



PROTON EXCHANGE COMPOSITE MEMBRANE BASED ON AB POLYBENZIMIDAZOLE AND CAESIUM DIHYDROGEN PHOSPHATE FOR HT-PEM FUEL CELLS

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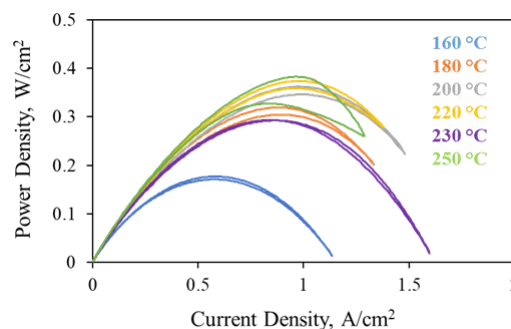
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Abstract

A new type of polybenzimidazole-based proton exchange composite membrane, poly(2,5-benzimidazole) (ABPBI)–CsH₂PO₄, was obtained. The possibility of application of the composite membrane in a hydrogen–air fuel cell operating at 160–250 °C was demonstrated. In the fuel cell tests, the maximum power density reached ~400 mW/cm² at 250 °C. The resulting data along with high open circuit voltage (0.92–0.95 V) indicate high quality and low hydrogen crossover of the membrane.



Key words: AB polybenzimidazole, caesium dihydrogen phosphate, proton-conducting membrane, hydrogen–air fuel cell.

Introduction

The development of novel proton-conducting solid and polymeric electrolytes has recently attracted significant attention due to their potential for practical application in electrochemical devices for a variety of purposes such as sensors, electrolyzers, fuel cells (FCs), *etc.* However, most known proton conductors operate in a narrow temperature range, limited in the high temperature region to a temperature of ~100 °C, associated with the evaporation of water (for example, Nafion® type membranes) and/or the change in the network of hydrogen bonds in crystalline or polymer structures. The rare exceptions are composite polymer electrolytes based on polybenzimidazole (PBI) doped with phosphoric acid (PA) for high-temperature polymer electrolyte membrane (HT-PEM) FCs and salt electrolytes based on hydrosulfates and dihydrogen phosphates of heavy alkali metals [1–6].

PBIs are the most widespread and demanded representatives of HT-PEM polymers for FC applications [7–16]. The AB polybenzimidazole (ABPBI) is based on cheap nontoxic industrial 3,4-diaminobenzoic acid (Fig. 1).

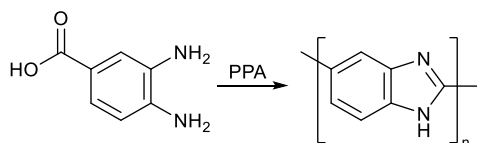


Figure 1. Synthesis of ABPBI in polyphosphoric acid (PPA).

3,4-Diaminobenzoic acid contains carboxy and *o*-phenylenediamine reaction centers in one molecule, which

greatly facilitates the loading during polymer production (no need to ensure an equimolar ratio of the monomers, as required in the classical PBI synthesis) [7, 17, 18].

Earlier solid acid FCs based on solid acid CsH₂PO₄ applied as an electrolyte were proposed [3]. Dihydrogen phosphate proton conductors based on CsH₂PO₄ have been widely studied, and their typical operating temperature range is 230–350 °C, since this material possesses high proton conductivity of about 10⁻² S/cm due to its transformation into the superionic phase at 232 °C [4].

However, the direct use of caesium dihydrogen phosphate (CDP) as a membrane involves practical challenges due to poor mechanical properties, such as brittleness of low-temperature (LT) phase and plastic deformation at high-temperature (HT) phase [19–21]. In previous reports [22, 23], it was outlined that the composites involving CDP and a polymer can effectively improve the mechanical properties of a membrane.

In this work, we report on the production of a composite material which comprises the ABPBI polymer with high chemical and thermal resistance, as well as the ability to transport protons in a PA-doped form, as a binder for an inorganic substances for the first time.

Results and discussion

The ability of high-molecular weight ABPBI to dissolve in a mixture of formic acid (FA) and trifluoroacetic acid (TFA), and the solubility of CDP in pure FA were used to prepare a proton conducting membrane for real FC test in the HT-PEM membrane electrode assembly (MEA). Separately prepared

solutions of ABPBI polymer and caesium dihydrogen phosphate with the addition of PA (3 mol of PA per 1 mol of ABPBI) were mixed and quickly poured onto a Teflon surface. After removal from the Teflon substrate, a sufficiently strong and elastic composite film was studied by electrochemical impedance spectroscopy (EIS) to assess its proton conductivity and was subsequently used as a proton exchange membrane in a hydrogen–air MEA at 160–250 °C. The ABPBI/CDP ratio in the membrane was 50/50 (vol/vol), and 3 mol of PA onto 1 mol of ABPBI were added.

Even at 100 °C, the membrane conductivity maintains high values throughout the entire humidity range, varying from $2.5 \cdot 10^{-4}$ S/cm in air to $7 \cdot 10^{-3}$ S/cm for a relative humidity close to 100% (Fig. 2).

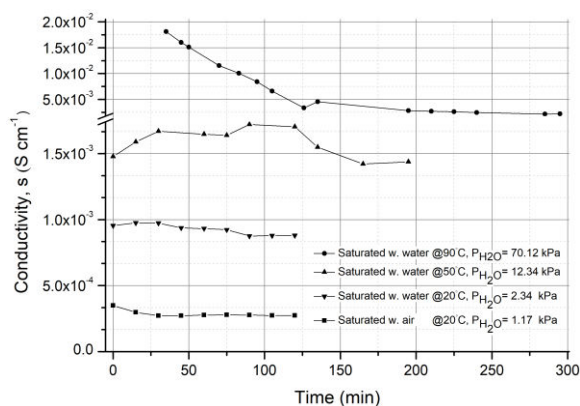


Figure 2. Dependences of the conductivity on the measurement time for the ABPBI/CDP (50/50 vol/vol) composite membrane at 100 °C under different humidification conditions.

It is worth noting that at 100 °C, the membrane already exhibits record conductivity, which continues to increase with rising temperature. The sample appeared to be stable at least up to 300 °C. This shows the absence of a significant amount of CsH_2PO_4 crystalline phase, and there are no inflections in the temperature conductivity curve associated with the CsH_xPO_y phase transition. It has well been shown that the PBI– CsH_2PO_4 composite membrane can be used in a new type of FC which operates at 160–250 °C.

The HT-PEMFC MEA test results are shown in Figs. 3 and 4.

As is seen from these figures, the maximum power density of the MEA reached at 250 °C (green line) was ~ 400 mW/cm². The MEA worked steadily at 180 °C for 250 h. The open circuit voltage (OCV) was 0.92–0.95 V, which corresponds to high membrane quality and assumably low hydrogen crossover through the membrane.

Experimental section

General remarks

Phosphoric acid (PA), polyphosphoric acid (PPA), 3,4-diaminobenzoic acid (DABA), formic acid (FA), trifluoroacetic acid (TFA) were purchased from Sigma-Aldrich and used as received. CsH_2PO_4 crystals were grown at room temperature by slow isothermal evaporation of PA (analytical grade) from aqueous solutions and caesium carbonate (analytical grade), taken in the equimolar ratio. The X-ray diffraction (XRD)

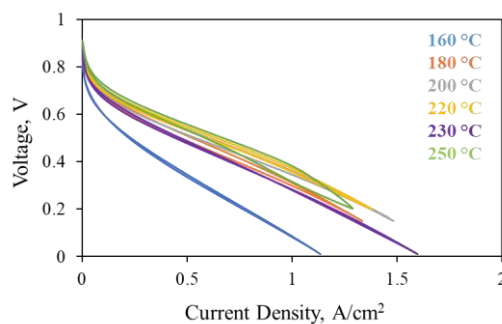


Figure 3. Polarization curves for the HT-PEM FC MEA with the ABPBI/CDP composite membrane at different temperature conditions.

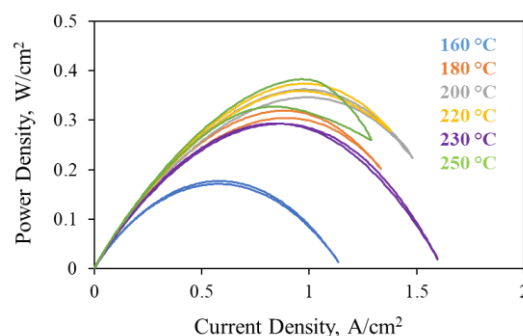


Figure 4. Power density curves for the HT-PEM FC MEA with the ABPBI/CDP composite membrane at different temperature conditions.

analysis of CsH_2PO_4 (P2₁/m) obtained fully corresponds to the crystallographic database (35-746).

As is seen from these figures, the maximum power density of the MEA reached at 250 °C (green line) was ~ 400 mW/cm². The MEA worked steadily at 180 °C for 250 h. The open circuit voltage (OCV) was 0.92–0.95 V, which corresponds to high membrane quality and assumably low hydrogen crossover through the membrane.

Synthesis of ABPBI in PPA solution

The synthesis of ABPBI is discussed in Ref. [18]. Briefly, PPA (84%, 75 g) was introduced into a three-necked flask equipped with a stirrer and a capillary for argon supply. The solution was heated to 120 °C under an argon flow. Thereafter, DABA monophosphate (25 g, 0.1 mol) was added portionwise under stirring. The stirring was continued for at least 2 h until a 25% homogeneous solution was obtained. A part of the reaction mixture was poured into Teflon cups and placed in a muffle furnace, preheated to 120 °C. The resulting reaction solutions in PPA were heated to 180–200 °C at a rate of 1 deg/min and kept for 16–24 h. In order to isolate the polymers, the solutions were treated with hot deionized water, ground, and then treated with 5% aq. ammonia for 3 days at ~ 20 °C. Afterwards, the product was extracted with MeOH in a Soxhlet apparatus for final removal of low molecular weight impurities. The polymer was dried under vacuum (10^{-2} Torr) for at least 2 h at 150 °C. The polymer yield was $\sim 99\%$. The intrinsic viscosity in sulfuric acid $[\eta]$ was 4.0 dL·g⁻¹ which corresponded to a molecular weight of 42 kg/mol.

Composite ABPBI–CDP membrane preparation

The ability of the high-molecular weight ABPBI to dissolve in a mixture of FA and TFA and the solubility of CDP in pure FA were taken into account for the membrane preparation. A separately prepared solution of the polymer in a mixture of FA and TFA and a separately prepared solution of caesium salt with PA addition were mixed and quickly poured onto a Teflon surface. The following component ratios were used to prepare the membrane for the MEA testing. A solution of 0.12 g (0.001 mol) of ABPBI in 2 mL of FA and 1 mL of TFA was mixed with a solution of 0.12 g (0.0005 mol) of CDP in 3 mL of FA containing 0.35 g of PA, then the mixture was poured onto a Teflon disc. The resulting ratio of PA to ABPBI was 3/1 (mol/mol). After drying, the ABPBI/CDP ratio was 50/50 (vol/vol) and 70/30 (wt/wt). The thickness of the films obtained was from 50–100 μm .

Electrochemical impedance spectroscopy

The impedance spectra were measured using a potentiostat – frequency response analyzer Smart P-45X with a FRA-24M electrochemical impedance measurement module (Elins, Russia) in a frequency range of 1 MHz–0.1 mHz. The measurements were performed in a two-electrode cell with Pt electrodes ($D = 8$ mm) pressed to the film sample. The parasitic impedance of the cell (residual inductance of wires, contact resistance, geometric capacitance) was found using an empty cell without a film sample and included in the equivalent circuit during the data processing.

MEA testing

The performance of the MEA with the ABPBI–CDP composite membrane was investigated using a standard testing fuel cell with two graphite flow field plates (Arbin Instruments, USA) with standard gas diffusion cathodes Celtec®-P Series 1000 MEA (BASF, Germany) [24] and polytetrafluoroethylene gaskets. The MEA working area was 5 cm^2 . The polarization curves were stabilized after 2–3 h of the cell voltage cycling and recorded at different temperatures and ambient pressure on an Elins P-200X Potentiostat (Electrochemical Instruments, Russia). The anode side was supplied with hydrogen (100 mL/min), the cathode side was supplied with atmospheric air (800 mL/min). FC voltage was scanned at a rate of 5 mV/s.

Conclusions

In this study, we developed a new type of proton exchange composite membrane, ABPBI– CsH_2PO_4 , which was shown to operate up to 250 $^\circ\text{C}$ based on the fuel cell test data. This membrane has the potential for practical application in high-temperature proton exchange membrane fuel cells and other medium-temperature electrochemical devices. The possibility to apply the ABPBI– CsH_2PO_4 (70/30 wt/wt) composite membrane in a hydrogen–air fuel cell operating at 160–250 $^\circ\text{C}$ was demonstrated. In the HT-PEM FC MEA tests, the maximum power density of the MEA reached ~ 400 mA/cm^2 at 200 $^\circ\text{C}$ with steady operation of the MEA at 180 $^\circ\text{C}$ for 250 h. The OCV was 0.92–0.95 V, which indicates high quality of the resulting composite membrane and assumably low hydrogen crossover through the membrane.

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References

1. Y.-L. Ma, J. S. Wainright, M. H. Litt, R. F. Savinell, *J. Electrochem. Soc.*, **2004**, *151*, A8. DOI: 10.1149/1.1630037
2. V. V. Sinityn, A. I. Privalov, O. Lips, A. I. Baranov, D. Kruk, F. Fujara, *Ionics*, **2008**, *14*, 223–226. DOI: 10.1007/s11581-007-0175-y
3. S. M. Haile, C. R. I. Chisholm, K. Sasaki, D. A. Boysen, T. Uda, *Faraday Discuss.*, **2007**, *134*, 17–39. DOI: 10.1039/b604311a
4. A. V. Nikiforov, R. W. Berg, N. J. Bjerrum, *Ionics*, **2018**, *24*, 2761–2782. DOI: 10.1007/s11581-017-2420-3
5. E. Afshari, M. Mosharaf-Dehkordi, H. Rajabian, *Energy*, **2017**, *118*, 705–715. DOI: 10.1016/j.energy.2016.10.101
6. I. A. Stenina, E. Y. Safronova, A. V. Levchenko, Yu. A. Dobrovolsky, A. B. Yaroslavtsev, *Therm. Eng.*, **2016**, *63*, 385–398. DOI: 10.1134/S0040601516060070
7. Q. Li, D. Aili, H. A. Hjuler, J. O. Jensen, High Temperature Polymer Electrolyte Membrane Fuel Cells. Approaches, Status, and Perspectives, Springer, Cham, **2016**. DOI: 10.1007/978-3-319-17082-4
8. S. S. Araya, F. Zhou, V. Liso, S. L. Sahlin, J. R. Vang, S. Thomas, X. Gao, C. Jeppesen, S. K. Kær, *Int. J. Hydrogen Energy*, **2016**, *41*, 21310–21344. DOI: 10.1016/j.ijhydene.2016.09.024
9. R. Zeis, *Beilstein J. Nanotechnol.*, **2015**, *6*, 68–83. DOI: 10.3762/bjnano.6.8
10. J. Escorihuela, J. Olvera-Mancilla, L. Alexandrova, L. F. del Castillo, V. Compañ, *Polymers*, **2020**, *12*, 1861. DOI: 10.3390/polym12091861
11. S. Moorthy, G. Sivasubramanian, D. Kannaiyan, P. Deivanayagam, *Int. J. Hydrogen Energy*, **2023**, *48*, 28103–28118. DOI: 10.1016/j.ijhydene.2023.04.005
12. Z. Zhou, O. Zholobko, X.-F. Wu, T. Aulich, J. Thakare, J. Hurley, *Energies*, **2021**, *14*, 135. DOI: 10.3390/en14010135
13. R. E. Rosli, A. B. Sulong, W. R. W. Daud, M. A. Zulkifley, T. Husaini, M. I. Rosli, E. H. Majlan, M. A. Haque, *Int. J. Hydrogen Energy*, **2017**, *42*, 9293–9314. DOI: 10.1016/j.ijhydene.2016.06.211
14. Q. Li, R. He, J. O. Jensen, N. J. Bjerrum, *Fuel Cells*, **2004**, *4*, 147–159. DOI: 10.1002/fuce.200400020
15. R. Rath, P. Kumar, L. Unnikrishnan, S. Mohanty, S. K. Nayak, *Polym. Rev.*, **2020**, *60*, 267–317. DOI: 10.1080/15583724.2019.1663211
16. E. Qu, X. Hao, M. Xiao, D. Han, S. Huang, Z. Huang, S. Wang, Y. Meng, *J. Power Sources*, **2022**, *33*, 231386. DOI: 10.1016/j.jpowsour.2022.231386
17. H. D. Chaudhari, R. Illathvalappil, S. Kurungot, U. K. Kharul, *J. Membr. Sci.*, **2018**, *564*, 211–217. DOI: 10.1016/j.memsci.2018.07.026
18. I. I. Ponomarev, Yu. Yu. Rybkin, Yu. A. Volkova, D. Yu. Razorenov, K. M. Skupov, Iv. I. Ponomarev, A. S. Senchukova,

- A. A. Lezov, N. V. Tsvetkov, *Russ. Chem. Bull.*, **2020**, *69*, 2320–2327. DOI: 10.1007/s11172-020-3036-8
19. I. N. Bagryantseva, V. G. Ponomareva, N. P. Lazareva, *Solid State Ion.*, **2019**, *329*, 61–66. DOI: 10.1016/j.ssi.2018.11.010
20. I. N. Bagryantseva, A. A. Gaydamaka, V. G. Ponomareva, *Ionics*, **2020**, *26*, 1813–1818. DOI: 10.1007/s11581-020-03505-9
21. Y. Li, J. Hu, H. Li, L. Chen, *J. Electrochem. Soc.*, **2022**, *169*, 024505. DOI: 10.1149/1945-7111/ac4d6e
22. I. N. Bagryantseva, V. G. Ponomareva, V. R. Khusnutdinov, *J. Mater. Sci.*, **2021**, *56*, 14196–14206. DOI: 10.1007/s10853-021-06137-0
23. I. Bagryantseva, D. Dormidonova, V. Ponomareva, *MATEC Web Conf.*, **2021**, *340*, 01044. DOI: 10.1051/mateconf/202134001044
24. T. J. Schmidt, J. Baurmeister, *J. Power Sources*, **2008**, *176*, 428–434. DOI: 10.1016/j.jpowsour.2007.08.055

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