Journal of Membrane Science 460 (2014) 160–170

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Quaternized polybenzimidazoles with imidazolium cation moieties for anion exchange membrane fuel cells

Li-cheng Jheng [a,b], Steve Lien-chung Hsu [a,*], Bi-yun Lin [c], Yi-lun Hsu [b]

[a] Department of Materials Science and Engineering, Research Center for Energy Technology and Strategy, National Cheng-Kung University, Tainan, Taiwan, ROC
[b] Green Energy and Eco-Technology Center, ITRI-S, Industrial Technology Research Institute, Tainan, Taiwan, ROC
[c] Instrument Center of National Cheng Kung University, Tainan, Taiwan, ROC

ARTICLE INFO

Article history:
Received 3 October 2013
Received in revised form
26 February 2014
Accepted 28 February 2014
Available online 12 March 2014

Keywords:
Polybenzimidazole
Imidazolium
Anion exchange membrane
Fuel cell

ABSTRACT

A new series of quaternized polybenzimidazoles (PBIs) having imidazolium moieties in the main-chain and/or in the side group were synthesized for use as anion exchange membrane (AEM) for fuel cells. The polymer structures were characterized by ^{1}H NMR, FTIR, and EDX analyses. The degree of imidazolium functionalization (DIF) of the quaternized PBI was also determined. The properties required for AEM, such as ion exchange capacity (IEC), water uptake, swelling ratio, hydrated number, and ionic conductivity were measured. The IECs of the quaternized PBIs were in the range of 0.96–1.49 mmol/g. The highest ionic conductivity of 2.72×10^{-2} S/cm was achieved at 80 °C. Besides, the thermal stability, mechanical properties, and alkaline stability of the quaternized PBI membranes were investigated. The results revealed that the thermal stability and mechanical properties of the membranes were acceptable, but the alkaline stability of the imidazolium moieties needs to be improved.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely investigated and tested for several decades. However, its mass commercialization is hampered by the high cost of both membranes and catalysts, as well as the low durability of catalysts [1,2]. Anion exchange membrane fuel cell (AEMFC) is a viable alternative to PEMFC, in which the charge carriers are hydroxide ions instead of protons. AEMFCs remain the advantages of alkaline fuel cells (AFCs), the primary ones which include: (1) a more efficient oxygen reduction reaction at the cathode compared to PEMFC [3,4]; (2) a reduced amount of the platinum catalyst or cheaper non-noble catalysts used, allowing further cost reduction [5–7]; (3) avoiding corrosion problems in acidic conditions so that graphite-based bipolar plates can be replaced by cheap and robust metal-based ones [8,9]; (4) the electro-osmotic drag associated with ion transport opposes the liquid fuel crossover, allowing wide choice of fuels [1,3]. Furthermore, the AEMFC can prevent the liquid electrolyte (e.g., KOH) leakage issue and reduce the carbonation phenomenon, which makes it more reliable and durable than AFC [2,3]. Hence, there has been considerably growing interest in AEMFCs in recent years.

Merle suggested that anion exchange membranes (AEMs) can be classified into three categories, including heterogeneous membranes, homogeneous membranes, and interpenetrating polymer networks [10]. The most common heterogeneous AEM is an ion-solvating polymer based membrane, which consists of a polymer matrix and an alkaline salt. This has been extensively developed for applications in secondary batteries in the last few decades [11,12]. In addition, some heterogeneous AEMs such as KOH/polyvinyl alcohol (PVA) complex, and KOH doped polybenzimidazole (PBI) have been suggested feasible as polymer electrolytes for fuel cells [13–15]. According to the recent works of Hou, alkaline doped PBI membranes exhibited good ionic conductivity, acceptable mechanical strength, high thermal stability, and low methanol permeability [16,17]. They reported that the ionic conductivity of the membrane at room temperature reached to 1.84×10^{-2} S/cm and the fuel cell performance at 90 °C showed a peak power density reaching 60.95 mW/cm^2 [17]. Furthermore, a KOH doped PBI membrane based alkaline directed ethanol fuel cell (ADEFC) with non-platinum catalysts has been demonstrated by Modestov and co-workers [18].

Quaternary ammonium functionalized AEMs are the most extensively developed homogeneous AEMs. However, most of them were prepared by the chloromethylation with chloromethyl ether and the following quaternization with aqueous trimethylamine [19–21]. Chloromethyl ether is carcinogenic and harmful to human health that makes the synthesis procedure environment unfriendly [22]. Therefore, it is desirable to develop alternative

* Corresponding author. Tel.: +886 6 2757575x62904; fax: +886 6 2346290.
E-mail address: lchsu@mail.ncku.edu.tw (S.-c. Hsu).

http://dx.doi.org/10.1016/j.memsci.2014.02.043
0376-7388

synthesis methods for quaternary ammonium functionalized AEMs [23] or to replace quaternary ammoniun with other cationic groups, such as pyridinium, phosphonium, guanidinium and imidazolium, as anion-exchange sites [1].

In contrast, homogeneous AEMs based on quaternized polymers with imidazolium groups have attracted increasing attention in recent years [24–31]. In comparison with quaternary ammonium functionalized AEMs, imidazolium functionalized AEMs exhibited better thermal and chemical stability, as well as comparable ionic conductivity [32,33]. Until now, a variety of imidazolium derivatives has been studied for AEMFCs, including N-methylimidazolium [27–29], C2-substituted dimethylimidazolium [25,31], and methylbenzimidazolium [24]. A quaternized PBI having imidazolium moiety in the main-chain, called poly(benzimidazolium), synthesized from water-insoluble PBI via a facile methylation process was suggested [34–36]. This impressive approach allows PBI to act as not only a heterogeneous AEM but also a homogeneous AEM, which was brought up by three different research groups almost at the same time. The fuel cell operation of ADEFC based on poly(benzimidazolium) was demonstrated by Hou et al. [35], and the alkaline degradation mechanism of poly(benzimidazolium) was investigated by Henkensmeier et al. [37]. Meanwhile, Thomas et al. studied the steric effect on the alkaline stability of poly(benzimidazolium) [38].

Quaternized PBIs used as homogeneous AEMs for fuel cells are of potential interest and worthy of further development. However, quaternized PBIs with imidazolium moiety in the side group have not been developed so far. Herein, we synthesized a series of quaternized PBIs having imidazolium moieties in the main-chain and/or side group. The properties of the quaternized PBI based AEMs with respect to IEC, water uptake, hydrated number, swelling ratio, ionic conductivity, mechanical strength and alkaline stability were investigated in the present work.

2. Experimental

2.1. Materials

Bis(chloroethoxy)ethyl ether, iodomethane, and potassium chromate (K_2CrO_4) were purchased from Alfa Aesar. Sodium sulfate (Na_2SO_4), sodium chloride, potassium hydroxide (KOH), and silver nitrate ($AgNO_3$) were obtained from SHOWA. All the solvents of ACS grade used in this work, including chloroform, diethyl ether, dimethyl sulfoxide (DMSO), acetone, tetrahydrofuran (THF), and methanol, were provided from ECHO Chemical Co., Ltd. Sodium hydride, calcium hydride and all the d-solvents used in this work including dimethyl sulfoxide-d_6 (DMSO-d_6), chloroform-d ($CDCl_3$), and potassium deuteroxide solution were purchased from Aldrich. DMSO was dried and purified by distillation over calcium hydride before use. All the reagents and solvents except for DMSO were used as received.

2.2. Synthesis of (Chloromethoxy ethoxy ethoxy ethyl) methylimidazolium chloride ([CM3EMI]cl)

Bis(chloroethoxy)ethyl ether (6.934 g, 0.03 mol) was placed in a 100 mL of two-necked flask reactor equipped with a magnetic stirrer and a condenser. The reactor was heated to 80 °C and methylimidazole (2.5862 g, 0.0315 mol) was subsequently added into it drop by drop. The reaction was carried out by stirring the mixture at 80 °C under nitrogen atmosphere for 24 h. After cooling to room temperature, the mixture was dissolved in chloroform. A viscous substance with pale yellow color was isolated by pouring the solution into excessive cold diethyl ether, and then it was concentrated under a reduced pressure. The viscous substance was dissolved in chloroform and isolated from diethyl ether again for further purification. After drying in a vacuum oven for 48 h at 100 °C, the resulting product [CM3EMI]Cl was obtained. The yield of [CM3EMI]Cl reached approximately 84%.

2.3. Synthesis of quaternized polybenzimidazole having imidazolium moiety in the side groups (sQPBI-X)

In a 250 mL of three-necked flask reactor, PBI powder (0.534 g, 1 mmol) and anhydrous DMSO (17.3 g) were added. The reactor was equipped with a magnetic stirrer, a dropping funnel, and a condenser. The mixture was vigorously stirred at 80 °C under nitrogen atmosphere until PBI was dissolved completely. Sodium hydride (0.048 g, 2 mmol) was dissolved in a proper amount (about 2 g) of anhydrous DMSO and then the solution was added into the reactor gradually within 10 min. While there was no longer gas releasing from the mixture, [CM3EMI]Cl (0.748 g, 2.5 mmol) solution in DMSO was added into the reactor. The mixture was heated to 100 °C and stirred under nitrogen atmosphere for 36 h. After that, the mixture was cooled to room temperature. After pouring the mixture into 200 mL of acetone and filtration, a precipitate was collected. The precipitate was respectively washed with acetone and de-ionized water twice to remove remaining substances. After drying at 100 °C in a vacuum oven for 24 h, the resulting polymer denoted as sQPBI-X was obtained. The sQPBI-X contains Cl^- anions as the counterions for the N-methylimidazolium cations in the side groups.

2.4. Synthesis of quaternized polybenzimidazole having imidazolium moiety in the main-chains (mQPBI-X)

In a 250 ml of three-necked flask reactor, PBI powder (0.534 g, 1 mmol) and anhydrous DMSO (17.3 g) were added. The reactor was equipped with a magnetic stirrer, a dropping funnel, and a condenser. The mixture was vigorously stirred at 80 °C under nitrogen atmosphere until PBI was dissolved completely. After a half amount of iodomethane (0.358 g, 2.5 mmol) was added, the mixture kept stirring at 80 °C under nitrogen atmosphere for 12 h. Subsequently, another half amount of iodomethane (0.358 g, 2.5 mmol) was added into the mixture and the temperature was raised to 100 °C. After stirring at 100 °C under nitrogen atmosphere for 24 h, the mixture was cooled to room temperature. After pouring the mixture into 200 mL of THF and filtration, a precipitate was collected. The precipitate was washed with de-ionized water and dried at 100 °C in a vacuum oven for 24 h. After drying, the resulting polymer denoted as mQPBI-X was obtained. The mQPBI-X contains I^- anions as the counterions for the benzimidazolium cations in the main-chains.

2.5. Synthesis of quaternized polybenzimidazole having imidazolium moieties in both the main-chains and side groups (msQPBI-X)

In a 250 mL of three-necked flask reactor, PBI powder (0.534 g, 1 mmol) and anhydrous DMSO (17.3 g) were added. The reactor was equipped with a magnetic stirrer, a dropping funnel, and a condenser. The mixture was vigorously stirred at 80 °C under nitrogen atmosphere until PBI was dissolved completely. Sodium hydride (0.048 g, 2 mmol) was dissolved in a proper amount (about 2 g) of anhydrous DMSO and then the solution was added into the reactor gradually within 10 min. While there was no longer gas releasing from the mixture, [CM3EMI]Cl (0.748 g, 2.5 mmol) solution in DMSO was added into the reactor. The mixture was heated to 100 °C and stirred under nitrogen atmosphere for 24 h. An excessive amount of iodomethane (0.86 g, approximately 6 mmol) was added into the mixture. The mixture kept stirring at 100 °C under nitrogen atmosphere for another 24 h. After that, the mixture was cooled to room temperature.