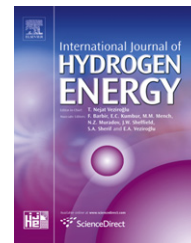


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Novel polyolefin/silicon dioxide/H₃PO₄ composite membranes with spatially heterogeneous structure for phosphoric acid fuel cell

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ABSTRACT

Novel composite membranes based on polyolefins for intermediate and high temperature (120–160 °C) phosphoric acid fuel cells with polymer matrices have been synthesized and their properties have been studied, including testing in operating fuel cells. In contrast to polybenzimidazoles uniformly swelling with H₃PO₄, which are typically used as membrane-separators in such a type of fuel cells, the proposed materials have heterogeneous internal structure with spatially separated condensed bundles of non-swelling rigid polymer-silica composite matrix and proton-conducting channels filled with phosphoric acid. Such a heterogeneous structure may potentially provide improved balance between proton conductivity and mechanical stability of the membranes in comparison with the homogeneously swollen PBI structures. The composite porous films based on polyethylene and polypropylene have been prepared in several different ways and filled with network of silicon dioxide. The SiO₂ phase forms hydrophilic three-dimensional well-percolated channels. The affinity between the SiO₂ phase and the liquid phosphoric acid is responsible for capillary retention of the liquid electrolyte in the porous matrix (phosphoric acid wets SiO₂ surface). Besides, the framework of SiO₂ phase enhances the mechanical stability of the membranes at high temperatures. Maximum proton conductivity of 0.033 S/cm is achieved at 160 °C for fuel cell with the obtained polyethylene-based membrane. The best performance is detected for fuel cells on polypropylene-based membrane, which provides 0.5 V at 0.4 A/cm² at 140 °C being supplied with hydrogen and air. The proposed concept is aimed to mimic spatially-non-uniform Nafion-type membranes instead of using uniformly swollen polybenzimidazoles.

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1. Introduction

The fuel cells (FC) are well known as a promising alternative to conventional power sources due to their high efficiency of energy conversion, low pollutant emission, etc. [1,2]. Among the different types of fuel cells, polymer electrolyte membrane fuel cells (PEFC) have several advantages such as rather simple system design, good pressure imbalance tolerance, convenient operating temperature range and relatively simple assembly procedure [3]. Such fuel cells are proposed as an attractive choice for portable, transport and stationary applications [1,4].

Perfluorosulfonic acid polymers, e.g. Nafion, are the most commonly used as polymer electrolyte membranes. They have rather high proton conductivity and simultaneously relatively good chemical and mechanical stability, optimal gas (im)permeability and acceptable durability [5]. However, high degree of water content in the membrane is required in order to maintain sufficiently high proton conductivity and, therefore, the operating temperature cannot be increased above 90–100 °C due to problems with water retention. Besides, mechanical stability of Nafion-type membranes decreases dramatically at the temperatures above 100 °C. Nevertheless, higher operating temperatures (120–180 °C) of FC ensure certain benefits. The most significant one is the improved catalyst tolerance towards possible residual impurities in the fuel, in particular, to carbon monoxide, that allows to exploit cheaper hydrogen fuel, thus simplifying CO-removal procedure and reducing corresponding expenses (i.e., fuel price) [6,7]. In addition, at these intermediate and higher operating temperatures one may expect enhanced electrode kinetics, furthermore, there are no problems with cathode overflowing (with water being generated) and heat utilization is also more effective (i.e., the temperature control is simpler) [6,7].

In recent years different polybenzimidazoles (PBI) have been recognized as a good choice of proton conducting membranes operating at intermediate and higher temperatures [8]. These materials have excellent mechanical property, thermal and chemical stability [9,10]. PBIs conduct neither protons nor electrons, but they may acquire proton conductivity when doped with some acid. Phosphoric acid is considered to be the most prominent liquid electrolyte for PBI matrices due to high proton conductivity of the thus obtained doped membranes even in an anhydrous form, very low vapor pressure and high thermal stability of the acid [11]. However, phosphoric acid deteriorates cathode reaction because of phosphate anion adsorption on the platinum surface and therefore one can hardly expect any improvements of the electrode kinetic due to increased operation temperature of the phosphoric acid fuel cells as compared to Nafion-based ones [12].

The conductivity of the PBI membrane doped with phosphoric acid depends on the acid content. The higher is the acid doping level of the membrane, the higher is the proton conductivity, but at the same time the mechanical stability of the matrix is more and more deteriorated. Thus, it is necessary to look for a certain compromise between these two factors. Extensive efforts have been made to improve proton

conductivity yet maintaining good mechanical strength or vice versa such as covalent cross-linking of the membrane, chemical modification, synthesis of copolymers and composite membranes [13–17]. Apart from PBI-based membranes, different other anhydrous proton-conducting membranes with appropriate properties have also been explored as attractive alternatives, e.g., based on polyimidazoles, polyethylene glycols and etc. [18–20].

Typically, doped PBI membranes and their analogs possess uniformly swollen, spatially homogeneous gel structures in distinct from Nafion-type membranes. Indeed, in contrast, Nafion structures at the nanoscale level consist of wide (a few nanometers) proton-conducting channels and dense network of hydrophobic polymer domains [21]. Due to this peculiar phase-separated internal structure, Nafion-type membranes combine high proton conductivity with good mechanical stability. Enhancement and control of the order degree (in particular, long-range order [22]) in the phase-separated picture is considered to be among the most promising approaches to develop materials suitable for FC with the performance to be achieved reasonable for real application [23]. It seems to be rather promising to implement similar spatial non-uniformity at the submicron level in the structure of the membranes doped with phosphoric acids. Therefore, we explore a concept to mimic Nafion-type membranes by introducing phase separation into the structure of polymer matrices doped with liquid H₃PO₄-electrolyte. Indeed, such a structure seems to be an attractive improvement for these membranes in order to attain optimum balance between proton conductivity and mechanical stability.

In order to introduce some spatial heterogeneity into a polymer matrix for phosphoric acid, the most explored approach nowadays is to start with a common PBI material and then to modify it, mainly, in such a way as to create some spatial features at the submicron- or nano-scale range. From this viewpoint, among typical recent examples one can mention introduction in PBI bulk of zwitterion-coated silica nanoparticles [24], silica nanocomposite [25], silica-riveted phosphotungstic acid [26], titania particles [27], nanotubes [28], nanodiamonds [29], silane-based cross-linkers [30] or acidic polymers for interpolymer complexation [31]. As a rule, more optimal balance between proton conductivity/mechanical stability/acid retention was typically reported in these works due to the influence of the properly tailored fillers [32], though, with a few examples [27,28], some lack of testing of the obtained composites in real operating fuel cells may be noticed in the relevant literature.

But, usual PBI materials tend to swell homogeneously in phosphoric acid. In our opinion, this strong tendency of the matrix should diminish any possible influence of filler onto its local spatial organization. Therefore, instead of introducing non-homogeneity into the spatial PBI structure, we propose to use non-swelling highly porous polymer materials, which already possess a non-homogeneous spatial structure. Somewhat similar concepts of using heterogeneous polymer and composite matrices of different nature—i.e., other than PBI—are known from recent literature, for example, when organosiloxane inorganic-organic hybrid net [33], polyvinyl alcohol-based compositions [34,35] or polyacrylamide

frameworks [36,37] were successfully explored as a reservoir for phosphoric acid with good retention capabilities. We propose here to use some cheap commercially available porous polymer nets and apply silica to modify the chemistry of their pores as well as to reduce the effective pore size in order to ensure durable phosphoric acid retention due to capillary forces.

Firstly, dense hard bundles of non-swelling polymer phase should ensure mechanical stability of the membrane as a whole much more efficiently than in the case of homogeneous PBI structure with strongly swollen plasticized polymer phase. Secondly, larger open percolated channels in between the non-swelling polymer bundles filled with phosphoric acid should provide membrane with better proton conductivity. Indeed, Garcia-Gabaldon et al. have proposed that specific effective conductivity of phosphoric acid is higher when it is localized in larger pores [38] and therefore proton conductivity of membrane with such a heterogeneous structure is expected to be higher at the same acid content. Further, we expect also better specific effective conductivity in our system due to the absence of any base macromolecules (e.g., PBI), which chemically interact with acid molecules (accept protons, form a salt) and disturb the proton-conducting network (Grotthuss mechanism) of hydrogen bonds in the H_3PO_4 phase. Thus, we suppose that the proposed membranes with spatially heterogeneous structure may be more effective for intermediate and higher temperature phosphoric acid fuel cells as compared to common uniformly swollen membranes of the PBI-type.

In the present study we report on new types of membranes based on polyalkenes (polyolefins) with spatially heterogeneous structure for operating at intermediate and higher temperatures (120–160 °C). These materials were previously used as electrolytes and fillers for low temperature PEFC [39–41] but here for the first time we use them as composite membranes to be doped with phosphoric acid for significantly higher operating temperatures. One important advantage of the polyolefins is that they are much cheaper as compared to PBIs as far as are produced in vast quantities. The main purpose of the work is to illustrate the concept of mimicking Nafion-type membranes with spatially non-uniform polymer-based matrices for phosphoric acid. Polyolefins do not swell in phosphoric acid and therefore we use them as highly porous polymer matrices to be filled with the liquid electrolyte. From this viewpoint the concept is somewhat similar to the classical design of a phosphoric acid fuel cell with inorganic matrices-separators. Power plants with classical phosphoric acid fuel cells are the only FC-systems, which are produced and sold in commercial purposes. Yet, there are many drawbacks of inorganic matrices mainly related to their fragility. The process of the matrix preparation may hardly provide sufficient degree of uniformity thus formation of some occasional defects—such as pinholes or just too large pores—is quite possible at small matrix thicknesses (the thinner is the matrix, the smaller are the ohmic losses in general) [42]. The presence of such defects reduces tolerance of FC towards possible pressure imbalance between gas-fed cathode and anode during operation. Another serious problem of the classical design of the phosphoric acid fuel cell is that the acid is easy to solidify during shutting-down procedure after

prolonged continuous operation and thereby during solidification may damage the porous structure of the matrix [43]. Usage of the more elastic, robust and easy-to-handle polymer matrices yet should provide better flexibility in assembling and starting-up/shutting-down cycles. The advanced spatially heterogeneous structure of the proposed polymer-based matrices is supposed to provide potentially better balance between proton conductivity and mechanical stability as compared to PBI membranes. It should be noted that the porous polyolefin based materials can retain phosphoric acid due to capillary forces. However, in order to ensure strong capillary retention the walls of the pores should have strong affinity towards phosphoric acid (wetting). Therefore, special fillers with the required affinity are to be introduced into the pores in order to prevent acid leakage. Using hyperbranched polyethoxysiloxane as a precursor, silicon dioxide phase is to be synthesized directly in the pores [44]. There is an advantage of using hyperbranched polyethoxysiloxane as compared to its low-molecular-weight analog, tetraethoxysilane, as far as it is nonvolatile and fills a porous structure of polymer uniformly throughout the whole volume of the polymer matrix. Previously, it was shown that this approach allowed us to produce SiO_2 phase, which formed a chemically linked well-percolated three-dimensional network inside the polymer matrix imparting additional mechanical stability of the composite [44,45].

The objectives of our investigation are the preparation of the polyolefin- SiO_2 composites doped by H_3PO_4 and testing their behavior in the operating fuel cells.

2. Experimental part

2.1. Materials

The following porous polymer membranes were used for further synthesis of proton-conducting composite membranes:

- Non-woven material (PP) based on isotactic polypropylene (JSC Kamenskvolokno, Rostov-on-Don, Russia) with a thickness of 85 μm , pore diameter smaller than 30 μm , porosity of 55%.
- Nanoporous film (PE) based on industrial film of high-density polyethylene ($M_w = 200000$, with thickness of 75 μm , percentage crystallinity of 60%, $T_{mp} = 130$ °C), prepared by crazing mechanism [46]. We applied uniaxial deformation of the initial film in heptane to 200% with the rate of 5 mm/min at room temperature and stabilized it in isometric conditions at 100 °C for 1 h in the electric drying closet SNOL 67/350 (Lithuania). Such a film has porosity of 50% and pore diameter of 5–9 nm.
- Microporous film such as hard elastic [47] (PE-h) based on high-density polyethylene (276 grade, density 0.96 g/cm³), prepared by the extrusion method of polymers melt at high flow rate with subsequent annealing, uniaxial stretching and heat setting (Institute of Macromolecular Compounds of RAS, Saint-Petersburg, Russia). The prepared membrane had thickness of 20 μm , porosity of 40–60%, and pore diameter of 200 nm.

Hyperbranched polyethoxysiloxane (HPEOS) ($M_w = 30000$, density 1.17 g/cm^3 , viscosity 18.8 cP , effective diameter of molecule $2\text{--}5 \text{ nm}$), prepared according to the procedure described in Ref. [48], and diethylphosphatoethyltriethoxysilane (DEPETEOS) (92%, density 1.03 g/cm^3 , $T_{mp} = 70 \text{ }^\circ\text{C}$, ABCR GmbH & Co KG production, Germany) were used as precursors. Fig. 1 shows chemical formulas of these compounds.

2.2. Preparation of composite membranes

Porous polymer membranes PP, PE and PE-h were impregnated for 2 h at room temperature with HPEOS or with mixture of HPEOS/DEPETEOS (molar ratio 2:1). Then films filled with organic silicon compounds were placed into desiccator over the 10% hydrochloric acid solution for 24 h. After the hydrolytic condensation reaction the samples were washed with distilled water and dried at room conditions for 24 h. The obtained polymer-silica composites were doped with 85% phosphoric acid solution for 24 h and named as PP/SiO₂ (mixt), PE/SiO₂ (mixt), PE/SiO₂, PE-h/SiO₂, where (mixt) means mixture of HPEOS/DEPETEOS. Some samples of PE/SiO₂ were heat-treated at $160 \text{ }^\circ\text{C}$ for 1 h in H₃PO₄ between plane-parallel glass plates with subsequent slow cooling to room temperature in furnace. It is further marked as PE/SiO₂-160.

2.3. Characterizations of composite membrane

SiO₂ content in the composite membrane was measured by thermogravimetric analyzer “Mettler TA4000”. The samples of undoped composite membrane were heated up to $700 \text{ }^\circ\text{C}$ with rate of $20^\circ/\text{min}$. Polymer was completely burnt down at such conditions, and the residual was ascribed to SiO₂.

Phosphoric acid content was evaluated by electronic balance AND ER-182A and calculated by the relationship: $\Delta m, \text{ wt } \% = 100\% \cdot (m_k - m_0)/m_k$, where m_k and m_0 are masses of doped and undoped composite membrane respectively.

The morphology of the samples (surface and volume) was studied using a scanning electron microscope JEOL JSM-

6390LA (Japan). In order to investigate bulk structure, cleavage surface of the films were made by brittle fracture in liquid nitrogen. All the samples were coated with a gold film with a thickness of $50\text{--}70 \text{ nm}$ on the sputtering device Giko IB-3 (Japan) before SEM observation. The silicon, carbon and phosphorous atom distribution was analyzed by energy dispersion spectrometry (EDS), using JEOL EX-54175JMH detector, combined with the microscope.

2.4. Fuel cell tests

The membrane-electrode assemblies (MEAs) were assembled with fuel cell hardware units (Arbin Instruments) including bipolar graphite plates with reagent supply system and current collectors. In order to ensure reliable comparison of different membranes we used commercial gas diffusion electrodes (GDE), which, in our experience, have very reproducible performance. The electrodes were taken from commercial Celtec-P Series 1000 MEA (PEMEAS). Such a MEA contains two electrodes and a PBI-membrane, but the latter can easily be removed and replaced with another one (before assembling), e.g., with the prepared composites or with some another PBI-based membrane, such as ABPBI. The electrodes consist of woven carbon fabrics with deposited active layers containing pure Pt catalyst (ca. 1 mg/cm^2 loading) on anode or Pt–Ni/C alloy catalyst (Pt ca. 0.7 mg/cm^2 loading) on cathode [12]. The electrodes were cut out as squares with area of 6.25 cm^2 . The active cell area was restricted by the open area in the gaskets and was taken as being equal to the total gas channels cross section area of 5 cm^2 square. The prepared composite membranes were doped with 85% phosphoric acid. For comparison purposes we also assembled MEAs with the same electrodes and cross-linked ABPBI membranes (delivered by FuMA-Tech company, Germany, in acid-free-form, thickness ca. $35 \text{ }\mu\text{m}$) doped similarly with 85% phosphoric acid. The sizes of all the tested membranes were chosen so as to be somewhat larger than the surface of electrodes. For assembly we used set of gaskets (PTFE-coated polyimide film for electrodes, thickness of $120 \text{ }\mu\text{m}$, Estrokom, Russia; PEEK film

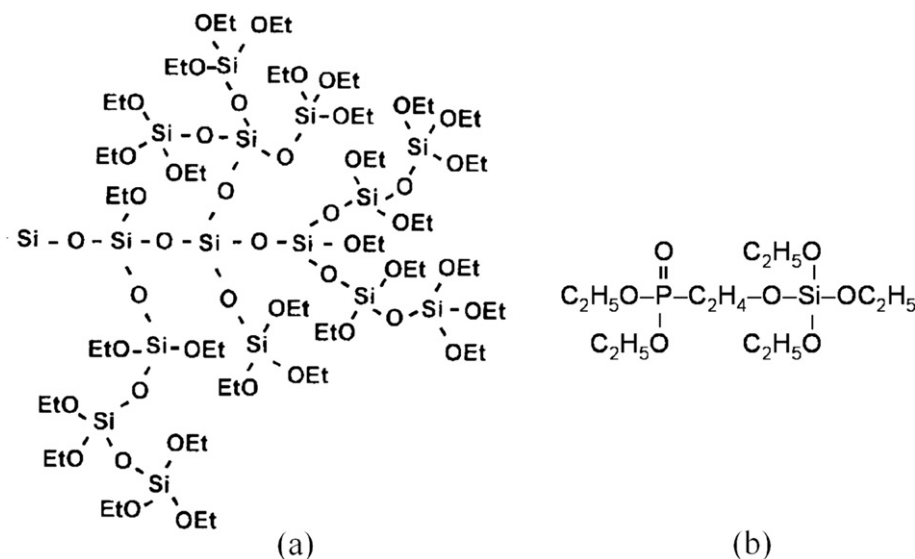


Fig. 1 – Chemical formulas of HPEOS (a) and DEPTEOS (b).

for membranes, thickness of 25 μm , APTIV[®], Victrex, UK). Gasket thicknesses were specially adjusted to match the electrode and membrane thicknesses.

The fuel cells were layer-by-layer assembled as showed in Fig. 2. Finally the assembly was screwed together by PTFE-coated bolts. A thermocontrolled hotplate (IKA RCT basic, IKA, Germany) was used to maintain the constant operating temperature, which was controlled by thermocouple embedded in the membrane electrode assembly cell in the proximity of the electrodes. Hydrogen and air were supplied without excessive pressure and without humidification to the fuel cell MEA (Hydrogen Generator: HOGEN GC Series, Proton Energy Systems Inc., USA). The air flow rate was in the range of 0.1–0.2 L/m and the hydrogen flow rate was slightly above the value corresponding to stoichiometric requirements.

The performance of the assembled fuel cells was tested using potentiostat/galvanostat PGSTAT 302 (Eco Chemie B.V., Netherlands) equipped with built-in frequency response analyzer module (FRA 2). During break-in procedures and stationary testing the fuel cells were operated at a constant current. The current–voltage profiles as well as the conductivity measurements were carried out several times per a day operation, which proceeded typically about 8 h. Typically, the MEAs were tested during many successive days, with shutting down for nights, up to several weeks in total. The conductivities of the membranes were evaluated by an a.c. impedance spectroscopy in galvanostat mode over the frequency range from 40 kHz to 0.1 Hz at different currents in the range of 0–0.4 A/cm² with perturbation amplitude 0.002 A/cm². The conductivities were calculated using the relationship $\sigma = d/SR$, where d and S are the membrane thickness and the active cell area, respectively, and R is the high frequency intercept of the impedance curve with the real axis on a complex impedance plane. In control experiments with a dummy cell we tested that all the non-membrane related non-distributed ohmic resistances, including contact resistances between the gas diffusion layer and the current collectors, etc., are much smaller as compared to the typically measured values with operating fuel cells.

The start-up procedure included heating up to the operation temperature, purging the cell with hydrogen and air at a temperature of 10° lower than the operation one and

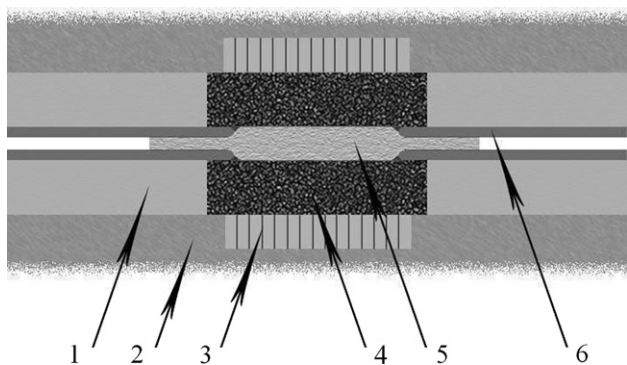


Fig. 2 – Scheme of the fuel cell MEA unit: (1) gaskets for electrodes, (2) bipolar graphite plate with gas channels, (3) gas channels, (4) electrode, (5) membrane, (6) gasket for membrane.

applying a load when the open circuit voltage was established. The load was adjusted as to obtain the voltage in the range from 0.35 to 0.55 V. The shutting down was carried out each day by switching off the load and gas supply and cooling the cell without any further precautions.

The hydrogen crossover current was measured by oxidation of hydrogen having penetrated through the membrane. H₂ and N₂ were supplied at the anode and cathode, respectively. The potential range of 0.1–0.6 V and scan rate of 1 mV/s were used in the linear sweep voltammetry to measure the crossover rate.

3. Results and discussion

3.1. Composition of the composite membranes

Initially, the polymer membranes were filled with silicon dioxide using only HPEOS as a precursor. However, we found out that the doping at room temperature was not effective enough for such composite membranes as H₃PO₄ content in these systems was only below 10 wt%. In order to increase the acid content two ways were tested as follows: 1) modifying component was added into the polymer membranes in addition to SiO₂ in order to increase the ability of the composite to absorb the acid (precursor mixture HPEOS/DEPETEOS were used), or 2) doping temperature were increased (PE/SiO₂-160 material was prepared in this way).

In the first case DEPTEOS was applied as a modifying additive. It comprises two types of functional groups: ethoxysilyl- and ethoxyphosphorous ones. During acid hydrolysis reaction the ethoxyphosphorous parts turns into phosphoric acid residues that are bound to the common SiO₂ frame by silanole groups. Presence of this modifying additive is supposed to increase the acid retention capability of the membrane during long-term operation of the fuel cells. The total H₃PO₄ content in the membrane was managed to be increased in 2–3 times. The obtained composite membranes chosen for further analysis are listed in Table 1 with indication on their SiO₂ and phosphoric acid content.

3.2. SEM study of composite membranes

Insertion of DEPTEOS in addition to HPEOS was found not to influence the morphology of the composite membranes noticeably. In Fig. 3, Fig. 4 and Fig. 5 one can see typical SEM micrographs of the cleavage surface of the silica-containing composite membranes, prepared from the three types of porous matrices, before the doping with H₃PO₄. It can be seen that the whole volume of the polymer material is filled uniformly with SiO₂ phase, which is confirmed by the mapping of Si and O elements with uniform distribution. However silicon dioxide phase is not monolithic, it has some cracks and empty spaces; especially at the interfaces between the polymer phase and the filler. These defects form channels, which are to be filled with phosphoric acid. It is necessary to note that the size of these channels is apparently much larger for PP/SiO₂ (mixt) that results in higher content of H₃PO₄ in the sample (Table 1).

Table 1 – Characteristics of composite membranes doped with phosphoric acid.

Membrane material	Precursors	Doping conditions	SiO ₂ , wt%	H ₃ PO ₄ , wt%	Thickness, μm
PP/SiO ₂ (mixt)	HPEOS/DEPETEOS	25 °C/24 h	40	30	85
PE-h/SiO ₂ (mixt)	HPEOS/DEPETEOS	25 °C/24 h	55	15	20
PE/SiO ₂ (mixt)	HPEOS/DEPETEOS	25 °C/24 h	30	25	50
PE/SiO ₂ -160	HPEOS	160 °C/1 h	35	35	50

When other above-mentioned methods of membrane conditioning were applied, the formation of conductive channels occurred differently. In this case, the doping procedure for PE/SiO₂-160 was carried out at 160 °C which is higher than melting point of PE. It appeared that at these conditions polymer melt sweated out of the volume on the surface and spread in a rather thin film (2–4 μm) (Fig. 6). As a result, phosphoric acid filled the released volume in the composite whereas polymer material migrated towards the surface. After such a treatment the H₃PO₄ content is dramatically increased almost in 8 times in comparison with the doping performed at room temperature. The distribution of the H₃PO₄ in the doped membrane through its thickness is uniform, according to the performed elements mapping. The phosphoric acid cannot penetrate into hydrophobic polymer phase and stay localized in the pores and cavities being stabilized here by capillary forces. The origin of this capillary retention is related to good wetting of the SiO₂ phase surface with liquid phosphoric acid. Usage of DEPTEOS as an agent modifying the chemistry of the pores surfaces may help to improve further the acid retention ability.

Thus, doping at the increased temperature is much more effective. Meanwhile the diameter of the conducting channels seems to increase. It should be emphasized that this surface layer of the polymer apparently does not prevent proton contact between the electrolyte in the SiO₂-rich phase and in the electrodes even at temperature lower than melting point of PE. It is due to many defects (pores and cracks) in the polymer layer, which provide the proton contact between the membrane and the electrodes. At higher temperature (160 °C) this polymer layer melts and, apparently, may partially migrate further into the porous electrodes. The presence of hydrophobic molten polymer phase in the electrodes should not deteriorate their performance. Indeed, the electrodes anyway contain large amount of Teflon as a hydrophobic

polymer phase. This phase is required to ensure gas transport through open pores, not overflowed with phosphoric acid.

On the other hand, this thin layer of the polymer at the surface of the as-prepared membrane is very beneficial during storage of the doped composite at room temperature. It seems that the polymer layer serves as a sealing of the liquid electrolyte inside the matrix. Indeed, we found out that such a membrane can rather efficiently retain acid at room temperature in the presence of humidity, especially in comparison with typical behavior of PBI membranes. Thus, we found out that the acid loss was not more than 4 wt% after three months of the storage. Processes similar to the ones that were observed during such a heat-treatment at 160 °C may be expected for the composite membranes when real fuel cells are assembled and operated at 160 °C.

3.3. Fuel cell performance test

The fuel cells with the composite membranes were tested at operation temperatures in the range of 120–160 °C. The selected results presented below for particular membranes are given for different operating temperatures. This is due to the fact that MEAs with different membranes show different non-monotonic dependencies of the performance on temperature. For example, MEAs with PE membranes show rather poor performance at 120 °C, even worse at 140 °C and dramatically improved at 160 °C. On the contrary, MEAs with PP membranes show quite reasonable performance at 140 °C but strongly degraded one at 160 °C.

Thus, fuel cells assembled with membranes based on PE show poor performance and tend to degrade at 120 °C. Such performance drop apparently may be attributed to the acid loss because of the leaching in the presence of water being generated. Similar situation is observed also for PBI membrane FC at 120 °C [49]. On the contrast, when the PE

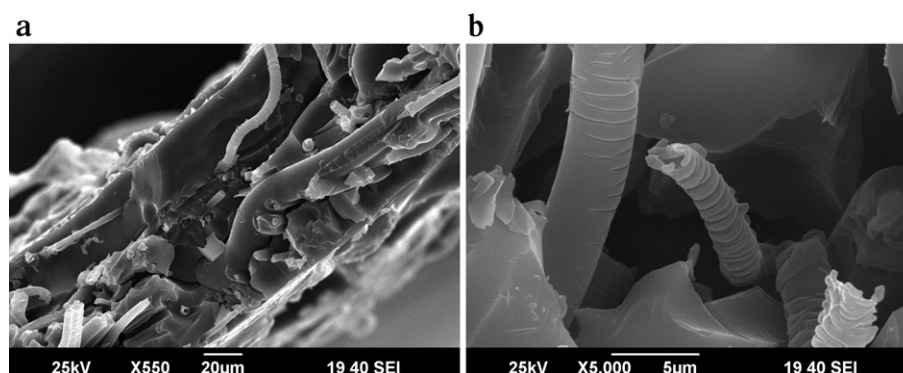


Fig. 3 – SEM micrograph of the cleavage surface of PP/SiO₂ (mixt) based on non-woven polypropylene.

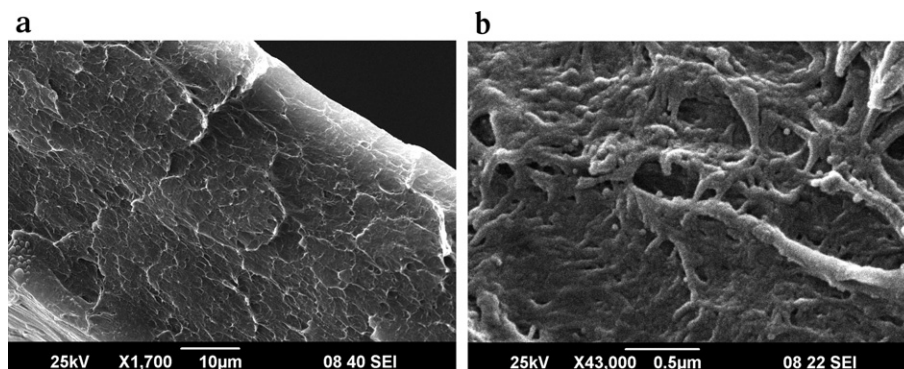


Fig. 4 – SEM micrograph of the cleavage surface of PE/SiO₂ (mixt) based on high-density polyethylene prepared by crazing procedure in the precursor mixture of HPEOS/DEPTEOS.

membranes were tested in FC at 160 °C, there were rapid performance improvements with time although the significant voltage drop was observed initially. Among the membranes tested in operating FC conditions the best performance was detected for PE/SiO₂-160 material. In Fig. 7 one can see the cell potential *V* versus current density *j* curves of a single fuel cell prepared with the PE/SiO₂-160 membrane. For comparison purposes we added reference typical curve for MEAs with ABPBI membranes and the same electrodes in Fig. 7. In 1–2 weeks of testing in the FC with the PE membrane seemed to reach the stable operation conditions as far as the further voltage growth rates became rather small. We assumed that stabilization of the fuel cell performance occurred, if the overall voltage increase rate at constant current density of $j = 0.4 \text{ A/cm}^2$ was less than 0.5 mV per hour during a full day of operation. This achieved performance was considered as final one and was used for comparison. The reasons of the noticeable performance improvement during continuous operation may be related either to increase of the membrane proton conductivity or to diminution of electrode polarization. Impedance spectroscopy allowed us to distinguish clearly that the major contribution here is the improvement of the membrane proton conductivity. We suppose that such behavior may be explained by effective enlargement of the channels filled with phosphoric acid. As mentioned above (see Introduction) larger channels are expected to provide

membrane with better proton conductivity (at the same acid content) thus decreasing ohmic losses and therefore better performance should be attained. On the other hand, larger channels may result in higher crossover through membrane and therefore the open circuit voltage (OCV) should noticeably decrease. In agreement with this expectation, indeed, some slight OCV reduction was observed while the MEA was yet operating with the total improvement of the performance. Apparently, the decrease of ohmic losses finally overcompensated the reduction of OCV.

Fig. 8 and Fig. 9 represent the cell potential *V* versus current density *j* curves of PP/SiO₂ (mixt) and PE-h/SiO₂ (mixt) membrane FC at 140 and 120 °C respectively (for comparison a reference curve for MEAs with ABPBI membranes and the same electrodes is also indicated here). The operation behavior of the composites is similar to PE membrane FC at 160 °C. Here again one may notice distinct performance improvement with time and final stabilization of the MEA operation. However PP/SiO₂ (mixt) membrane showed a significant drop in fuel cell performance initially that can be caused by the leakage of free acid. The fuel cell operation at 160 °C is characterized by very low OCV, therefore poor voltage–current curves were recorded and rather fast degradation was observed as well.

Table 2 summarized OCV and finally achieved voltages at 0.4 A/cm² of PE/SiO₂-160, PP/SiO₂ (mixt) and PE-h/SiO₂ (mixt) membrane fuel cells. The best performance result was

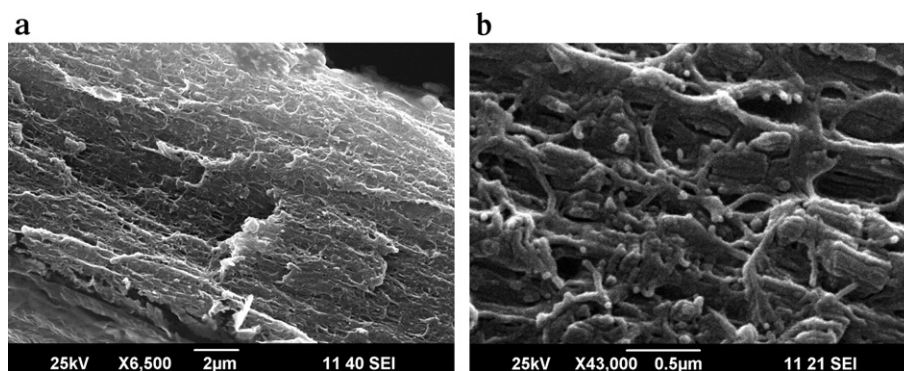


Fig. 5 – SEM micrograph of the cleavage surface of PE-h/SiO₂ (mixt) based on high-density polyethylene prepared by the extrusion method.

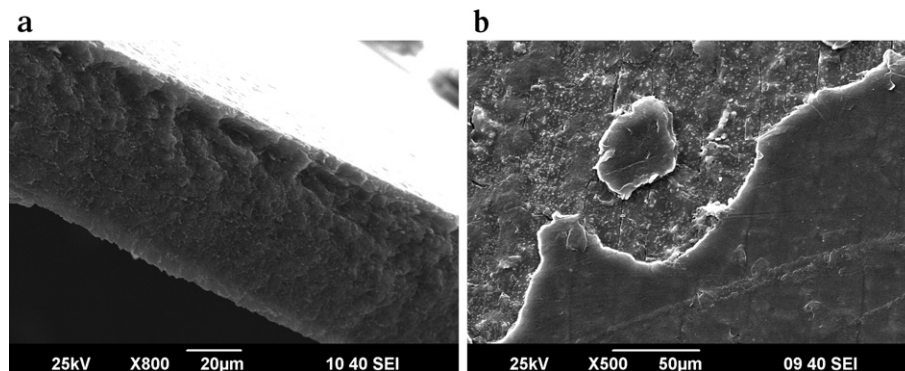


Fig. 6 – SEM micrograph (a) of the cleavage fracture surface and (b) membrane surface of PE/SiO₂-160 based on silica-containing PE doped with H₃PO₄ at 160 °C.

obtained using PP/SiO₂ (mixt) composite membrane at 140 °C and 0.5 V at 0.4 A/cm² was reached. Comparing the OCV of the tested fuel cell at 160 °C with the one at lower temperature (120 and 140 °C) we detected significant voltage drop with increasing temperature, which is much higher than OCV reduction typically measured by us for PBI-matrices (the values typically achievable with the same electrodes and ABPBI membranes are also indicated in Table 2 for comparison, see also Refs. [50,51]). This might be attributed to polymer softening as well as to membrane pore growth. Indeed, the measured hydrogen penetration through the membrane is increased as well, therefore mixed cathode overpotential apparently diminishes the open circuit voltage.

3.4. Conductivity and crossover measurements

The membrane resistances were evaluated by an a.c. impedance spectroscopy. Impedance curves analysis showed that PE membrane resistance was continuously increasing with time during operation at 120 °C. This result confirms our

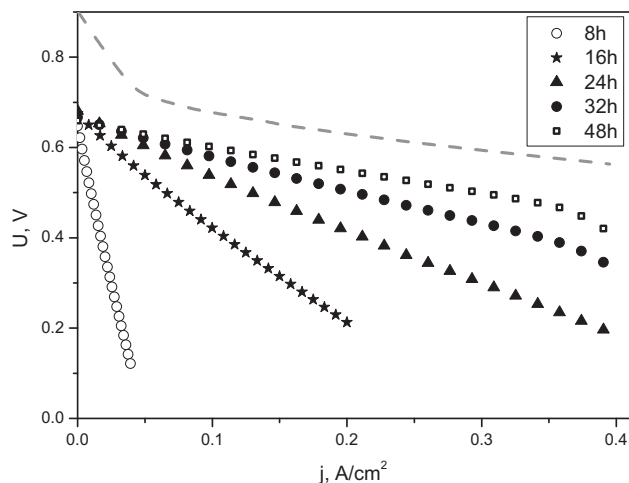


Fig. 7 – Cell potential *V* versus current density *j* curves of MEA assembled with PE/SiO₂-160 matrix at various times and 160 °C operation temperature. Reference typical curve for ABPBI membranes (160 °C, the same electrodes) is indicated as a dash line.

assumption about acid leaching from the membrane at this not sufficiently high temperature.

In Fig. 10 one can see impedance curve evolution while performance improvements were observed. It was found out that the membrane resistance—which can be evaluated as a high frequency intercept with the real axis—is reduced by an order of magnitude. Hence, the apparent performance improvements are due to the decrease of ohmic losses. However it should be noted that some diminution of electrode polarization were also detected, but they were minor and not very significant in affecting total performance as compared to resistance changing. The final conductivity and resistance are listed in Table 3. The lowest resistance and best conductivity is demonstrated by PE/SiO₂-160 membrane, nevertheless the highest performance is attained by the MEA with PP/SiO₂ (mixt) membrane. It can be explained by the difference of the open circuit voltages.

Hydrogen crossover test showed that crossover current increased with decreasing membrane resistance as represented in Fig. 11. Summarized results of conductivity, crossover measurements and OCV indicate that membrane

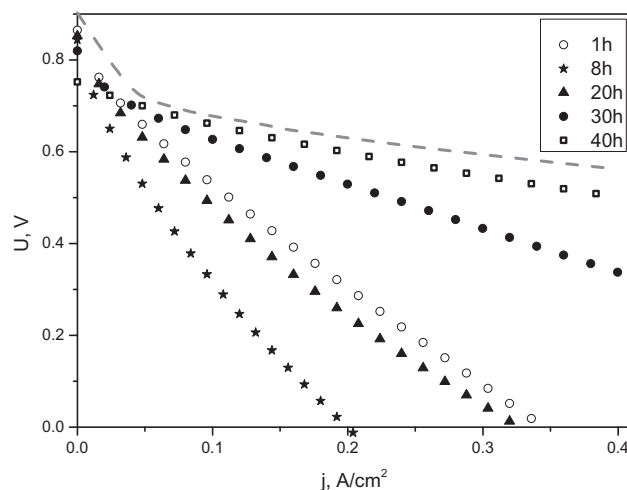


Fig. 8 – Cell potential *V* versus current density *j* curves of MEA assembled with PP/SiO₂ (mixt) matrix at various times and 140 °C operation temperature. Reference typical curve for ABPBI membranes (160 °C, the same electrodes) is indicated as a dash line.

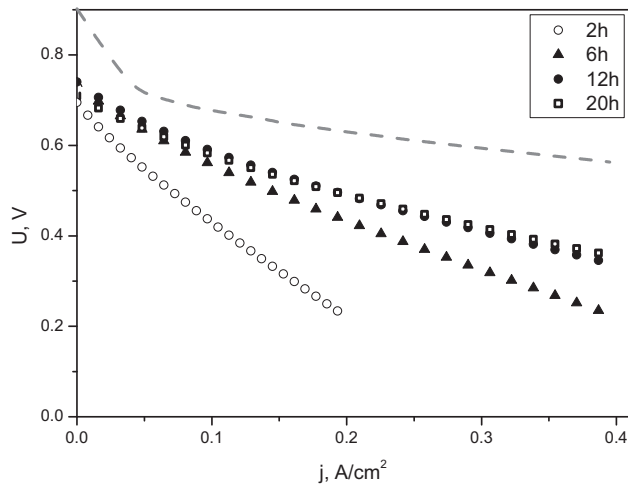


Fig. 9 – Cell potential V versus current density j curves of MEA assembled with PE-h/SiO₂ matrix at various times and 120 °C operation temperature. Reference typical curve for ABPBI membranes (160 °C, the same electrodes) is indicated as a dash line.

structures have changed during operation and this can be attributed to effective growth of channels filled with phosphoric acid. It is also detected that in 1–2 weeks stable operation is achieved and we suppose that filler structures finally restrict and stabilize the pore sizes at a certain level. The control of the channel sizes provides possible way to achieve optimum membrane structure with improved balance between proton conductivity and mechanical stability. Yet, low OCV values remain to be serious problem to be solved. We may hope to solve this problem by varying the nature of filler and its content, thus improving the fuel cell performance in general. Also, affecting the filler structure and distribution, one may hope to influence the final size of proton-conducting channels.

3.5. Post-mortem MEAs analyses

After finishing extensive testing of the membranes in operating MEAs we performed their cleavage with subsequent SEM analyses of the cleaved surface with mapping of the main

Table 2 – Open circuit voltages (OCV) and finally achieved voltages U at current density $j = 0.4 A/cm^2$ of composite membranes. The operation temperature is indicated in brackets indicated in brackets.

Membrane	OCV, mV	U , mV ($j = 0.4 A/cm^2$)
PP/SiO ₂ (mixt)	730–800 (140 °C) 550–600 (160 °C)	480–500 (140 °C)
PE-h/SiO ₂ (mixt)	700–750 (120 °C) 350–400 (160 °C)	330–350 (120 °C)
PE/SiO ₂ -160	880–900 (120 °C) 650–700 (160 °C)	380–400 (160 °C)
ABPBI (for comparison)	900–930 (160 °C)	560–570 (160 °C)

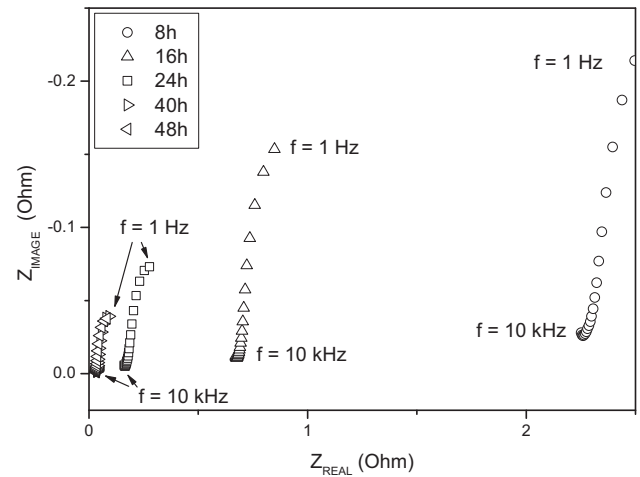


Fig. 10 – AC-impedance diagrams of MEA assembled with PE/SiO₂-160 matrix at various times, 160 °C operation temperature and zero current density.

Table 3 – Selected values of final values of resistances per unit area r and conductivities σ of composite membranes as measured in operating fuel cells after achieved stabilization. The operation temperature is indicated in brackets.

Membrane	R , ohm cm^2	σ , S/cm
PP/SiO ₂ (mixt) (140 °C)	0.29	0.029
PE-h/SiO ₂ (mixt) (120 °C)	0.5	0.004
PE/SiO ₂ -160 (160 °C)	0.15	0.033

elements distribution. Typical example is presented in Fig. 12. One can see the general still uniformly heterogeneous morphology of the composite membranes (Fig. 12a and c), which is retained after long-term operation. Further, one can see that Si-rich phase remains to be localized in the membrane only.

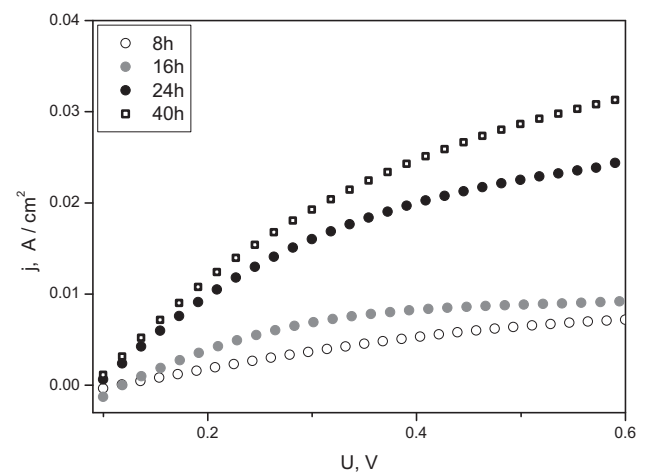


Fig. 11 – Hydrogen crossover current density versus cell potential V of a single fuel cell prepared from PE/SiO₂-160 at various times and 160 °C operation temperature.

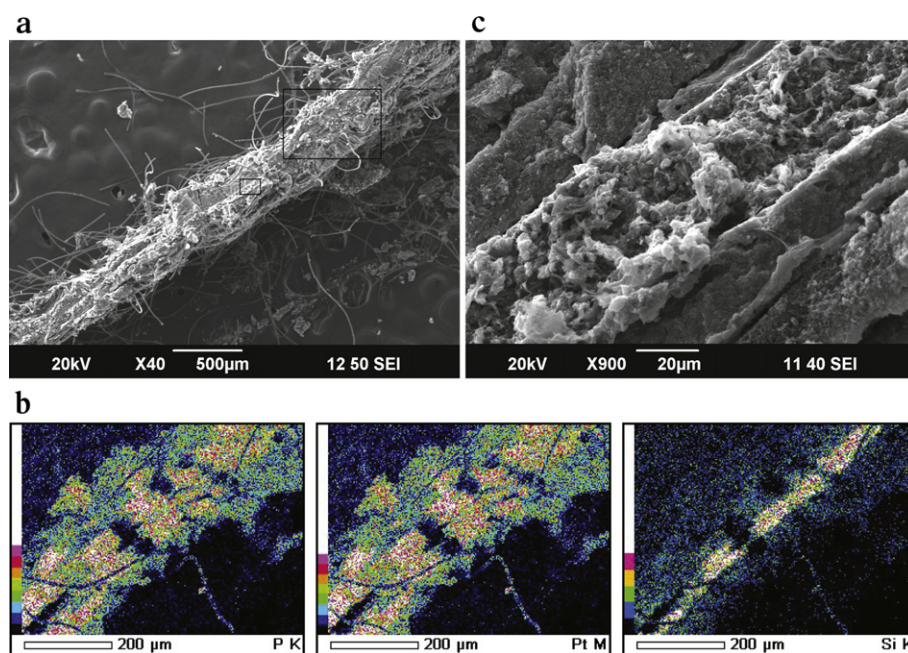


Fig. 12 – SEM micrographs, showing general morphology of the cleaved MEAs with PE membrane after long-time operation (a), elemental distribution (P, Pt, Si) at the surface of the cleavage (b), and the morphology of the membrane at higher magnification (c). Larger rectangle in image (a) corresponds to area used for elements mapping (b), and smaller rectangle in image (a) corresponds to area rescanned at higher magnification (c).

On the contrast, Pt penetrates almost everywhere, where the P-containing phase (H_3PO_4) is localized. This is indicative of strong Pt dissolution in the electrodes during continuous long-time operation during testing procedure. Therefore, Pt dissolution mechanism seems to be one of the most important degradation processes affecting durability of the fuel cell with the prepared composite matrices. This is rather typical problem for phosphoric acid fuel cells in general, which is to be solved by optimizing not the membranes, but electrodes.

Thus, in this work the best performance is detected with PP/SiO₂ (mixt) membranes, which demonstrated 0.5 V at 0.4 A/cm² (Table 2). Yet, this value is somewhat lower than typically achievable with PBI membranes and the same electrodes at the same conditions (air stoichiometry, etc.) in our lab [50,51]. Indeed, for comparison, in our practice MEAs typically provide about 0.6 V when assembled with meta-PBI membranes and about 0.56–0.57 V when assembled with ABPBI membranes (Table 2) during testing at 0.4 A/cm². Nevertheless, this is only a first try of the completely new concept and further optimization seems to be possible. Most importantly, one needs to reduce typical sizes of the spatial heterogeneity in the composite. If we do intend to mimic Nafion-type membranes, the characteristic size of the heterogeneity should be closer to the nano-scale range. This may help to solve the problem of low OCV values. Provided this problem is solved, at least, ca. 100 mV of the overpotential may be compensated (see Table 2) and thus the performance should be comparable to MEAs assembled with meta-PBI membranes.

Thus, the proposed composite membranes are supposed to be promising because they possess clearly visible heterogeneous structure (Figs. 3–5), which persists after doping with

phosphoric acid, assembling in MEA and long-time testing in the operating FC (Fig. 12c). Therefore, they can potentially afford to attain better balance between functional membrane properties in comparison with typical PBI materials, which are known to have spatially homogeneous structure when doped with phosphoric acids unless some specific routes to introduce and preserve heterogeneity are explored [52–54].

4. Conclusions

In this work we successfully prepared novel heterogeneous three-component proton-conducting membranes consisting of 1) porous polymer matrix based on polyolefins that provides good mechanical properties of the membrane, 2) silicon dioxide three-dimensional frame that improves compatibility of the polymer and electrolyte as well as increases stability of the composite, and of 3) phosphoric acid that serves as a proton-conducting liquid electrolyte.

The single fuel cell tests assembled with the composite membranes showed that significant performance improvements are observed with time after break-in at particular temperature depending on the membrane types. Stable performance is attained within 1–2 weeks of operation. This behavior is attributed to the growth of conducting channels. The best performance is demonstrated by PP/SiO₂ (mixt) membrane fuel cell, which provides 0.5 V at 0.4 A/cm² being supplied with hydrogen and air as reactants. The obtained results prove that further development of the composite membranes for intermediate and high temperature FC is promising as far as their heterogeneous structure is retained

during long-term FC operation and thus may potentially ensure better balance between proton conductivity and mechanical stability. Therefore, better performance in comparison to the FC on typical PBI-based membranes is to be achieved.

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