Solid State Ionics 278 (2015) 144–151

Contents lists available at ScienceDirect

Solid State Ionics

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

Synthesis and characterization of novel anion exchange membranes containing bi-imidazolium-based ionic liquid for alkaline fuel cells

Ji-Lin Wang *, Lu-Lu Wang, Rui-jiang Feng, Yang Zhang

College of Chemistry, Chemical Engineering and Environmental Engineering, Liaoning Shi Hua University, Fushun 113001, PR China

ARTICLE INFO

Article history:
Received 16 December 2014
Received in revised form 11 April 2015
Accepted 10 June 2015
Available online 23 June 2015

Keywords:
Anion exchange membrane
Bi-imidazolium
Ionic liquid
Fuel cell
Chemical stability

ABSTRACT

Novel anion-exchange membranes (AEMs) were prepared via in situ assembly of N-dodecyl-imidazole and 1,4-dibromobutane to construct the bi-imidazolium functionalized cationic liquid monomer, butanediyl-1,4-bis(N-dodecylimidazole bromide) into the isopropanol dispersions of quaternized chitosan, and followed by anion exchange with OH^-. The morphology and characteristic properties of the resultant membranes, such as ion exchange capacity (IEC), anionic conductivity, and chemical stability were investigated. The membrane containing 15% mass fraction of butanediyl-1, 4-bis(N-dodecylimidazole bromide) shows that the anionic conductivity at 80 °C up to 41.9 mS cm^{-1} and keep better long-term stability for 300 h in 1 mol dm^{-3} KOH methanol solution than in 1 mol dm^{-3} KOH aqueous solution. The introduction of hydrophobic alkyl side chain of the imidazole rings could drive the N^+ ionic clusters to aggregate and promoting OH^- mobility in AEMs. The results of this study suggest that the AEMs based on bi-imidazolium cations with long alkyl side chain have good perspectives for alkaline fuel cell application.

1. Introduction

The modern technology of electrochemical energy conversion, such as fuel cells, prefers the use of solid polymer electrolytes (SPEs) instead of traditional liquid electrolytes [1]. An SPE is a conductive membrane, which serves as a physical separator between the anode and the cathode with the function of transporting ions and blocking electrons. Nowadays, the most popular SPE for proton conduction is Nafion [2–4], which is a sulfonated fluoropolymer membrane developed by DuPont in the late 1960s [3]. The working circumstance of the fuel cell with Nafion membrane is acidic because Nafion is a strong acid ($pH \approx 0$). Therefore, it has to face several serious problems: (1) slow methanol oxidation kinetics [5–7], (2) poisoning of CO intermediate on the Pt catalyst surface [8], (3) high methanol permeability through the polymer membrane [9–12], and (4) high costs of the Nafion membrane and noble metal catalysts, which have been one of the major barriers to the widespread application of Nafion-based fuel cells [13]. An alternative route to solve this problem is to develop alkaline exchange membranes (AEMs) [14], in which the charge carrier is OH^- rather than H^+, thus they can work under alkali circumstance, where the electrochemical reactions are more facile than they're in acidic medium, and non-noble metals can be used as catalyst [15,16], making the fuel cell more cost effective [17].

An ideal AEM should possess good hydroxide ion conductivity, high mechanical strength, low swelling ratio, and good chemical stability [18,19], which are fundamentally influenced by the cationic groups [20]. Presently, many cationic species have been developed, including tertiary sulfonium [20], quaternary ammonium [21–23], guanidinium [24], phosphonium [25], imidazolium [26–28], benzimidazolium [29,30], phosphatranium [31], and metal cations [32]. However, alkaline stability of the cationic species mentioned above under high pH environment and an elevated temperature continue to be a major barrier for alkaline fuel cell commercialization. It is especially true for AEMs based on quaternary ammonium types, which belong to the more common cationic species in AEMs. That was due to the fact that hydroxide ions could degrade the quaternary ammonium cation sites on the polymeric AEMs via direct nucleophilic substitution or Hofmann elimination reaction [33]. Compared with quaternary ammonium cations, however, quaternary phosphonium cations also exhibited poor alkaline stability [34], and the conductivity of guanidinium cation based AEMs decreased quickly after long-term durability test (380 h) in 0.5 M NaOH solution at elevated temperature (80 °C) [24]. It was worthwhile to mention that among the cationic species mentioned above, imidazolium cation based AEMs showed competitive alkaline stability and potential application in anion exchange membrane fuel cells (AEMFCs) [35]. The fact that the AEMs based on imidazolium cations exhibit good alkaline stability is probably due to the resonance effect of the conjugated imidazole rings, which weaken the interaction of imidazolium groups and hydroxide ions. These results mentioned above demonstrate a feasible approach for the synthesis and practical applications of alkaline imidazolium-type ionic liquids (ILs) functionalized AEMs, and should

---

* Corresponding author at: School of Petrochemical Engineering, Liaoning Shi Hua University, Fushun 113001, PR China. Tel.: +86 24 56860869.
E-mail address: wangjilin1978@163.com (J.-L. Wang).

http://dx.doi.org/10.1016/j.ssi.2015.06.010
0167-2738/

be expected to promote the widespread use of AEMFCs. Unfortunately, presently, the relevant literatures are mainly focused on taking advantage of the good alkaline stability of imidazole but ignore another important problem that is anionic conductivity. Even though, in order to enhance the OH^- conductivity, increasing the IEC seems to be an easier choice. But in fact it is not a good choice because high IEC is always accompanied with excessive water uptake [36,37], a severe side effect that causes the AEMs to significantly swell or even dissolve at elevated temperatures [38]. Hence a smarter and more practical strategy to boost the OH^- conductivity of AEMs is to improve the OH^- mobility while keeping the IEC at a moderate level. Such a promotion in the OH^- conducting efficiency can be realized by introducing additional hydrophobic structures, it is possible to drive the ionic clusters (hydrated ions and surrounding water molecules) to be aggregated, so as to generate bigger ionic clusters and to facilitate the formation of interconnected, broad ionic channels. Such a suitable ion-aggregating structure is expected to benefit the OH^- conduction [39].

In this work, bi-imidazolium functionalized AEMs for alkaline fuel cells were synthesized. An ionic liquid monomer, butanediyl-1, 4-bis (N-dodecylimidazole bromide) has been assembled in situ with the proper QCS casting solution. The resulting membranes were converted to OH^- form by changing the anions in the ionic liquid moiety of the membrane with hydroxide anions, as shown in Scheme 1.

Properties of the composite membranes synthesized in this paper, such as ion exchange capacity (IEC), hydroxide conductivity, morphology and chemical stability in high pH solution were investigated. We hope that the long hydrophobic side chain (dodecyl) into the imidazole structure will drive the ionic clusters (N^+) to be aggregated and partially the N^+ active site was dispersed into the imidazole rings, which could weaken the interaction of imidazole groups and hydroxide ions to prolong the stabilization time of AEMs in alkaline solution. As for the Gemini structure of ionic liquid, based on imidazole was used to build the structure, which with two long hydrophobic alkyl chains and two imidazole rings, that structure will make the ionic liquid doped in membrane was not easy run off with the increasing of volume for membrane under the swelling of membrane adsorb water.

2. Experimental

2.1. Materials

(2, 3-epoxypropyl) trimethylammonium chloride (EPTMAC, purity ≥ 95%) was purchased from Shandong GuoFeng Fine Chemistry Factory. Chitosan and aqueous glutaraldehyde (GA, 50 wt.%) were obtained from Sinopharm Chemical Reagent Co., Ltd. The deacetylation degree of the chitosan was 95%, which was determined according to Ref. [40]. N-dodecyl-imidazole and 1,4-dibromobutane were provided by Sigma-Aldrich. All the reagents used were analytical grade. The QCS in chloride form was synthesized by quaternization of chitosan in isopropanol with EPTMAC at 85 °C for 10 h and it was afterwards isolated and purified according to the reference described elsewhere [41]. Quaternization degree of the QCS was $35.02(\pm 2.7)$ %, which was determined by titration with a standard $AgNO_3$ solution [42]. The same quaternization degree of QCS was hereafter used for all the membrane preparations. The de-ionized water employed in all experiments was prepared with a Millipore Milli-Q system.

2.2. Methods

2.2.1. Membrane preparation

In a 100 mL round-bottom flasks equipped with a magnetic stirrer and a condenser, 1.0 g chloride form QCS ($DQ = 35.02(\pm 2.7)$ %) was dispersed in 25 mL isopropanol solutions in a nitrogen atmosphere at room temperature. Then a required amount of N-dodecyl-imidazole and 1,4-dibromobutane (the molar ratio was 2:1) and the mixture were refluxed for 24 h at 80 °C. After rotatory evaporation to get rid of the solvent, the product was vacuum dried at 80 °C. Then a given amount of the product synthesized above was dissolved in 20 mL 2% (v/v) acetic acid aqueous solution in N_2 atmosphere at room temperature. A given amount of crosslinker GA (2%, v/v) aqueous solution was then added dropwise to the mixture at a feeding rate of 0.5 mL min^{-1} to crosslink the QCS. The mixture was stirred at room temperature for 30 min and it was then sonicated for another 30 min. The resultant mixture was poured onto a glass plate and the solvent was then evaporated in an oven at 40 °C until a constant weight was reached. Alkaline doping of the membranes was performed by immersing them in 1.0 mol L^{-1} KOH solution at room temperature for 24 h. The membranes were then washed thoroughly with de-ionized water and dried at 50 °C until a constant weight was reached to obtain the hydroxide form membranes. The structure of the composite membrane synthesized in this paper was illustrated in Scheme 1. The obtained membranes were termed as QCS-$(\text{bi-imidazolium})_x$, where x denoted the half of doping percent of N-dodecyl-imidazole in the composite membrane. It was worthwhile to mention that a GA content of 2% (wt.%) was chosen to prepare all the membranes.

2.2.2. Instruments and techniques

The FT-IR spectra of the membrane samples were recorded on a Perkin-Elmer Spectrum One (B) spectrometer (Perkin-Elmer, America) and all the samples were prepared as KBr pellets. NMR spectra of the ionic liquid was recorded on a ^{1}H NMR spectrometer (AV ANCE III 400, Bruker Company, Germany) in $CDCl_3$ and was calibrated with tetramethylsilane (TMS) as the internal standard. Thermo gravimetric analysis (TGA) was performed on a TGA 290C analyzer (Netzsch Company, Germany) at a heating rate of 10 °C min^{-1} under N_2 atmosphere. The mechanical strength of the dry membranes was determined with an instrument CMT6502 (SANS Company, China). Dumbbell-shaped membrane samples of 25 mm × 4 mm were prepared and the measurements were carried out by setting a constant separating speed of 5.00 mm min^{-1} under ambient atmosphere. Tensile stress at break E was obtained by Eq. (1) [43].

$$E = \frac{F}{A_0} \tag{1}$$

where F is the applied force at break, A_0 is the initial cross-section area of the sample which is equal to $4 \times L$ mm^2, and L is the thickness of the membrane.

2.2.3. Water/methanol (MeOH) uptake and swelling of the membranes

Membrane samples were soaked in de-ionized water/MeOH for 24 h at room temperature to monitor the variations in weight and dimensions of the wet membranes. The weight and the dimensions of the wet membranes (P_{wet}) were measured rapidly after wiping the excessive surface water/MeOH with a tissue paper, and those of the dry membranes (P_{dry}) were obtained by drying the samples at 50 °C in a vacuum oven until a constant weight was reached. The water/MeOH uptake and swelling of the membranes was calculated by Eq. (2):

$$\text{water/MeOH uptake (swelling) } (\%) = \frac{P_{wet} - P_{dry}}{P_{dry}} \times 100\% \tag{2}$$

2.2.4. Ion exchange capacity

The anion exchange membrane in hydroxide form was washed thoroughly with de-ionized water and then dried in a vacuum oven at 60 °C to obtain a constant dry weight (w_{OH} in gram). It was afterwards immersed in a 0.1 mol L^{-1} HCl standard solution at ambient temperature for 48 h under continuously stirring to neutralize the hydroxide ions containing in the membrane. The mole number (equivalent) of the neutralized hydroxide ions (n) was determined by back titration of the remanent acid with a 0.1 mol L^{-1} KOH standard solution. Ion exchange