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Novel sulfonated Nafion®-based composite membranes with pillararene as selective artificial proton channels for application in direct methanol fuel cells

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ARTICLE INFO

Article history:
Received 18 February 2015
Received in revised form
30 June 2015
Accepted 15 July 2015
Available online 22 August 2015

Keywords:
DMFC
Nafion
Pillararene
Composite membranes
Proton conductivity
Methanol permeability

ABSTRACT

Proton exchange membranes (PEM) are critical components of low temperature fuel cells. Most PEMs are made of perfluorinated sulfonic acid polymers such as Nafion®. However, Nafion has a high methanol permeability which is limiting its applicability in direct methanol fuel cells (DMFCs). Here, we report on novel sulfonated pillar[5]arene/Nafion composite membranes with improved properties for application in DMFCs. The properties of the novel composite membranes were investigated under a range of synthesis and operating conditions. Under most conditions, the novel composite membranes exhibited properties far superior than Nafion. For example, the proton conductivity of the sulfonated pillar[5]arene's (10 wt.%)/Nafion composite membrane was 0.145×10^{-4} S cm^{-1} at 80 °C, while methanol permeability was 2.43×10^{-6} cm^2/s. Proton selectivity was increased up to two-fold compared to Nafion-recast membrane. The likely mechanisms for improvements were discussed. Overall, these results indicate that these novel composite membranes are promising for application in DMFCs.

Introduction

Direct methanol fuel cells (DMFCs) are thought to be one of the most promising power generating systems, with great commercial value for applications e.g., in portable electronic devices [1,2]. DMFCs can be made very compact and lightweight, they are relatively simple systems with a high energy density, they benefit from a convenient fuel, and could be developed into safe, convenient and economical portable power sources [3,4]. When fully developed, DMFCs have the potential to be used in small power stations, spacecrafts,

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http://dx.doi.org/10.1016/j.ijhydene.2015.07.073

microelectronics such as cell phones, laptop computers, cameras, and more. DMFCs could one day replace lithium ion and other storage batteries.

The proton exchange membrane (PEM) is a key component in DMFCs allowing separation of anodic and cathodic compartments to prevent methanol crossover, yet allowing transfer of protons from the anode to the cathode. Consequently, the performance and price of PEMs determine to a large extent the performance, life, and cost of DMFCs. Despite the success of perfluorinated sulfonic membranes such as Nafion® as proton exchange membrane in fuel cells, there are several drawbacks when it used in DMFCs: (1) The methanol permeability of Nafion is high. Methanol crossover will result in a reduced potential and poisoning of the platinum catalyst at the cathode, ultimately leading to a drop in the fuel cell performance [5,6]. (2) The cost of perfluorinated sulfonic membranes is high because of the complex preparation process [6,7]. (3) The dimensional stability of Nafion is poor. There could be a 10%–20% size difference between wet and dry conditions [8–10].

To reduce methanol crossover, several methods, such as synthesizing new polymers, chemically and physically cross-linking, blending, acid–base composite grafting and dispersing suitable fillers in polymers, have been explored [11–15]. A promising approach has been to incorporate inorganic nanoparticles into Nafion membranes to suppress methanol crossover. $Na_2Ti_3O_7$ nanotubes/Nafion composite membranes were prepared by Wei et al. [16]. With just 5 wt.% $Na_2Ti_3O_7$ nanotubes, composite membranes showed improved selectivity of protons over methanol; they performed better at low temperature (298 K) than high temperature (353 K). Similarly, 6 wt.% $TiO_2 - SO_4^{2-}$/Nafion composite membranes exhibited 33% reduced methanol permeability with just a slight decrease in proton conductivity [17]. The relatively high proton conductivity was believed to be the result of proton channels formed by sulfonic acid groups attached to nanomaterials. Similar results have been obtained by others though often, the reduced permeability to methanol was obtained at the expense of weaker mechanical properties, lower proton conductivity, and/or markedly higher cost [18–28]. Ideally, the added materials should decrease methanol crossover, increase the water holding capacity of the membrane and/or create more proton channels to promote proton conductivity.

Recently, pillar[5]arene (Fig. 1) was studied by Si et al. [29] as an artificial proton channel to selectively conduct protons in a lipid bilayer. It was shown that protons migrate in Grotthus mechanism through water wires formed in pillar[5]arene backbones efficiently, but other ions including Li^+, K^+ and Cl^- can barely pass through pillar[5]arene. This phenomenon was explained by the size mismatching of the ions with the cavity surrounded by the ether and ester groups [29]. Since the inner diameter of pillar[5]arene is only about 6.5 A [30], which is about one order of magnitude smaller than that of inorganic nanomaterials [16,17,21], we hypothesized that methanol molecules (diameter ~2.8 A) would thus experience a much larger resistance to pass through the pillar[5]arenes compared to H_3O^+ molecules (diameter ~1.6 A). Therefore, pillar[5]arenes have the potential to selectively conduct protons over methanol. Here, we report a novel way to increase the selectivity of proton exchange membranes by incorporating pillar[5]arene molecules into Nafion membranes. Then, the pillar[5]arene/Nafion composite membranes were sulfonated in the hope of increasing the proton conductivity. The structure, proton conductivity, and methanol permeability of the composite membranes were characterized.

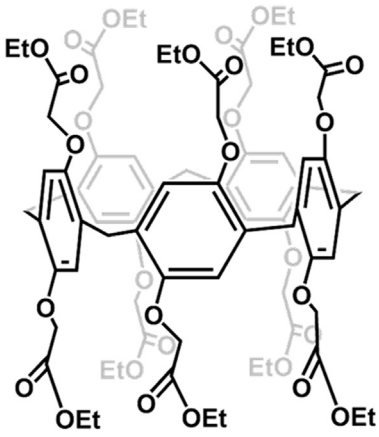

Fig. 1 – Chemical structure of pillar[5]arene.

Experimental

Materials

The 5 wt.% Nafion solution and N,N-Dimethylformamide (DMF) were purchased from Fisher Scientific (Pittsburgh, PA); anhydrous methanol and sulfuric acid (H_2SO_4, 98%) were purchased from VWR (Radnor, PA). Pillar[5]arene (white crystal powders) was synthesized by Jun-Li Hou's group in the Department of Chemistry at Fudan University, China. Details of the synthesis method can be found in Refs. [30,31]. Deionized water was used throughout this study.

Preparation of Nafion-recast membrane and pillar[5]arene/Nafion sulfonated composite membranes

The 10 wt.% pillar[5]arene/Nafion composite membranes were prepared by a solvent casting technique. The low-boiling-point alcohols in the Nafion solution were first removed by distillation at 50 °C and reduced pressure. DMF was then added until a 5 wt.% Nafion-DMF solution was obtained. Different amounts of Pillar[5]arene powder were then added to the Nafion-DMF solution and the solution was mixed for 30 min in an ultrasound bath. The resulting white solution was let to stand for 20 min and was then poured into a clean glass dish and dried for 24 h at 60 °C. The procedure was repeated with 0 wt.%, 3 wt.%, 5 wt.%, 7 wt.% and 10 wt.% of pillar[5]arene in Nafion to investigate the effects of that parameter. 10% pillar[5]arene was the upper limit in this study as when exceeding 10 wt.%, pillare[5]arene molecules cannot be evenly dispersed in the membrane by ultrasonication.

Sulfonated membranes were prepared by immersing in concentrated sulfuric acid (98%) solution for 1 h, 2 h, 2.5 h or