. Methylene chloride was distilled off, and residual solvent was removed in vacuum 20 mbar at 70 °C for 8 h. The viscous liquid of light yellow color was obtained.



Scheme. Synthesis of protic ionic liquid BG-TFSI.

^{1}H NMR technique was used to characterize the structure of BG-TFSI. ^{1}H NMR spectra were recorded in DMSO-d_6 on a Varian Gemini-2000 (400 MHz) spectrometer using TMS as internal standard. The vibrational properties of ionic liquid were carried out using a Bruker Tensor-37 FT Infrared spectrometer. The sample was prepared as a tablet with KBr. The spectrum was collected over the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} in a dry atmosphere.

Thermal gravimetric analysis (TGA) was made using a Q-1500D thermal analyzer. About 100 mg of sample was heated from 30 °C to 1000 °C with a heating rate of 10 °C/min in air.

The ionic conductivity was measured with the help of impedance spectrometer Solartron SI 1260 in the temperature range 25 – 170 °C.

Results and discussion

Figure 1 contains ^{1}H NMR spectrum of BG-TFSI. The triplet signal at 0.89 ppm is assigned to methyl protons (d) of butyl radical. The sharp peaks at 1.44 and 1.31 ppm are the signals of methylene protons (b) and (c), respectively. The sharp and splitting peak at 3.1 ppm is assigned to protons (a) of NCH_2 group. The broadening and splitting peaks in the region 6.5-7.8 ppm are assigned to the resonance of guanidine protons C-NH-C, C-NH_2 and C=NH_2^+.

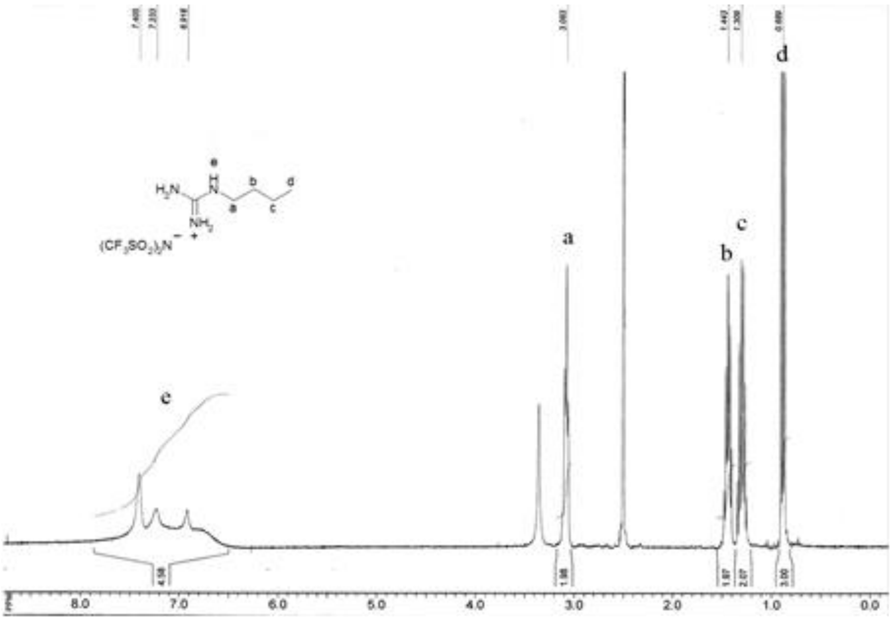


Fig. 1. ^{1}H NMR spectrum of BG-TFSI.

The infrared spectrum of ionic liquid BG-TFSI (Fig. 2) is characterized by a strong absorption band located at 1645 cm^{-1} and broad bands in the region 3200-3600 cm^{-1}. The high-frequency modes are assigned to symmetric and asymmetric bands of NH_2 groups and the band at 1645 cm^{-1} to the scissoring mode of the NH_2 units [18]. The weak but distinct peak observed at 2941 cm^{-1} is assigned to the asymmetric stretching vibration of CH_2 of disordered alkyl chains [19]. The symmetric stretching CH_2 mode expected to be around 2875 cm^{-1}, contributes therefore to the broadening of the band whose maximum is located at 2881 cm^{-1}. The bands at 2966 and 2881 cm^{-1} are respectively attributed to asymmetric and symmetric stretching vibrational modes of methyl groups. The band at 1467 cm^{-1} is assigned to the bending vibrations of CH_2 groups [20]. The strong intensity bands are located at 1658 cm^{-1} for the C=N stretching vibration mode, at 1344 cm^{-1} and 1128 cm^{-1} for the SO_2 antisymmetric and symmetric stretching modes and at 1186 cm^{-1} and 1051 cm^{-1} for CF_3 antisymmetric stretching and the C-C stretching modes, respectively [21].

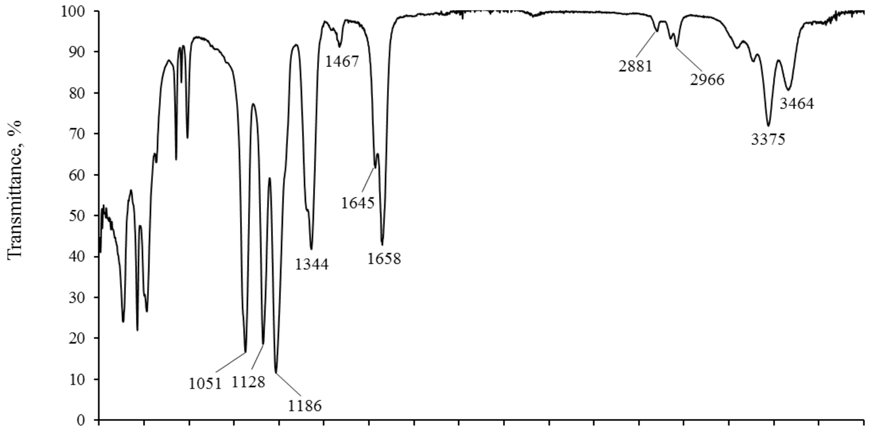


Fig. 2. IR spectrum of BG-TFSI.

According to TGA data, the ionic liquid has the thermal degradation point (5% weight loss) of 348 °C, and the maximum degradation rate is observed at 426 °C (Fig. 3, Table 1). The obtained data are similar to those for other reported PILs comprising TFSI anion [2, 3, 10] and indicate sufficient thermal stability of BG-TFSI for high temperature fuel cell applications.

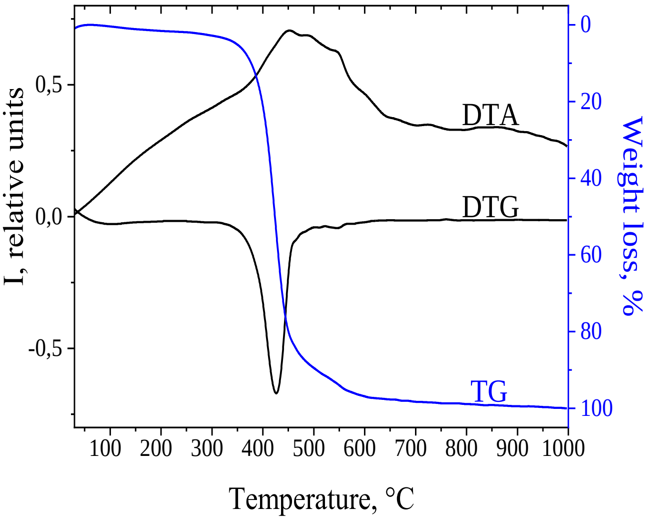


Fig. 3. TGA curves of BG-TFSI.

Frequency dependences of real and imaginary components of the electrical conductivities of BG-TFSI (Fig. 4) indicate the ionic mechanism of conductivity. At low frequencies (up to 0.1 Hz) the conductivity of the system has the lowest value due to the accumulation of charges on electrodes that block the surface by a double electrical layer [22]. The increase of ionic conductivity is observed with increasing frequencies up to 10^2 Hz and the maximum on the bottom curve indicates a decrease in the capacitance of the electrical double layer at the electrode. Further frequency growth leads to charge dissipation when moved through the system [17]. The ionic conductivity of BG-TFSI is around 10^{-3} S/cm at room temperature and increases by almost one order of magnitude at 170 °C (Fig. 5, Table 2) that indicates its availability as a proton conducting electrolyte for high-temperature fuel cells. It should also be noted that the hydrophobicity of BG-TFSI is an important advantage, since it can prevent its leaching from the polymer-electrolyte membrane during fuel cell operation [6].

Table 1. **TGA data for BG-TFSI**

Sample	$T_{\Delta m=5\%}$, °C	$T_{\Delta m=10\%}$, °C	$T_{\Delta m=20\%}$, °C	$T_{\Delta m=50\%}$, °C
BG-TFSI	348	377	398	424

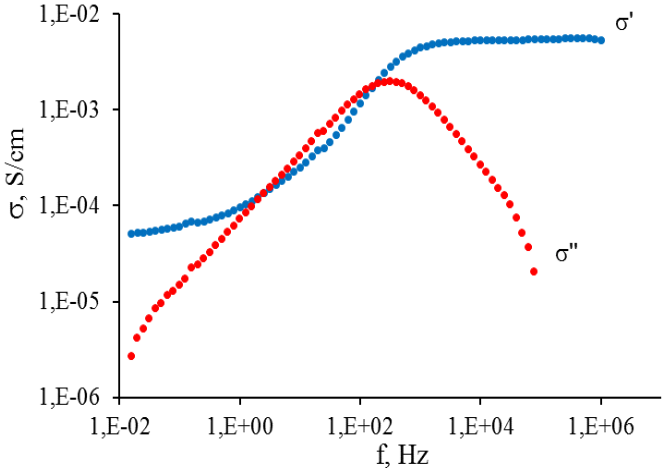


Fig. 4. Frequencies dependences of real (σ') and imaginary (σ'') components of the ionic conductivity of BG-TFSI at 20 °C.

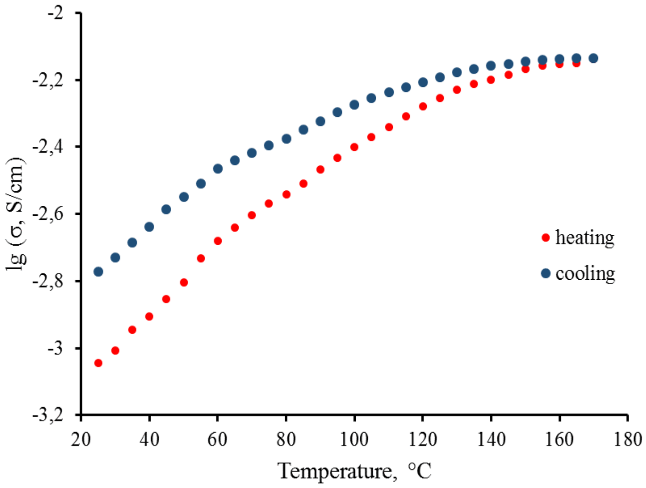


Fig. 5. Ionic conductivity (at frequency of 1 kHz) of BG-TFSI as a function of temperature.

Table 2. **Ionic conductivity of protic ionic liquid BG-TFSI as a function of temperature**

Sample	σ, S/cm			
	25°C	80°C	130°C	170°C
BG-TFSI	$9.1 \cdot 10^{-4}$	$2.9 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	$8 \cdot 10^{-3}$

As earlier noted, there are two types of charge transport mechanism in PILs: vehicle (molecular diffusion) and Grotthus-type (proton migration in the hydrogen-bonded networks). N-butylguanidinium cation of BG-TFSI contains five exchangeable protons which may ensure an efficient proton hopping conduction mechanism. The last one involves thermal activation and follows Arrhenius law as a function of temperature:

$$\ln\sigma = -E_a/RT + \ln\sigma_0$$

where σ_0 is the maximum electrical conductivity at infinite temperature ($S\cdot cm^{-1}$), E_a is the activation energy ($kJ\cdot mol^{-1}$) which indicates the energy needed for an ion to jump to a free hole, R is the universal gas constant (8.314 $J\cdot mol^{-1}\cdot K^{-1}$), and T is the absolute temperature (K).

Thus, the activation energy for ionic conductivity characterizes the difficulty level of ions migration under the electric field. In the Arrhenius diagram (Fig. 6), the dependence of ionic conductivity on temperature ($\ln\sigma$ vs 1000/T) is linear in the range from 40 to 140 °C for BG-TFSI. The activation energy E_a calculated from the slope value (Fig. 6) is 16.4 kJ/mol. This value is close to E_a values reported for other guanidinium based PILs, 1-butylguanidinium tetrafluoroborate (E_a = 17 kJ/mol) [17] and guanidinium nonaflate (E_a = 19 kJ/mol) [23]. Overall, the obtained results indicate that the presence of butyl radical in guanidinium cation does not prevent efficient proton transfer in BG-TFSI.

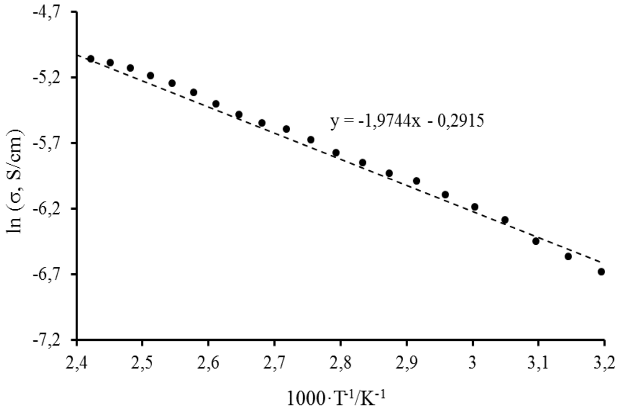


Fig. 6. Arrhenius plot of ionic conductivity for BG-TFSI

Conclusions

New hydrophobic protic ionic liquid comprising monosubstituted guanidinium cation, N-butylguanidinium bis(trifluoromethylsulfonyl)imide (BG-TFSI), has been synthesized by a simple two-step method. The first stage involves condensation between guanidine hydrochloride and butylamine to prepare water soluble precursor N-butylguanidine hydrochloride (BG-Cl). At the second stage, BG-Cl was converted into the water-immiscible ionic liquid BG-TFSI by anion exchange reaction with lithium bis (trifluoromethylsulfonyl)imide in water solution. According to TGA data, the ionic liquid has the thermal degradation point (5% weight loss) of 348 °C which indicates its sufficient thermal stability for use in high-temperature fuel cells. The ionic conductivity of BG-TFSI determined by the electrochemical impedance method was found to be $9\cdot10^{-4}$ S/cm at room temperature. This value increased by almost one order of magnitude at temperatures above 100 °C thus reaching an acceptable level for use in fuel cells. The activation energy E_a calculated from the Arrhenius plot for BG-TFSI was found to be 16.4 kJ/mol which is close to E_a values reported for other guanidinium based ionic liquids. The obtained data also indicate that the proton transport in BG-TFSI is dominated by Grotthus-type (hopping) mechanism.

The liquid state of N-alkyl substituted guanidine salt BG-TFSI is an important advantage over most common guanidine salts which have high melting points. Thus, room temperature PIL can provide a satisfactory level of proton conductivity over a wide temperature range.

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Новий протонпровідний електроліт для високотемпературних паливних елементів на основі гідрофобної солі гуанідину

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Солі гуанідину є перспективними протонними провідниками завдяки високому вмісту у складі їх катіона протонів, здатних до обміну. Це забезпечує ефективне перенесення протонів вздовж сітки водневих зв’язків між донорними і акцепторними групами. Однак високі температури плавлення солей гуанідину є істотним недоліком для їх використання як протонпровідних електролітів. Порушення симетрії гуанідинієвих катіонів заміщенням водневих атомів на алкільні радикали зменшує температуру плавлення солей, а також їх протонну провідність. У цій роботі синтезовано монозаміщену сіль гуанідину - біс(трифторметилсульфоніл)імід N-бутилгуанідинію (БГ-ТФСІ) двостадійним методом. Сполука є протонною іонною рідиною, яка не змішується з водою. Будову БГ-ТФСІ підтверджено методами ядерного магнітного резонансу та інфрачервоної спектроскопії. Згідно з результатами термогравіметричного аналізу, іонна рідина має температуру початку деструкції (втрата маси 5%) 348 °С, що свідчить про її достатню термічну стійкість для використання у високотемпературних паливних елементах. Іонна провідність БГ-ТФСІ, визначена методом електрохімічного імпедансу, становить $9 \cdot 10^{-4}$ См/см за кімнатної температури і зростає майже на один порядок за температур вище 100 °С. Таким чином, іонна рідина має необхідний рівень провідності для застосуванн як електроліту в паливних елементах. Енергія активації іонної провідності E_a, визначена із залежності Ареніуса для БГ-ТФСІ, становить 16.4 kJ/mol і є близькою до величин E_a для інших солей гуанідину. На основі отриманих результатів можна припустити, що протонний транспорт в БГ-ТФСІ відбувається переважно за стрибковим механізмом (Гротгуса). Результати роботи засвідчили перспективність протонної іонної рідини БГ-ТФСІ як електроліту для паливних елементів, які функціонують за підвищених температур і відсутності зволоження. Гідрофобність іонної рідини є важливою перевагою, оскільки може запобігати її вимиванню з полімер-електролітної мембрани при роботі паливного елементу.

Ключові слова: сіль гуанідину, протонна іонна рідина, іонна провідність, протонпровідний електроліт