



Hydroxide-ion selective electrolytes based on a polybenzimidazole/graphene oxide composite membrane



Bor-Chern Yu^a, Yi-Chun Wang^a, Hsin-Chun Lu^a, Hsiu-Li Lin^b, Chao-Ming Shih^a,
S. Rajesh Kumar^a, Shingjiang Jessie Lue^{a, c, d, *}

^a Department of Chemical and Materials Engineering and Green Technology Research Center, Chang Gung University, Guishan District, Taoyuan City 333, Taiwan

^b Department of Chemical Engineering and Materials Science and Fuel Cell Center, Yuan Ze University, Chung-Li, Taoyuan City 320, Taiwan

^c Department of Radiation Oncology, Chang Gung Memorial Hospital, Guishan District, Taoyuan City 333, Taiwan

^d Department of Safety, Health and Environmental Engineering, Ming-Chi University of Technology, Taishan District, New Taipei City 243, Taiwan

ARTICLE INFO

Article history:

Received 28 January 2017

Received in revised form

1 June 2017

Accepted 9 June 2017

Available online 12 June 2017

Keywords:

Graphene oxide (GO)

Polybenzimidazole (PBI)

Spin coating

Alkaline fuel cell

Cell performance

ABSTRACT

The objectives of this work are to prepare and characterize poly[2,2'-m-(phenylene)-5,5'-bibenzimidazole]/graphene oxide (PBI/GO) solid electrolyte for direct alcohol alkaline fuel cell (DAAFC) applications. GO nanosheets are coated onto a PBI surface using a spin coater to construct the PBI/GO composite membrane. The PBI/GO composite membrane exhibits an ionic conductivity of $2.53 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C, which is improved by 72–93% when compared with the pure PBI membrane. In addition, the methanol permeability is reduced by 18–25% by incorporating GO onto the PBI top surface. The peak power density (P_{max}) of the PBI/GO electrolyte reaches 200 mW cm^{-2} when using alkaline methanol as fuel with Pt-based catalysts, or 120 mW cm^{-2} when fed with an ethanol and alkaline solution mixture at 80 °C. Replacing the Pt-based catalysts with Hypermec™ catalysts resulted in P_{max} of 40 and 100 mW cm^{-2} , for methanol and ethanol fuel cells, respectively. These superior DAAFC power outputs are ascribed to the improved anion conduction of the KOH doped GO and the suppressed methanol cross-over from high aspect ratio GO as the alcohol barrier layer.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Fuel cells are electro-chemical conversion devices able to transform chemical energy into electrical energy and thereby function as alternative power resources [1,2]. Recently, low-operating temperature (<80 °C) fuel cells, including acidic direct alcohol fuel cells (DAFCs) [3] and alkaline DAFCs have been proposed for mobile and portable applications [4,5]. As a key component of acidic DAFCs, Nafion from DuPont has been used as a cationic-exchange membrane (CEM) due to its high chemical resistance and outstanding physical strength [6,7]. CEMs can transport protons from anode to cathode and act as a barrier to separate the fuel and oxidant streams [8,9]. The bottlenecks for acidic DAFCs in commercialization are slow redox kinetics, platinum-based electrocatalysts, high fuel permeability, CO

poisoning, complex water management and their high cost [10–12]. In contrast, alkaline DAFCs employing an anion-exchange membrane (AEM) are a potential alternative to DAFCs employing a CEM and have attractive merits [13,14]. The advantages of alkaline DAFCs include suppressed fuel cross-over, enhanced electro-chemical kinetics, easy water management and reduced cost [15–18].

Methanol, being rich in hydrogen, has become a popular fuel in addition to hydrogen. Consequently the use of direct methanol alkaline fuel cells (DMAFCs) in alternative energy applications has gained significant attention [19–21]. During DMAFC operation, the hydroxide anion acts as a charge carrier and transfers from cathode to anode, which is contrary to the proton migration direction in acidic direct methanol fuel cells (DMFC) [22]. Thus, the electro-osmotic effect of anions accompanies reduced methanol cross-over through the electrolyte film. The electrochemical reactions of methanol oxidation [23] and oxygen reduction [24] are easily accelerated in an alkaline solution than those of acidic medium. Water molecules are generated at the anode and compatible with

* Corresponding author. Department of Chemical and Materials Engineering, Chang Gung University, Guishan District, Taoyuan City 333, Taiwan.

E-mail address: jessie@mail.cgu.edu.tw (S.J. Lue).

the methanol aqueous solution in the DMAFCs, thus eliminating the cathode flooding issue and decreasing water management complexity as compared with proton-exchange DMFC [19,25]. Thus, the cell voltage and power density (P_{\max}) was improved in alkaline DMFC than those of acidic DMFC [26,27]. In addition, alkaline fuel cells achieve cost reduction benefits (~70–80%) by using less expensive membrane electrolytes and non-platinum (Pt) catalysts [28]. Therefore, DMAFC development has increased in the last decade.

Most of the extensively studied alkaline AEMs contain quaternary ammonium (QA) groups to increase ionic conductivity and fuel cell performance [17,29]. However, the QA groups were unstable in alkaline medium when exposed to high pH, elevated temperature (>60 °C) and long-term operations [30] due to the strong nucleophilic attack of QA by OH^- ions, Hoffman elimination and the degradation of polymeric backbones [31]. These reactions cause the membrane to lose its structural stability, change its molecular weight and suffer serious fuel cross-over, thus limiting fuel cell performance [32]. More recently, some other functional head-groups containing phosphonium [33], guanidinium [34], and benzimidazolium ions [35] have been explored to overcome the problems of QA groups. Among these, the benzimidazolium moiety is most stable in alkaline conditions due to its π -conjugated structure and the five-membered heterocyclic ring of its imidazolium ions [36].

Polybenzimidazole (PBI, poly [2,2-(*m*-phenylene)-5,5-benzimidazole]) [37] is one members of the benzimidazolium family and has two imidazole functional groups per repeating unit. PBI is extremely flexible and is an amorphous polymer with good film-forming ability and an excellent electrolyte membrane for fuel cells. Among the different PBI structures described by Quartarone et al. [38], the meta form of PBI is more stable in both acidic and alkaline conditions. However, this PBI structure represents an ionic and electronic insulator, while the $-\text{N}=\text{}$ and $-\text{NH}-$ functional groups in the imidazole-ring may become ionic conductors by doping with alkaline [27] or with acids [39]. Most PBI membrane research has focused on acid doping for high-temperature proton exchange membrane fuel cells (PEMFCs) [40]. Nevertheless, alkali-doped PBI membranes can also achieve high-quality performances when operating with alcohols [27] or with hydrogen [41] fuels. For alkali doping, the chemical bonding between PBI and KOH occurs via two possible mechanisms. One is hydrogen bonding between the PBI backbone of $-\text{N}=\text{}$ and OH^- ions from KOH, where K^+ is the counter ion; the other is the interaction between PBI chains of $-\text{NH}-$ and K^+ ions due to neutralization that occurs between OH^- ions from the alkaline conditions and H in $-\text{NH}-$ groups of PBI [42,43]. These bonding formation mechanisms prevent KOH leakage from the PBI skeleton [44]. The neutralization and/or hydrogen bonding between PBI and KOH promote an increase in hydroxide ion transportation [27,45]. The PBI skeleton increases the alkaline retention for long-term operation (more than 500 h), resulting in an improvement in chemical stability [42]. Similarly, Ali et al. have demonstrated that 25 wt% KOH doped PBI membranes are highly stable up to 200 days at 88 °C by preventing hydrolysis of the polymeric backbone [46]. This stable alkali-doped PBI membrane can enhance hydroxyl conductivity and fuel cell performance.

In our previous study, we showed that KOH-doped PBI exhibited more than two times higher selectivity (1.12×10^5 vs. 0.4×10^5 S s cm^{-1}) and power density ($P_{\max} = 159$ vs. 46.5 mW cm^{-2}) than the acid-doped PBI electrolyte at 90 °C [27]. Similarly, Xing and Savadogo observed that KOH-doped PBI has a higher ionic conductivity (9×10^{-2} S cm^{-1}) than acid-doped PBI film (5×10^{-2} S cm^{-1}) [47]. Hou et al. reported that the KOH-doped PBI membrane showed good ionic conductivity (10^{-2} S cm^{-1}) and

suppressed alcohol permeability (10^{-7} $\text{cm}^2 \text{S}^{-1}$), which resulted in a P_{\max} of 31 mW cm^{-2} on methanol and 60.9 mW cm^{-2} on ethanol fuel cells using a Pt-based electrocatalyst [43,45]. Furthermore, Modestov et al. and Katzfub et al. have demonstrated that non-Pt based electrocatalysts also promote higher P_{\max} values of 100 mW cm^{-2} on ethanol and 120 mW cm^{-2} on methanol, using a KOH-doped PBI membrane [48,49]. The literature reports clearly indicate that KOH doping in the PBI membrane provides a facile method for an efficient electrolyte for alkaline fuel cells.

Recently, different nanofillers such as LaFeO_3 [50], fumed silica [17,51], chitosan [52], carbon nanotubes [22], and graphene oxide (GO) [53] have been incorporated into a KOH-doped polymeric matrix for DMAFCs. Among these nanofillers, GO may act as a potential nanofiller to block the passage of fuel through the polymeric electrolyte, resulting in the suppression of methanol permeability [54]. According to Bharadwaj and Cussler models, the molecular permeant rate is suppressed and is related to the GO loading, aspect ratio, and orientation angle in the polymeric matrix [55,56]. One of our earlier studies indicated that GO nanosheets spin-coated onto a Nafion-212 membrane suppressed methanol permeability (60%) and increased the P_{\max} by 100% compared with pristine Nafion [53]. Therefore, the hybrid GO fillers in the polymeric matrix were used to increase tortuous paths for methanol permeation.

The effect of GO incorporation into polymer electrolytes on the ionic conductivity is not conclusive. Nafion/GO composite membranes have been reported to have decreased ionic conductivity using hot-pressing [57], dip-coating [58], spin-coating [53], layer-by-layer [59] and direct blending methods [60]. The direct blending of GO in quaternized polysulfone membrane also results in decreased conductivity [61]. In contrast, PVA/GO [62] and PBI/GO [18,63] blended composite membranes show increased ionic conductivity compared with the pristine membranes. Further investigations performed by several groups illustrate the ionic conductivity is dependent on the GO content for optimal polymer/GO blend composites [54]. There is an optimal GO loading for PBI [64,65], Nafion [66], and sulfonated polyimide [67], depending on the compatibility and composition of GO, polymer and possible solvent. Hence, the role of GO on the ionic conductivity of polymer electrolyte membrane remains controversial.

In order to prepare efficient membrane electrolytes for DAAFC, both low fuel permeability and high ionic conductivity are top criteria. In this study, GO nanosheets are spin-coated onto a PBI membrane to fabricate a dual-layer PBI/GO composite with a well-aligned structure. The interfacial adhesion between GO and the PBI matrix improves when the same PBI is used as a binder, which is demonstrated by strengthening of the mechanical properties of the composite. The PBI/GO composite membrane has a higher dimensional stability than that of the pristine PBI membrane. The GO introduces a barrier function to suppress methanol permeability. The ionic conductivity of the composite is enhanced due to better interfacial compatibility. Direct alcohol (methanol and ethanol) alkaline fuel cells using the developed composite were assembled using Pt- and non-Pt-based catalysts, and their fuel cell performances were determined.

2. Experimental

2.1. Preparation of GO nanosheets, PBI solution, and PBI film preparation

We prepared exfoliated GO nanosheets from graphite powder (Sigma-Aldrich, St. Louis, MO, USA) using potassium permanganate (Nihon Shiyaku Industries, Ltd., Japan) and sulfuric acid (Sigma-Aldrich), similar to modified Hummers' method [68]. The X-ray diffraction (XRD, Model D5005D, Siemens AG, Munich, Germany)

Download English Version:

<https://daneshyari.com/en/article/5475876>

Download Persian Version:

<https://daneshyari.com/article/5475876>

[Daneshyari.com](https://daneshyari.com)