



High temperature polybenzimidazole membrane electrode assemblies using pyridine-polybenzimidazole as catalyst layer binder



Po-Hao Su^a, Joy Cheng^a, Jia-Fen Li^a, Yi-Hsiang Liao^a, T. Leon Yu^{a,b,*}

^a Department of Chemical Engineering & Materials Science, Yuan Ze University, Chung-Li, Taoyuan 32003, Taiwan

^b Fuel Cell Center, Yuan Ze University, Chung-Li, Taoyuan 32003, Taiwan

HIGHLIGHTS

- Higher pyridine content catalyst binder enhances catalyst layer H₃PO₄ loading.
- Higher pyridine content catalyst binder enhances fuel cell performance.
- Higher pyridine content catalyst binder enhances H₃PO₄ binding sites.

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ABSTRACT

We synthesize four pyridine-polybenzimidazoles (PyPBIs) and one polybenzimidazole (PBI) from a tetramin monomer (i.e., 3,3'-diamino benzidine (DABZ)) and two dicarboxylic acid monomers (i.e., isophthalic acid (IPA) and 2,6-pyridinedicarboxylic acid (PyA)) with PyA/IPA molar ratios of 6/4 (i.e., PyPBI-64), 5/5 (i.e., PyPBI-55), 4/6 (i.e., PyPBI-46), 3/7 (i.e., PyPBI-37), and 0/1 (i.e., PBI-11). The PyPBIs and PBI with molecular weight of $\sim 1.0\text{--}1.3 \times 10^{-4} \text{ g mol}^{-1}$ are used as Pt–C (Pt on carbon support) binders for fabricating gas diffusion electrodes (GDEs) and are doped with H₃PO₄ to prepare membrane electrode assemblies (MEAs). We demonstrate that both the H₃PO₄ loading of the GDE and the fuel cell performance of the MEA at 160 °C with unhumidified H₂/O₂ fuel increase with the increase of PyA monomer content of the PyPBI (or PBI) binder in the GDEs according to the sequence of PBI-11 < PyPBI-37 < PyPBI-46 < PyPBI-55 < PyPBI-64. The higher PyA content PyPBI provides more binding sites for H₃PO₄ in GDE and enhances fuel cell performance.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is considered as one of the most promising next generation clean energy technologies, because of its high efficiency and non-polluting nature. In the past two decades, researchers [1–5] have made efforts to develop hydrocarbon membranes for PEMFCs working at high temperatures. Compared to Nafion-based low temperature PEMFCs, the high temperature PEMFCs (HT-PEMFCs, 120 °C < Temp < 200 °C) have the following advantages: higher rapid electrode kinetics, greater tolerance to the CO impurities in the hydrogen fuel stream, and easy water–thermal management [6,7]. One of the most promising proton exchange membranes

(PEMs) suitable for HT-PEMFCs is the polybenzimidazole doped phosphoric acid (PBI/H₃PO₄) membrane [1,2], in which H₃PO₄ acts as proton-conducting carrier, and no water is needed for proton-conduction in the membranes. The PBI/H₃PO₄ membrane has shown to possess high proton conductivity at 120–200 °C with low humidity, good mechanical strength, excellent chemical and thermal stability, and is employed with greater success than other PEMs in HT-PEMFCs [8,9].

The combination of an effective contact at the three-phase boundary, that is, high Pt catalyst utilization, good proton conduction, and facile H₂ and O₂ (or air) transport to the Pt active sites in the catalyst layer (CL), is necessary for a high-performance membrane electrode assembly (MEA) [10,11]. The MEA of a PBI/H₃PO₄ based HT-PEMFC consists of a PBI/H₃PO₄ PEM, anode and cathode CLs, and gas diffusion layers (GDLs). The three major components of a CL are: Pt–C (Pt on a carbon support), H₃PO₄, and PBI, in which H₃PO₄ acts as a proton conductor, PBI serves as a binder of Pt–C and also as an ionomer for fixing H₃PO₄ in the CL to avoid leakage of H₃PO₄ from the CL to the GDL. The concentrations of the H₃PO₄ and PBI ionomer

* Corresponding author. Department of Chemical Engineering & Materials Science, Yuan Ze University, Chung-Li, Taoyuan 32003, Taiwan. Tel.: +886 3 4638800x2553; fax: +886 3 4559373.

E-mail address: cetlyu@saturn.yzu.edu.tw (T.L. Yu).

in the CLs as well as the microstructure morphology of the Pt–C, PBI, and H₃PO₄ components play important roles in determining the properties and performance of CLs [12–21].

In an HT-PEMFC, a high concentration of H₃PO₄ is necessary to achieve sufficient proton conductivity within the PEM and the CLs. Thus a good ionomer catalyst binder for retaining H₃PO₄ in CL is an important issue for a high performance HT-PEMFC. In this study, instead of using PBI binder, we used pyridine-polybenzimidazole (PyPBI) as a Pt–C catalyst binder for fabricating gas diffusion electrodes (GDEs) of PBI/H₃PO₄-based MEAs. Four PyPBIs synthesized from a tetramin monomer (i.e., 3,3',4,4'-diamino biphenyl (DABZ)) and two dicarboxylic acid monomers (i.e., 2,6-pyridinedicarboxylic acid (PyA) and isophthalic acid (IPA)) with initial [PyA]/[IPA] fed molar ratios of 6/4–3/7, and one PBI synthesized from DABZ and IPA (see the chemical reaction scheme in Fig. 1). We demonstrated that the PyA pyridine group in the PyPBI binder enhances the binding of H₃PO₄ molecules in CLs and raises the fuel cell performance.

Comparing with the Nafion-based GDEs, in which water and Nafion ionomer are proton conductors, the kinetics for O₂ reduction on Pt–C within the pure H₃PO₄ is slow because of the strong adsorption effect of H₃PO₄ and H₂PO₄^{−1} on the Pt active sites and the low solubility and diffusivity of the O₂ in pure H₃PO₄ [22]. Li et al. reported that a combination of H₃PO₄ with PBI can increase the O₂ solubility and suppress adsorption of H₃PO₄ and H₂PO₄^{−1} on the Pt-active sites, thus enhancing the Pt catalytic activity of O₂ reduction [23]. In the present study, we fabricated GDEs using low molecular weight (MW, $M_w = 1.0–1.3 \times 10^{-4}$ g mol^{−1}) PyPBI and PBI binders mixed with Pt–C, LiCl, and N,N'-dimethyl acetamide (DMAc) solvent catalyst ink solutions. The low MW PyPBI (or PBI) binders and LiCl reduce inter-polymer hydrogen bonding of PyPBI (or PBI) and help dispersion of PyPBI (or PBI) in the catalyst ink solutions [24] and in CLs. As a result, there is an increase in the PyPBI (or PBI) binding sites for H₃PO₄ molecules in the CLs and Pt catalytic activity is enhanced [25]. In all the MEAs, the [Pt–C]/[PyPBI (or PBI)] weight ratio in a CL was fixed at 19/1, which was similar in value to the [Pt–C]/[PBI] weight ratio of 20/1 suggested in the literature [14,26]. In this study, we used a high MW PBI ($M_w = 1.74 \times 10^5$ g mol^{−1}) cross-linked with epoxy resin to prepare membranes. These cross-linked PBI membranes were doped with H₃PO₄ and were used as PEMs for fabricating MEAs [27].

2. Experimental

2.1. PBI synthesis

PBI was synthesized from DABZ (Aldrich Chem. Co.) and IPA (Aldrich Chem. Co.) using polyphosphoric acid (PPA, Aldrich

Table 1
Monomer fed quantities for PyPBIs and PBI syntheses.

Sample designation	DABZ mole (g)	PyA mole (g)	IPA mole (g)	Initial fed C:N:H ^b	Polymer ^a C:N:H ^b
PyPBI-64	1.0 (214)	0.6 (100)	0.4 (66)	1.00:0.283:0.09	1.00:0.278:0.09
PyPBI-55	1.0 (214)	0.5 (84)	0.5 (83)	1.00:0.277:0.09	1.00:0.268:0.09
PyPBI-46	1.0 (214)	0.4 (67)	0.6 (100)	1.00:0.270:0.09	1.00:0.256:0.09
PyPBI-37	1.0 (214)	0.3 (50)	0.7 (116)	1.00:0.265:0.09	1.00:0.247:0.09
PBI	1.0 (214)	0.0	1.0 (166)	1.00:0.246:0.09	1.00:0.229:0.09

^a Elemental analyses data of synthesized polymers.

^b C:N:H in atomic ratio.

Chem. Co.) as a solvent. The detailed polymerization procedures were similar to those reported in the literature [27,28]. 4200 g PPA was mixed with DABZ and melted at 200 °C under a N₂ atmosphere for more than 3 h to obtain a homogeneous mixture. Subsequently, IPA was mixed into the solution to initiate polymerization. The quantities of the monomers fed into the reaction flask for PBI synthesis are listed in Table 1. The PBI was polymerized under a N₂ atmosphere at 210 °C for 48 h. After terminating the polymerization, the product mixture was poured into distilled water to precipitate the PBI product. The precipitated PBI was milled into a powder and then mixed with a 1 N NaOH aqueous solution under stirring for 2 h. During stirring, the NaOH aqueous solution was exchanged every 30 min to remove residual PPA. The PBI was subsequently rinsed with deionized water several times to remove residual NaOH and then dried under vacuum at 120 °C for 4 h.

2.2. Fractionation of the as-synthesized PBI to obtain a low MW and a high MW PBIs

The as-synthesized PBI, obtained in Section 2.1, was fractionated by solvent extraction using an N-methylformamide (NMF; a poor solvent of PBI) and N-methyl pyrrolidinone (NMP; a good solvent of PBI) mixture to obtain a low MW PBI. A 16 g mass of the as-synthesized PBI was added to a solvent mixture comprising 35 g of NMF (Aldrich Chemical Co.) and 15 g of NMP (Aldrich Chemical Co.) and stirred at 30 °C for 3 h. The resulting solution was then filtered to obtain filtrate and residual solid. The solvent of the filtrate was evaporated at 150 °C under vacuum for 2 h to obtain the solid PBI-11, which had a weight average MW of $M_w = 1.1 \times 10^4$ g mol^{−1} determined as described in Section 2.5. The residual solid was designated as PBI-174, which had a $M_w = 1.74 \times 10^5$ g mol^{−1}. The MWs of PBI-11 and PBI-174 were determined using a GPC as described in Section 2.5.

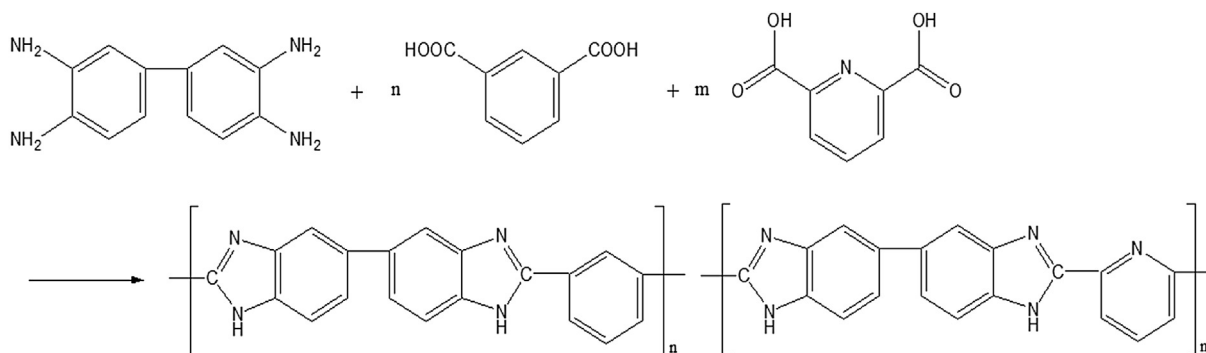


Fig. 1. Recation scheme of PyPBI from a tetramin monomer, i.e., 3,3',4,4'-tetraminbiphenyl (DAB), and two dicarboxylic acid monomers, i.e., isophthalic acid (IPA) and 2,6-pyridinedicarboxylic acid (PyDA).

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