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A chemical approach for probing the interphase boundary between polymer electrolyte membrane and HT-PEM fuel cell carbon nanofiber anode

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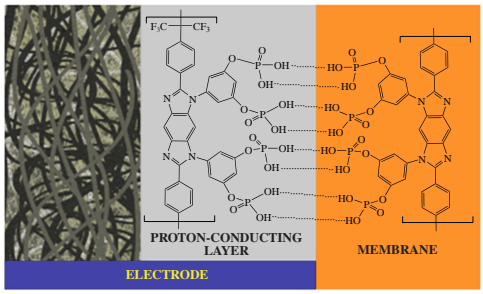
Interphase boundary interactions are essential for high-temperature polymer electrolyte membrane fuel cell membrane electrode assembly (MEA) operation. Interactions between the self-phosphorylating polybenzimidazole (PBI)-6F coating on a carbon nanofiber electrode and the self-phosphorylating proton-conducting membrane during MEA operation would improve the cell performance. The presented approach represents a novel path for the development of a PBI membrane-based MEA.



Keywords: polymer electrolyte membrane, carbon nanofiber, proton-exchange membrane, high-temperature polymer electrolyte membranes, proton-conducting membrane, interphase boundary, fuel cells, self-phosphorylating membrane, membrane electrode assembly, gas-diffusion electrode.

Improving the interface between the gas diffusion electrode (GDE) and the proton-conducting membrane (PCM) in the membrane electrode assembly (MEA) is a critical issue for all types of PCM-based fuel cells (FCs) and may result in a significant enhancement of the performance characteristics of hydrogen/air high-temperature polymer electrolyte membrane fuel cells (HT-PEMFCs).[1–14] Polybenzimidazoles (PBIs)[15–27] have found widespread application as PCMs due to their ability to act as carriers for phosphoric acid (PA), forming stable complexes with high proton conductivity at 120–200 °C. In the commercial HT-PEMFC membrane electrode assembly (MEA) Celtec®-P Series 1000 MEA (BASF, Germany), the PA doped *m*-PBI (see Online Supplementary materials, Figure S1) membrane (Celazole®, PBI Performance Products, The InterTech Group, USA)[28] is used (6–10 of PA molecules per polymer unit). One of the significant challenges related to such a system in terms of its stable and long-term operation is a potential loss of part of PA due to water release in the catalytic oxygen reduction reaction (ORR) at the FC cathode. In order to partially reduce and compensate for the effect of FC leaching from the membrane and the MEA gas-diffusion electrode (GDE), phosphorylated PBIs were applied.[29–33] However, these polymers, like other organyl phosphates, are highly expensive and now are of academic interest only. In addition, neither the issue of PA leaching from GDE for such polymers nor the challenge of improving interfacial boundaries in the MEA has yet been fully addressed. The potential for addressing the existing challenges has emerged following the discovery of self-phosphorylating PBI membranes, produced through polyamidation of N-substituted aromatic tetraamines with methoxy-groups, followed by thermocyclization and PA doping[34] (Figure S2). During MEA operation with these membranes (160–180 °C), the MeO-groups in the PBI were phosphorylated (see Figure S2), leading to a sharp increase in power of FCs as a result of an increase in the proton conductivity of the membrane and a decrease of its ohmic resistance.[34,35]

Earlier,[36,37] we presented a fundamentally new approach to the production of materials based on carbon nanofiber (CNF) mats with deposited platinum (Pt/CNF). For them, the issues of improving the interphase boundaries and creating a continuous proton-conducting surface over the surface of carbon nanofibers from the triple boundary to the PCM are also of key importance. Some progress in solving the aforementioned issues has been achieved by applying a thin layer of a proton-conducting polymer to a Pt/CNF GDE.[35,38] The best results have been achieved by using a novel self-phosphorylated polymer with a hexafluorinated 6F bridge group (PBI-6F), obtained from PA-6F (Figure S3), which possesses hydrophobic properties imparted to the polymer.[35] This polymer exhibits excellent gas permeability for H_2 and O_2, which is essential for gas transport to the triple phase boundary. In the past,[39] the PA doped PBI-O-PhT membrane (see Figure S1) developed at the INEOS RAS was applied as a PCM. This membrane is not inferior to the commercially available Celazole® membrane in terms of its characteristics. However, the results obtained for the MEA were somewhat inferior to the performance characteristics of the commercial Celtec® P1000 MEA, possibly due to interphase imperfections[40] at the junction between the Pt/CNF mat electrode and the PCM.

In this study, a self-phosphorylated PBI (PBI-4MeO-BP) based on N^1,N^5-bis(3,5-dimethoxyphenyl)-1,2,4,5-benzenetetramine and biphenyl-4,4′-dicarbonyl dichloride has been applied as a PCM together with the aforementioned Pt/CNF GDE coated with PBI-6F for HT-PEM fuel cell MEA assembling, for the first time. All solvents and precursors were obtained from

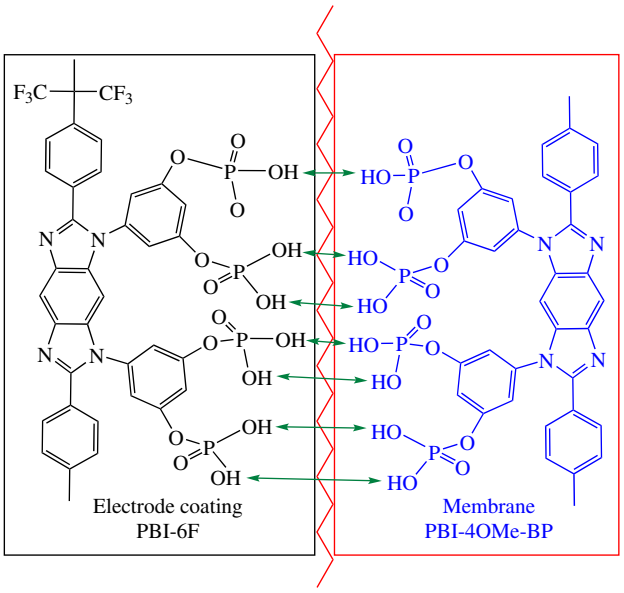


Figure 1 Possible way of interaction between self-phosphorylated membrane PBI-4OMe-BP and self-phosphorylated electrode coating PBI-6F.

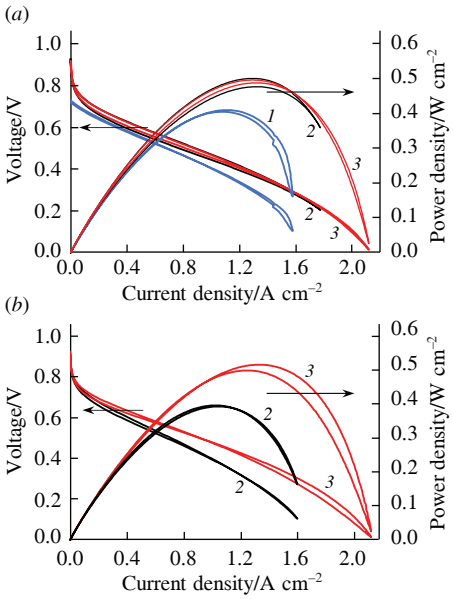


Figure 2 Polarization and power density curves (forward and reverse) for MEA 1 (*1*, blue), MEA 2 (*2*, black) and MEA 3 (*3*, red) at (*a*) 180 °C and (*b*) 200 °C.

TCI Europe (Belgium) and were used as received. The syntheses of N^1,N^5-bis(3,5-dimethoxyphenyl)-1,2,4,5-benzenetetramine and a self-phosphorylating polymer for the anode modification (PBI-6F) were described previously.[35] Polymer PBI-4OMe-BP was synthesized in a similar manner to PBI-2OMe-BP as reported.[34] We assumed that after self-phosphorylation of the PBI-4MeO-BP membrane and PBI-6F polymer coating applied to the GDE, a continuous proton-conducting contact would occur at the PCM–GDE interphase, resulting in a reduction of ohmic losses in the operating MEA (Figure 1).

The aforementioned assumptions regarding the potential for improving the interphase between PCM and GDE have been validated through the MEA tests. The performance of the hydrogen/air HT-PEM fuel cell MEAs (5 cm^2 working area) was studied using a standard test fuel cell with two graphite flow field plates (Arbin Instruments, USA) with standard gas diffusion cathodes (Celtec®-P Series 1000 MEA)[28] at 180 and 200 °C (for additional experimental details on the HT-PEMFC and Pt/CNF GDE, see Online Supplementary Materials).

The first MEA (MEA 1) included the PBI-O-PhT membrane and the pure Pt/CNF anode without the self-phosphorylating PBI-6F coating. The second MEA (MEA 2) included the PBI-O-PhT membrane and the Pt/CNF anode coated with the self-phosphorylating PBI-6F coating. The third MEA (MEA 3) included both the self-phosphorylating PBI-4OMe-BP membrane and the Pt/CNF anode coated with the self-phosphorylating PBI-6F coating. Comparative polarization curves for three different MEAs are presented in Figure 2.

Figure 2(*a*) shows that power density values for MEAs 2 and 3 (for both the Pt/CNF anode was coated with the self-phosphorylating PBI-6F coating, but different membranes were applied) are higher than the ones for MEA 1. At the same time, the power density peaks for MEA 2 and MEA 3 are almost identical (at 180 °C and 1.3 A cm^{-2}, the maximum power density values were 0.50 and 0.49 W cm^{-2}, respectively). However, with raising temperature to 200 °C [Figure 2(*b*)], the power density maximum for MEA 2 (PBI-O-PhT membrane and Pt/CNF anode coated with the self-phosphorylating PBI-6F coating) drops down to 0.39 W cm^{-2}, while the one for MEA 3 is even increasing up to 0.52 W cm^{-2}. Self-phosphorylating membrane PBI-4OMe-BP with self-phosphorylating anode covered by PBI-6F (MEA 3) reached the highest current density of 2.1 A cm^{-2} (at 20 mV); and the power density maximum was 0.52 W cm^{-2} at 1.4 A cm^{-2}.

In summary, the truly new in this work is a combination of the self-phosphorylating PBI-based membrane with the self-phosphorylating PBI-6F coating applied to the Pt/CNF-based anode, which results in improved HT-PEMFC performance due to possible enhancement of proton-conducting contacts in the MEA.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7562.

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