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Comparative study on the proton conductivity of perfluorosulfonic and polybenzimidazole based polymer electrolyte membranes

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Abstract: The polymer electrolyte membrane (PEM) electrolysis provides a sustainable solution for production of hydrogen with high purity. The most commonly used PEM, the perfluorosulfonic acid membrane (Nafion®), successfully works at temperatures up to 80°C, however above 90-100 ºC Nafion® it loses both conductivity and mechanical stability. Therefore, there is a need for development of PEM with different chemical structure capable to resist elevated temperatures. This work presents a comparative study on the properties of two commercial and three laboratory prepared PBI membranes applicable for preparation of membrane electrode assemblies for high temperature PEM water electrolysis. The proton conductivity is measured at temperatures up to 170 ºC applying the method of impedance spectroscopy. It is found that the conductivity decreases in the order $\sigma_{Celtec®-P} > \sigma_{p-PBI} > \sigma_{m-PBI} \geq \sigma_{ABPBI}$. The differences are discussed in connection with the polymer structure and type of proton transfer mechanism related to the polymer structure and PA doping level.

Key words: PEM, polybenzimidazole membrane (PBI), proton conductivity, high temperature water electrolysis

INTRODUCTION

Polymer electrolyte membrane (PEM) electrolyzers can operate at much higher current densities compared to classical alkaline electrolyzers achieving values above 2 A.cm^{-2}, while they reduce the operational costs and potentially, the overall cost of electrolysis [1]. The solid electrolyte also allows essential reduction of system dimensions ,low gas crossover rate, and wide range of power input (economical aspect). The letter is due to the fact that the proton transport across the membrane responds quickly to the power input, not delayed by inertia as in low molecular liquid electrolytes. In the alkaline electrolyzers the hydrogen permeability through the diaphragm increases at high loads, yielding a larger concentration of hydrogen on the anode (oxygen) side thus, creating hazardous and less efficient conditions. In contrast with the alkaline electrolysis, PEM electrolysis cover practically the full nominal power density range [1,2]. One could speculate that PEM electrolysis could reach 100% of the nominal power density derived from a fixed current density and the corresponding cell voltage. This is due to the low permeability of hydrogen through Nafion (less than 1.25.10^{-4} cm^{3}s^{-1}cm^2 for Nafion® 117 at standard pressure,80 ºC and 2 mA.cm^{-2}) [3].

In the recent years the high temperature PEM water electrolysis (HT-PEWE) operating in the temperature range from 100 to 200 ºC has been recognized as a promising technology to meet the contemporary technical challenges since the increase in the operational temperature affects favorably the energy demand for the splitting of water to hydrogen and oxygen [4]. The realization of HT-PEWE is a driving force for developing of proton exchange polymer membranes capable to work at such severe conditions [3, 5]. The most critical issues beside the proton conductivity are the thermal, chemical and mechanical stabilities of the polymer materials at these elevated temperatures [6, 7].

Phosphoric acid doped polybenzimidazole (PBI) membranes have been investigated and successfully used in PEM fuel cells at elevated temperatures (HT-PEFC) because of their excellent thermo-chemical stability, low gas permeability, high mechanical stability and good proton conductivity [7, 8]. Since the chemical processes occurring in hydrogen PEM fuel cells and in water electrolysis are reversible, it is expected that the PBI membranes doped with phosphoric acid could work successfully also in HT-PEWE [9]. The number of commercial HT-PEM is very limited. At the same time there is an intensive research on developing of

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new products with broad variations in their chemical composition [10].

This work presents a comparative study on the conductivity of two commercial products and three laboratory prepared polybenzimidazole based membranes dotted with phosphoric acid at broad range of experimental conditions (temperature, humidity, gaseous atmosphere).

EXPERIMENTAL

Membranes

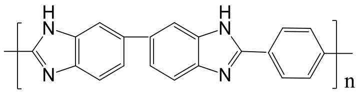
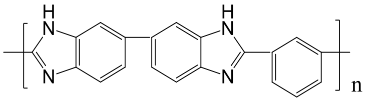
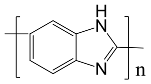
The commercial products tested are Nafion® 117 (perfluorosulfonic acid) and Celtec®-P type (para-polybenzimidazole doped with H_3PO_4). It is well known that Nafion® 117 optimal working temperature is 80 ºC and higher temperatures affect the mechanical stability and conductivity of this membrane [11]. The optimal working temperature of Celtec®-P according the literature is 160-170 ºC [12]. In this study before measurements the Nafion® 117 membrane is activated in 0.05 M sulfuric acid using a standard activation procedure - boiling in 3% H_2O_2, rinsing in boiling water, thenboiling in 0.5 M H_2SO_4, and finally rinsing in boiling water (at least 1 h for each step) [13]. The e Celtec®-P type membrane is dotted with 70% phosphoric acid and hold in special air free box, since long exposure in air leads to humidification changes of the phosphoric acid, affecting the membrane conductivity.

Three types of PBI based membranes poly[(2,2-(p-phenylen)-5,5-bisbenzimidazole], poly[2,2-(m-phenylen)-5,5-bisbenzimidazole] and poly(2,5-benzimidazole), denoted as p-PBI, m-PBI and ABPBI respectively were prepared and chemically modified. They differ in chemical structure of the building monomer (Table 1), the method of preparation, and the amount of the doping o-phosphoric acid (PA) inside the polymer electrolyte matrix [8].

The p-PBI membrane is prepared using 2% p-PBI solution from BASF, applying the sol-gel method developed by Xiao [14]. The solution is heated up to 200 ºC under stirring and left for 72 hours at open air. The formed dry polymer film is immersed in 70% o-phosphoric acid for conditioning. Thus obtained p-PBI membrane contains 5 wt.%. p-PBI and 95 wt.% of 70%PA and has an elastic module of 3.5MPa [15].

The ABPBI membrane is synthesized using a modified Eaton's reagent (8 wt% P_2O_5 in methane sulfonic acid) containing sulfuric acid.

Table 1. Conductivity of Celtec®-P and laboratory prepared PBI/PA membranes calculated from the impedance spectra measured at 160°C

Membrane	Structure of the building monomer	Conductivity [S.cm^{-1}]			Ea [kJ.mol^{-1}]
		Wet air 20%RH	Air 1st heat	Air 2nd heat	Air 2nd heat
Celtec®-P		0.24±0.02	0.22±0.02	0.19±0.01	14.2±0.2
p-PBI/PA		0.21*	0.19±0.01	0.13±0.01	21.1±0.2
m-PBI/PA			0.10±0.005	0.08±0.005	22.8±0.5
ABPBI/PA			0.09±0.006	0.08±0.005	20.6±0.4

*The conductivity of the same membrane measured from [21]

The 3,4- diaminobenzoic acid single monomer precursor is purified by a simple charcoal procedure. Then a thin film is spread using doctor blade technique and left to sol-gel transform in open atmosphere for 48h, washed with water and ammonia solution and dried at room temperature. The obtained dry polymer film is subsequently doped with 85% o-phosphoric acid.

The preparation of the m-PBI membrane is done identically by the described procedure for the ABPBI membranes with two different monomers – diaminobenzidine and isophtalic acid used for the synthesis of meta-PBI in Eaton's reagent.

Test cell

The experiments are carried out in self-made test cell presented on Fig. 1. It consists of working chamber (Fig.1a) and a Teflon holder (fig. 1b). The temperature in the chamber can be precisely controlled from up to 200ºC. The heater is

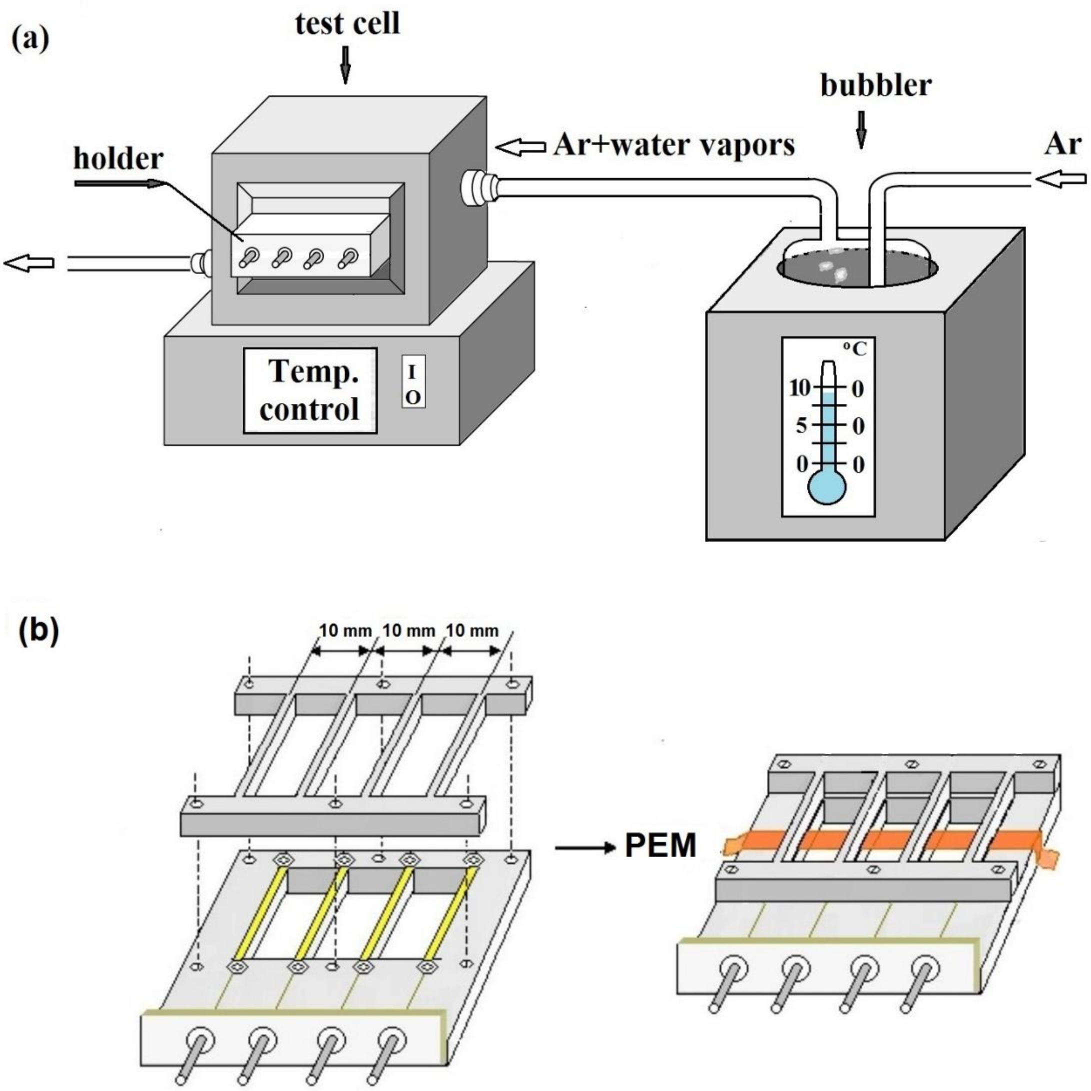


Fig.1. Laboratory test cell for measurement of polymer electrolyte membrane conductivity:
a) working chamber with temperature controller; b) membrane holder with sensing contacts/electrodes.

designed as a non-inductive bifilar winding to avoid disturb on impedance measurements. The humidity in the cell is ensured by flow of argon passing through heated water bubbler and controlled by the temperature.

The design of the Teflon holder ensures maximum contact with the gaseous flow, i.e. maximum humidification of the measured membrane. Two, three or four sensing contacts/electrodes are located on the holder, giving a possibility to use 4-probe method or to test different sections of the membrane as well as of samples with different length (1, 2, and 3 cm) by 2-electrode scheme.

Conductivity measurements

The characterization of the membranes is performed by impedance spectroscopy, using Phase Sensitive Multimeters Newtons4th Ltd. PsimetriQ-PSM1700 equipped with Newtons4th Impedance Analysis Interface (IAI). The measurements are carried out in the frequency range 1MHz-1Hz with sampling rate of 10 points per decade, and ac amplitude ≤ 100 mV. The conductivity is calculated from the determined resistance using the equation:

$$\sigma = \frac{l}{Rdw} \qquad (1)$$

where σ is the membrane conductivity, l - the length between the electrodes, R - the membrane resistance, d - the membrane thickness, and w - the membrane width.

RESULTS AND DISCUSSIONS

Commercial membranes

To get consistent results for the newly developed PBI membranes, the reliability of the developed test cell and the measuring procedure is verified, measuring the proton conductivity of two commercial products with well-known characteristics, namely the Nafion® 117 and Celtec®-P membranes. Different test procedures are applied. The first one consists of gradual increase of temperature from 25 ºC at high levels of humidity (RH=95% at 100°C and RH ≈20% at 160-170 °C) and recording of the impedance spectrum stepwise at different temperatures. Figure 2 presents the Nyquist plot of Nafion® 117 and Celtec®-P at room temperature. The Nyquist plot consists of part of semicircle in the high frequency range and characteristic spike due to diffusion and polarization in the low frequency range. The resistance of the membranes (R) is determined by the low frequency intersection of the semicircle with Z_{re} axis as pointed (the arrows in fig. 2).

The conductivity is not a monotonic function of the temperature for both type of membranes (fig. 3). Initially the conductivity of Nafion® 117 increases with temperature, reaches maximum value 0.13 S.cm^{-1} around 60^{o}C, and then decreases to 0.11 S.cm^{-1-}at 80 °C. The proton conductivity is a function of both temperature and membrane water content (water content is defined as the molar ratio of water molecules per SO_3H^- group) [16,17]. Reike and Vanderborgh have established that at the decrease in the conductivity at temperatures above 60 ^{o}C is not related with the starting drying process since the water content is still high enough. Using FTIR they have showed that at these temperatures fractions of the sulfonic acid groups are no longer ionizedand do not participate in the proton transfer which results in decrease of membrane conductivity [16].

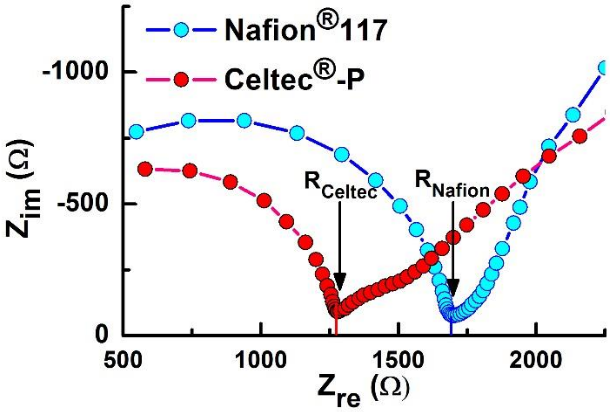


Fig. 2. Impedance Nyquist plot of commercial membranes Nafion® and Celtec®-P at room temperature

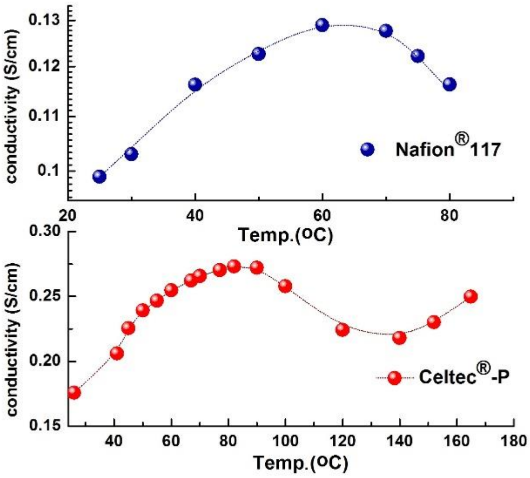


Fig. 3. Temperature dependence of the conductivity of Nafion® 117 and Celtec®-P.

With the increase of temperature the conductivity of Celtec®-P membrane reaches maximum value of 0.27 S.cm^{-1} around 90^{o}C, then decreases to passes through a minimum (σ=0.22 S.cm^{-1} around 140^{o}C, and begins to increase again reaching 0.24 S.cm^{-1} at 160 ^{o}C (Fig 3).

The second series of tests is carried out at constant temperature (80^{o}C and 170 ^{o}C for Nafion® 117 and Celtec®-P, respectively). Once it is reached, the humidification flow in the chamber is interrupted and a dry Ar flow is introduced in the chamber. The results obtained are compared in fig.4. They show that as soon as the dry argon is delivered in the test chamber, the conductivity of Nafion® 117 decreases dramatically. In contrast, after an initial decrease the conductivity of Celtec®

P stabilizes at 0.11 $S.cm^{-1}$ which is a very good value for dry condition.

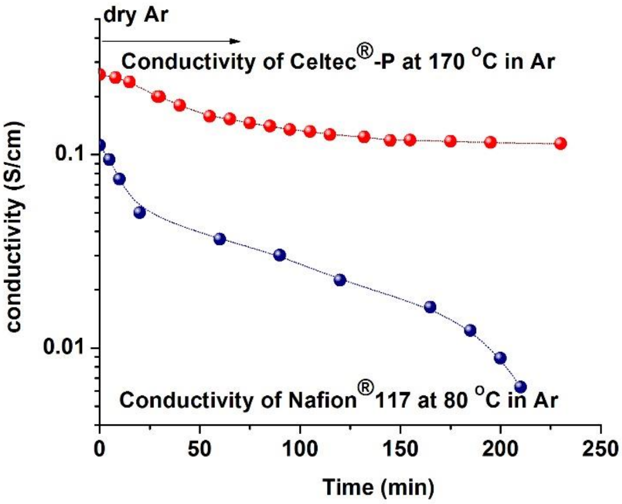


Fig.4. Time dependence membranes conductivity, calculated from the impedance spectra in dry Ar of Nafion® 117 at 80 °C and Celtec®-P at 170 °C.

These results are consistent with the conductivity values for both commercial membranes reported in the literature for Nafion® 117 [16, 19, 20] and Celtec®-P [21]. They are logical and expected since the proton conducting mechanism for both membranes is completely different. In the case of Nafion® 117 the transport of protons requires presence of superacid polymer electrolyte/water clusters in the volume of the membrane. The proton transport occurs by a vehicle mechanism, in which the water molecules forming hydronium ions carry the protons to the adjacent sulfonic sites. In the absence of water, i.e. under dry conditions or above temperatures of 80 ºC, the predominant proton transport mechanism is direct hopping between sulfonic sites and Nafion® conductivity decreases significantly. In Celtec®-P the protons move predominantly through the phosphoric acid H-bond intermolecular network (at high PA doping levels) and partially through the PBI N-heterocycles of the polymer chains. The transport in this type of membranes is dominated by the so called proton hoping (Grotthuss) mechanism [18].

Laboratory prepared membranes

It has b verified that while Nafion® 117 is efficient at high humidity, the experiments PBI-based membrane Celtec®-P performs very well at low humidity. Therefore, the the con laboratory prepared p-PBI, m-PBI and ABPBI membranes together with Celtec®-P are tfurther ested in an open system (i.e. in air) without additional moistening. The experiments are carried out in the temperature range 25÷170ºC. The obtained conductivity-temperature dependencies are presented in Fig. 5. The as prepared membranes at room temperature contain some amount of adsorbed water which with heating gradually evaporates. The leakage of that absorbed water in turn, influences the conductivity of the membranes (Fig. 5a). To avoid this inconsistency in the test conditions, a second series of measurements is performed immediately after the first one as the temperature was changed in opposite direction cooling down the system gradually form 160 ºC to – form of the test samples measurements. These results are presented in (fig. 5b). For comparison, the values of the proton conductivity calculated from both sets of impedance spectraare summarized in Table 1. As it is seen the conductivity decreases in the order $\sigma_{Celtec®-P} > \sigma_{p-PBI} > \sigma_{m-PBI} \geq \sigma_{ABPBI}$ The best result among the laboratory prepared samples is obtained for p-PBI membrane, however its proton conductivity is lower compared to that of the commercial Celtec®-P membrane. The values for m-PBI and ABPBI at 160 ºC are close to those obtained by Choi et.al. (σ_{m-PBI}=0.0951 $S.cm^{-1}$ and σ_{ABPBI}=0.0832 $S.cm^{-1}$ [22]).

The mechanism of proton conductivity can be recognized from the temperature dependence [23-25]. Since the PBI membranes possess high glass transition temperature (T_g), the dependence of conductivity on temperature should obey the Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} exp\left(-\frac{E_a}{RT}\right), \qquad (2)$$

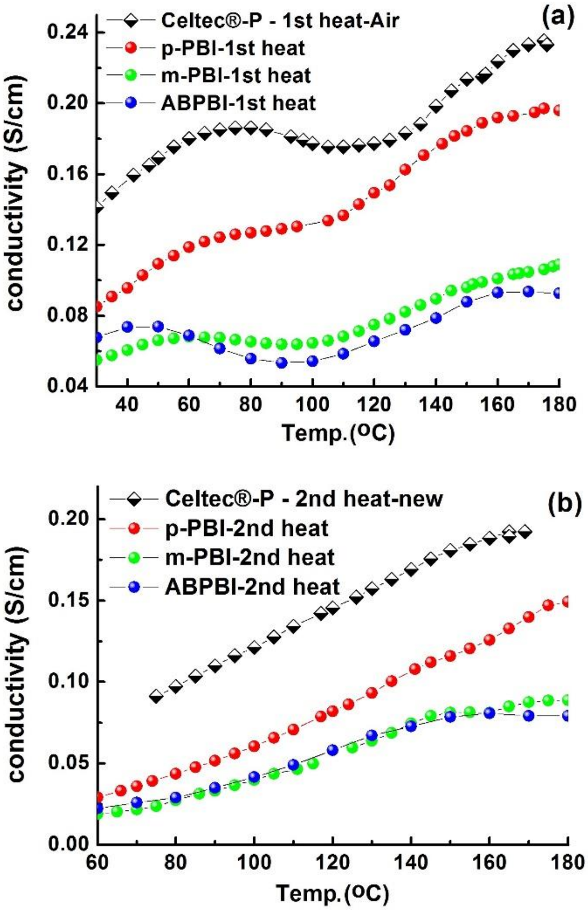


Fig. 5. Temperature dependence of conductivity of Celtec®-P and laboratory prepared PBI-membranes, in air: (a) first heat; (b) second heat.

where σ is the conductivity, σ_0 is a pre-exponential factor, E_a - activation energy, R - the gas constant and T – the absolute temperature.

The results presented in Fig. 6 confirm this assumption. The linearity of the Arrhenius plot ln(σT) vs T^{-1} sustains in wide temperature range (up 150°C) for the all membranes tested. This means that the proton transport is controlled by the hopping mechanism. Using a linear fit, the activation energies are determined from the slope of PBI-membrane compared to Celtec®-P mean that a higher potential barrier is needed for the proton transfer which in turn, results in lower conductivity of this membrane, despite the almost equal amount of doping PA in both samples. The explanation of this difference should be sought in the structural variation of the membranes. On the other hand, the difference in the calculated activation energies of the three laboratory prepared PBI membranes under study are comparatively low, suggesting that the mechanism of ion transport is the same. Hence, it can be concluded that the difference in the conductivity is mainly due to the different levels of PA doping. Over 150°C a deviation from Arrhenius dependence is observed. It is connected to dehydration of the phosphoric acid, formation of pyrophosphoric acid ($H_4P_2O_7$), and in result, to drop in the membrane conductivity.

As mentioned before the proton transport in PBI membranes is dominated by the hoping Grotthuss mechanism. According to Ma [26], the conductivity in these type membranes is realized by proton hoping through paths via different hydrogen bonds, depending on different factors such asd the doping level, RH, and temperature. At high acid doping level and water content and/or at high humidity, the protons are hopping through acid-water path (H_3PO_4…H-O-H…$H_2PO_4^-$) and phosphoric acid chains (H_3PO_4…$H_2PO_4^-$) as the former path dominates. This correlates with the measured highest conductivity of Celtec®-P, in wet Argon, as well as with the higher conductivity of the first scan of the impedance with the increasing temperature, where water is still present in the membranes. At low RH or dry conditions, there is deficiency of hydrogen bonds, i.e. of donor/acceptor pairs and the main proton transport is carried out through the phosphoric acid chains i.e. path (H_3PO_4…$H_2PO_4^-$) with small contribution of the (N-H^+…$H_2PO_4^-$) path, which resultsin decrease of conductivity. The calculated value of E_a for Celtec®-P is close to that of the pure H_3PO_4 [25], suggesting that the protons hop through the long phosphoric acid chains (H_3PO_4…$H_2PO_4^-$). The higher activation energies of the laboratory prepared PBI/PA membranes could be explained with the shorter phosphoric chains, interrupted from N-H^+…$H_2PO_4^-$ and N-H^+…N-

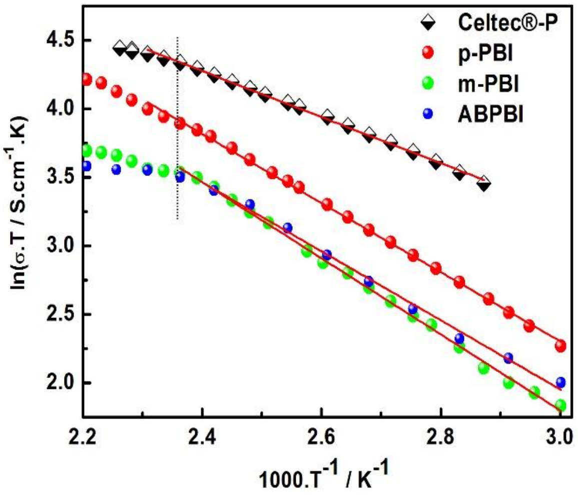


Fig. 6. Arrhenius plot: ln(σ.T) vs. 1/T of Celtec®-P and laboratory prepared PBI-membranes.

H^+… bonds. Thus, the observed differences in the conductivity of the polymer electrolyte membranes under investigation can be explained with the type of the ion transport determined by the polymer structure as well as the acid doping level.

CONCLUSIONS

The performed comparative study on proton-conductivity of polymer electrolyte membranes (perflourosulfonic acid Nafion® and a polybenzimidazole based membrane dotted with phosphoric acid Celtec®-P) and three laboratory prepared PBI based samples (p-PBI, m-PBI, and ABPBI) demonstrated that the applied testing procedure based on electrochemical impedance measurements is a reliable approach for screening and preselection of various type of polymer The results obtained showed that the conductivity of the home prepared p-PBI, m-PBI and ABPBI membranes are comparable with the best commercial product of that type available on the market and could be used for preparation of membrane electrode assemblies. .

The best performance of 0.19 $S.cm^{-1}$ at 160 ºC and very good stability at elevated temperatures without degradation showed the p-PBI membrane, which is considered as the most perspective for practical applications in HT- PEM water electrolysis.

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СРАВНИТЕЛНО ИЗСЛЕДВАНЕ НА ПРОТОННАТА ПРОВОДИМОСТ НА ПЕРФЛУОРОСУЛФОНИРАНИ И ПОЛИБЕНЗИМИДАЗОЛ БАЗИРАНИ ПОЛИМЕРНИ ЕЛЕКТРОЛИТНИ МЕМБРАНИ

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(Резюме)

Електролизата на вода в клетки с полимерна електролитна мембрана (ПЕМ) осигурява производство на водород с висока чистота. Най-често използваната ПЕМ, перфлуоросулфонова мембрана (Nafion®), успешно работи при температури до 80 °C. Над 90-100 °C тя губи както проводимостта, така и механичната си стабилност. Следователно, съществува необходимост от разработването на ПЕМ с различна химична структура, устойчива на по-високи температури. Тази статия представя сравнително изследване на протонната проводимост на две търговски и три лабораторно подготвени полибензимидазол (ПБИ) базирани мембрани, приложими за високотемпературна ПЕМ електролиза на вода. Проводимостта е измервана при температури до 170°C с импедансна спектроскопия и е установено, че намалява в реда Celtec®-P>p-PBI>m-PBI≥ABPBI. Разликите са обсъдени в контекста на механизма на протонния трансфер, свързан със структурата на полимера и степента на дотиране с фосфорна киселина.