Journal of Power Sources 393 (2018) 99–107

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Arylether-type polybenzimidazoles bearing benzimidazolyl pendants for high-temperature proton exchange membrane fuel cells

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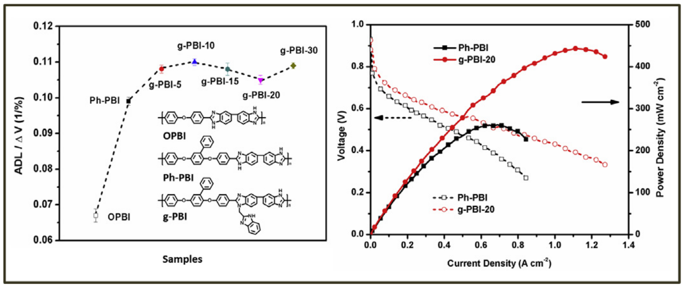
HIGHLIGHTS

- Grafted PBIs were prepared by an effective N-substituted method without catalyst.
- Grafted PBI membranes exhibited increased tensile stress, PA uptake rate and ADLs.
- The highly PA-doped g-PBI membranes had excellent dimensional-mechanical stability.
- PA-doped g-PBIs showed high proton conductivity and good fuel cell performance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Polybenzimidazole
Grafting
High-temperature proton exchange membrane
Phosphoric acid doping behavior
Dimensional-mechanical stability

ABSTRACT

Phosphoric acid-doped polybenzimidazole membranes offer great potential for high-temperature proton exchange membrane applications due to their high proton conductivity at high-temperature and low-humidity conditions. However, it remains a major challenge in fabricating high-performance membranes with both high proton conductivity and good mechanical strength. Here, a series of polybenzimidazoles with increased imidazole groups are obtained by incorporating some benzimidazole groups onto an arylether-type polybenzimidazole backbone via a simple and efficient N-substituted reaction without catalyst. This arylether-type polybenzimidazole is verified to exhibit good solubility under extremely high molecular weight, and it provides the possibility for fabricating the high mechanical strength membranes at high phosphoric acid doping levels. It is of interest to find that the introduction of additional bulky benzimidazole moieties even enhance the mechanical strength of the membranes, and at the same time, significantly improve their acid doping levels, acid doping rate and proton conductivity. Importantly, the acid-doped grafted membranes show superior dimensional-mechanical stability even at high acid loading. With an acid doping level of 22.1, the grafted membrane displays a high conductivity of 212 mS cm^{-1} at 200 °C without humidification. A H_2/O_2 fuel cell based on this membrane has a peak power density of 443 mW cm^{-2} at 160 °C.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have drawn significant attention due to their many attractive features, such as environmental friendliness, high efficiency, high power density and moderate operation conditions which provide their potential

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https://doi.org/10.1016/j.jpowsour.2018.05.011
Received 9 January 2018; Received in revised form 27 April 2018; Accepted 3 May 2018

applications in transportation and in stationary and portable electronics [1,2]. There is currently increasing interest in operating PEMFCs at high temperature (100–200 °C) and low-humidity conditions. Compared with low operating temperature (< 100 °C) limited by the water-based proton-conduction mechanism (vehicle mechanism) of low-temperature proton exchange membranes (PEMs), high operating temperature brings several distinct advantages, including a higher tolerance of the anode to CO poisoning, increased catalyst efficiency, simplified water/thermal management and improved resistance to fuel impurities [3–5]. High-temperature PEMs (HT-PEMs), as an essential efficiency-determining component of HT-PEMFCs that separate the two electrodes and provide a proton conducting medium, have become an active field of research consequently. Among the membrane materials for elevated operating temperatures, phosphoric acid doped polybenzimidazole (PA-PBI) membranes are considered to be the most promising HT-PEM candidates because of their low cost and high performance.

Polybenzimidazole (PBI) is an amorphous rigid polymer with high thermal stability, good chemical resistance and excellent mechanical strength. Phosphoric acid (PA) is a good electrolyte with high thermal stability and low vapor pressure at elevated temperatures. In PA-PBI membranes, there are two possible mechanisms for proton conduction: (i) vehicular, i.e., motion assisted by carrying molecules; and (ii) Grotthuss, i.e., jumping from one site to another one along a hydrogen-bond chain. The proton transport mechanisms are strongly dependent on PBI/PA ratio, i.e., the PA doping levels (ADLs: defined as the number of moles of doping PA per mole PBI repeat unit) [6]: (1) hopping directly along the nitrogen sites of PBI chains, which is relevant only for undoped PBI; (2) hopping from the N–H sites to the phosphoric acid anions. This contribution is relevant for ADL < 2 (calculated by the PBIs which contain two benzimidazole groups in one repeat unit); (3) hopping along the phosphoric acid anions (ADL > 2). This term is associated to the presence of free acid, and can contribute a strong increase of the conductivity; (4) hopping via water molecules. This term, which is concurrent with the previous one, is more significant at high temperature. The proton transport mechanisms in PA-PBI systems were deeply investigated by the Kreuer group through addressing the transport mechanisms in pure PA, PA-H_2O solutions, and PA-PBI systems [7–10]. These transport characteristics allow PBI membranes to operate at high temperatures up to 200 °C.

Until now, relatively few PBI structures have been investigated for PA-PBI systems, the most widely investigated PBI has been the commercially available *m*-PBI (poly[2,2′-*m*-(phenylene)-5,5′-bibenzimidazole]). Based on *m*-PBI, many efforts have been made to improve the ADLs of PA-PBI membranes in order to enhance their proton conductivity. For instance, since the affinity of basic sites to PA molecules, PBIs containing additional nitrogen heterocycles (e.g. pyridine and imidazole) were synthesized to increase ADLs [11–15]. Other functional groups, such as hydroxyl, amino and sulfonic acid groups, were also incorporated into PBI main chains to improve membrane properties [14,16–21]. Increasing the free volume of PBI membranes by introducing flexible and bulky groups into the rigid PBI chains or incorporating inorganic nanoparticles into the membranes could also improve ADLs [15,22–25]. Altering PA-PBI membrane formation techniques by a sol-gel method has been demonstrated as an effective way to fabricate PBI membranes with high ADLs and proton conductivity as well [19,23,26]. In addition, PBI based nanocomposites [25,27–31], polymer blends [32–35], and porous materials [36–38] have been built as the strategies to enhance the performance.

While these attempts have indeed yielded significant enhancements in improving ADLs and thereby increasing conductivity, high ADLs result in large dimensional swelling and the deterioration of the mechanical strength of PA-PBI membranes, leading to greatly reduced HT-PEMFC performance and durability. Generally, high linear molecular weight is preferred for PBIs in order to endow the corresponding membrane with enough mechanical strength to sustain more acids. However, for *m*-PBI, to avoid insolubility due to its rigid backbone and the strong hydrogen bond interactions between imidazole groups, PBIs with a relatively low molecular weight (M_w) in a range of 23–40 kDa have to be mainly used for membrane fabrication [39]. This molecular weight only allows a moderate ADL of 6–10, resulting in relatively low proton conductivity (e.g. $< 100\ \mathrm{mS{\cdot}cm^{-1}}$) even at high test temperature of 150 °C [19,24]. Covalent cross-linking is a useful method to strengthen the polymer matrix. Compared with the linear PBI membranes, cross-linked PBI membranes exhibited enhanced mechanical strength and dimensional stability at the similar ADLs [36,40–42]. However, the introduction of cross-linker component would lower the relative content of imidazole groups in PBI membranes, and thereby reduce the ADLs and proton conductivity. As is evident from the above discussion, each of these approaches possesses advantages and disadvantages. Thus, the trade-off between ADLs (i.e. conductivity) and membrane dimensional-mechanical stability is still a tough and unresolved challenge in the study of PA-PBI membranes. Recently, exploring PBIs with novel chemical structures has been considered as an avenue to tailor the membrane properties and break the singularity of the established membrane systems based on PA-doped *m*-PBI for improving the overall desired properties of HT-PEMs. It is hopeful that a preferred PBI matrix can be obtained by combining a rational designed PBI backbone with a reasonable modification of functional groups.

An arylether-type PBI (Ph-PBI) having a well unity of high molecular weight and superior solubility was obtained in our previous work and it exhibited high dimensional-mechanical stability at high ADLs [43]. As a continuous effort to further enhance the performance of PBI-based membranes and create more PBI systems beyond *m*-PBI, in the present work, a series of PBIs with more imidazole groups were synthesized by grafting the benzimidazole groups onto flexible Ph-PBI backbones through a simple and efficient N-substituted reaction without catalyst. The additional bulky *N*-heterocyclic pendants were expected to enhance the acid uptake capability of PBI membranes by disrupting the dense packing of molecular chains and creating larger free volume, meanwhile, to provide extra basic sites for the acid doping and proton conduction. The properties related to their applications in HT-PEMFCs, such as PA-doping behaviors, dimensional-mechanical stability, proton conductivity and fuel cell performance, were investigated in detail.

2. Experimental section

2.1. Materials

Phenylhydroquinone (97%, Sigma-Aldrich Ltd.), 4-fluorobenzonitrile (99%, Energy Chemical Co.), 3,3′-diaminobenzidine (DAB) (97%, Aladdin Reagent), 2-chloromethylbenzimidazole (96%, Aladdin Reagent) and 4,4′-oxybis(benzoic acid) (98%, Alfa Aesar Reagent) were used as received without purification. Phosphorus pentoxide-methanesulfonic acid (PPMA) solution was prepared by dissolving phosphorus pentoxide (Beijing Chemical Reagent, China) into methane sulfonic acid (Aladdin Reagent) in the mass ratio of 1:10 [44]. *N,N*-Dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were purchased from Tianjin Tiantai Fine Chemicals Co. Ltd., China. Sodium bicarbonate ($NaHCO_3$), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), ethanol, acetone and toluene were obtained from Beijing Chemical Reagent, China.

2.2. Synthesis of arylether-type PBIs bearing benzimidazolyl pendants and preparation of the membranes

Ph-PBI precursor was synthesized by the condensation polymerization of Ph-COOH and DAB in PPMA, and the detailed synthetic procedure was reported in our previous work (Scheme 1 (a)) [43].

^{1}H NMR of Ph-PBI (500 MHz, DMSO-d6): δ(ppm) 12.93 (s, 2 H), 8.22 (dd, 4 H), 7.90 (d, 2 H), 7.46 (ddd, 12 H), 7.27–6.88 (m, 4 H). M_w: