Poly(ethylene glycol) plasticized poly(vinyl alcohol)/poly(acrylamide-co-diallyldimethylammonium chloride) as alkaline anion-exchange membrane for potential fuel cell applications

Tianchi Zhou [a,b], Jing Zhang [a], Jingfu Jingfu [a,1], Gaopeng Jiang [a], Jian Zhang [c,**], Jinli Qiao [a,b,*]

[a] College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, PR China
[b] Yancheng Institute of Technology, 9 Ying'bing Road, Yancheng 224003, China
[c] College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Zone 6 Chaohui, Hangzhou, Zhejiang 310014, PR China

ARTICLE INFO

ABSTRACT

This study reports a novel alkaline anion-exchange membrane from poly(vinyl alcohol)/poly(acrylamide-co-diallyldimethylammonium chloride) by incorporating poly(ethylene glycol) as a plasticizer and modified by chemical cross-linking method (PVA/PAADDA/PEG). The membranes are characterized by infrared spectra (FT-IR), scanning electron microscope (SEM) and thermogravimetric analysis (TG). The conductivity, water uptake, ion exchange capacity (IEC), and chemical stability of membranes are determined to evaluate their applicability in alkaline direct methanol alkaline fuel cells (DMAFC). The anionic conductivity (OH$^-$-conductivity) is found to be greatly dependent on the content of PAADDA and PEG in the PVA matrix. The conductivities of up to 1.53×10^{-3} S cm^{-1} at 25 °C and 8.5×10^{-3} S cm^{-1} at 80 °C are achieved for PVA/PAADDA/PEG in a mass ratio of 1:0.25:0.25. The membranes also show good alkali and oxidative stability. An open-circuit voltage of 0.85 V and an initial power density of 15.4 mW cm^{-2} of ADMFC with the membrane (=1:0.25:0.25 by mass), 2 M methanol, 2 M KOH, and humidified oxygen are achieved at room temperature.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Anion-exchange membrane fuel cells (AEMFCs) research have recently made a noticeable comeback from proton-exchange membrane fuel cells (PEMFCs) dominant era, primarily due to the distinct advantages when operating in an alkaline environment such as cathode reaction kinetics and resistance polarization [1,2]. The inherently faster and much easier kinetics of the oxygen reduction reaction (ORR) in alkaline environment than in acid medium leads to the use of non-noble and non-precious metal electrocatalysts such as silver (Ag) and nickel (Ni), making AEMFCs a potentially low cost technology compared to PEMFCs, which employ platinum (Pt) catalysts [3,4]. Moreover, due to the less corrosive nature of an alkaline medium, higher durability is expected for AEMFCs. In addition, the water management is also improved due to the electro-osmotic drag transporting water away from the cathode, thus the so-called alcohol 'crossover' problem is highly reduced because of the opposite movement of OH$^-$ anions to the movement of H$^+$ ions in acidic membrane [5,6].

Nowadays, some new alkaline anion-exchange membranes (AAEMs) have been evaluated for use in AEMFCs, where the membranes are constructed mainly from copolymers whose quaternized comonomers feature an anion as the charge carrier, such as polysulfone (PSO) [7,8], fluorinated polymers including poly(ethylene-co-tetrafluoroethylene) (PETFE) and poly(vinylidene fluoride) (PVDF) [6,9], copolymer of 4-vinylpyridin and styrene [10], poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) [11] and polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene [12]. However, these polymers are generally of high price and their quaternization is complex process. In addition, the stability of the quaternary ammonia groups has to be improved which are likely to decompose in concentrated alkali solutions, especially at elevated temperatures (above 60 °C) via by either an E$_2$ Hofmann elimination or by an SN$_2$ substitution reaction [13–15]. But as of now, very few AAEMs reported could fulfill all the aforementioned requirements and the development of AAEMs with desirable properties is still a key issue [16,17]. In our recent work, we have developed the new

* Corresponding author at: College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, PR China. Tel.: +86 21 67792379; fax: +86 21 67792159.
** Corresponding author at: College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Zone 6 Chaohui, Hangzhou, Zhejiang 310014, PR China.
E-mail addresses: zhanggom@zjut.edu.cn (J. Zhang), qiaojinli@hotmail.com, qiaojl@dhu.edu.cn (J. Qiao).
[1] Present address: Volvo Cars Technology (Shanghai) Co., Ltd., China.

families of cost-effective, readily prepared OH⁻ conducting membranes based on chemically cross-linked poly(vinyl alcohol) (PVA) polymer networks by incorporating the water soluble quaternized copolymer [poly(acrylamide-co-diallyldimethylammonium chloride), PAADDA] as anion charge carriers. Incorporation of the above concepts promoted the membrane excellent hydrolytic (dimensional stability) and the alkaline stability with reasonable OH⁻ conductivity [18,19].

As a continuing effort in improving the membrane performances, in this study, PVA/PAADDA based semi-interpenetrating polymer network was proposed by incorporating PEG as a plasticizer variant. In particular, the presence of hydrophilic and hydrophobic moieties in PEG gives it unique ability to be soluble in both aqueous and organic solvents, and to be blended with other polymers such as PVA [20–22]. By PEG addition, flexibility and the mechanical properties of alkaline membrane could be improved because of its special plasticizing effect which can loosen the membrane's network structure. Furthermore, the hydroxyl portion of PEG could lead to the formation of the strong hydrogen-bonding together with PVA and PAADDA, thus providing the membrane high thermal stability. PAADDA was synthesized by acrylamide (AA) and dimethyldiallyl-ammonium chloride (DMDAAC) through free radical copolymerization [23] and, was chosen as the cationic polyelectrolyte for its dual function both as an alcohol barrier and an OH⁻ conductor [18,19]. PVA was chosen as the polymer matrix for its easy preparation, biodegradability [24], perfect methanol tolerance effect and chemical stability with excellent film forming property [25,26]. To avoid the poor stability in aqueous solutions and reducing membrane swelling and improving mechanical stability, the membrane was modified by cross-linking the PVA main chain with acetal ring formation using aldehyde cross linker. PVA/PAADDA/PEG semi-IPNs was thus formed through the reaction of the hydroxyl groups (—OH) of PVA with the aldehyde groups (—CHO) of glutaraldehyde cross-linker in the presence of a strong acid, as has been proposed by many researchers [27–30]. The membrane characteristics including OH⁻ conductivity, ion-exchange capacity, water uptake, membrane morphology, thermal behavior, alkali and oxidative stabilities of the PVA/PAADDA/PEG membrane were addressed to evaluate their applicability in direct methanol alkaline fuel cells.

2. Experimental

2.1. Synthesis of PAADDA

To a 250 ml, round-bottomed flask equipped with a mechanical stirrer, a thermometer, nitrogen inlet and out tubes, 42.06 g DMDAAC and 7.93 g AA were mixed in a 7:3 molar ratio, then 116.69 g deionized (D.I.) water was added to form a 30% (w/w) monomer solution. The polymerization solution was warmed to 60 °C, and 1% amount (w/w, which was equivalent to total monomers amount) of initiator ((NH₄)₂ S₂O₈/NaHSO₃), was added with stirring during a period of 2–3 h to initiate the polymerization, and then the solution was continuously polymerized at 60 °C for 3–4 h (the total polymerization time at 60 °C was controlled to 6 h). Finally, the polymerization solution was further heated to 80 °C for 1 h. The copolymer was precipitated with ethanol filtered and washed for several times, then dried in a vacuum to constant weight at 60 °C. The reaction process is described as Fig. 1.

2.2. Membrane preparation

A stock 10%PVA (99% hydrolyzed, average molecular weight M_W = 86,000–89,000, Aldrich) aqueous solution was prepared by dissolving PVA in D.I. water at 70 °C. Appropriate amounts of
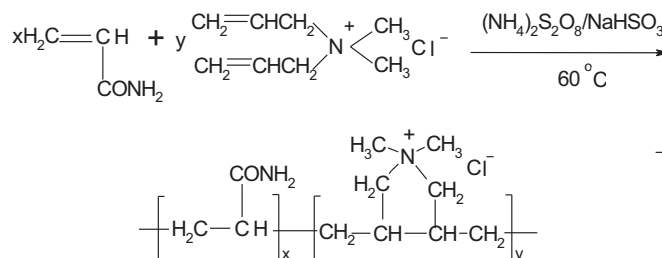

Fig. 1. The synthesis routine of poly(acrylamide-co-diallyldimethylammonium chloride).

PAADDA (home-made) and PEG600 (Aldrich) aqueous solution was separately prepared, then above solutions (PVA, PAADDA and PEG600) were mixed in different proportions under stirring for at least 4 h to make sure that the new solution was completely homogeneous, followed by addition of GA (25 wt% glutaraldehyde solution in water, SCRC) to react at 30 °C for 20 min. Cross-linking proceeded between the —OH of PVA and the —CHO of GA in the polymer due to an acid-catalyzed reaction upon addition of a small amount of HCl to the solution. The resulting solution was poured into plastic petri dishes, and the water was evaporated under ambient conditions. When visually dry, the chemically cross-linked membranes were peeled from the plastic substrate with the thickness of about 70–90 μm. Before the use, the samples of square pieces of membranes (ca. 1.5 cm × 2 cm) were soaked in 1.0 M KOH solution overnight to convert it from Cl⁻ form into OH⁻ form, then washed with D.I. water until pH neutral and finally stored in D.I. water for measurements. It should be mentioned that considering the difficulty in characterizing membranes definitively in OH⁻ form, for example, by excluding CO₂ rigorously as in a glove box, the anion conductivities reported here are all based on the membranes in bicarbonate form (i.e., exposure to air) without further correction. The structure of chemical modified PVA/PAADDA/PEG network system is illustrated in Fig. 2.

2.3. Membrane characterizations

The FT-IR spectra of PVA-PAADDA membranes were recorded using Shimadzu-4200 FT-IR spectrometer with a wavenumber resolution of 4 cm⁻¹ in the range 500–4000 cm⁻¹. Samples in the form of thin films were sandwiched between two KBr plates and placed in the cell to be measured. Air was employed as a background reference.

The composite morphology was evaluated using an FEI Sirion 200 field-emission scanning electron microscope (SEM) operating at 5 kV. Prior to observations, the membrane samples were
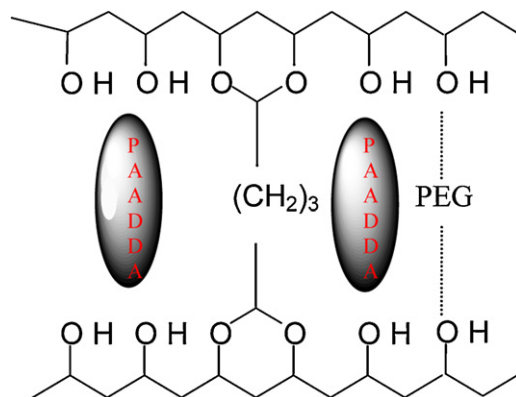

Fig. 2. Inner structure of chemically cross-linked PVA/PAADDA/PEG alkaline membrane.