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Synthesis and characterization of novel cross-linked quaternized poly(vinyl alcohol) membranes based on morpholine for anion exchange membranes

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ABSTRACT

A series of novel cross-linked and quaternized poly(vinyl alcohol) (QPVA) anion exchange membranes were prepared for application in alkaline anion exchange membrane fuel cells. These membranes, with excellent electrical and thermal properties, were prepared via a relatively simple procedure, by using nontoxic and mild 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC), made in the laboratory, as a quaternization reagent to graft aliphatic morpholine ring units that acted as the fixed charged groups, followed by reacting the remaining unreacted hydroxyl groups with different amounts of bisphenol-A epoxy resin (DGEBA) and alkalization. The reaction products were characterized by nuclear magnetic resonance (^{1}HNMR), Fourier transform infrared (FTIR), elemental analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and electrochemical methods. The membranes exhibited good thermal stability below 210 °C. The ionic conductivity can be as high as 5.21×10^{-2} S·cm^{-1} at 60 °C in water.

1. Introduction

Currently, ion exchange membranes are being used in many fields [1–5]. One of the most important applications is their usage in fuel cells, because of the high demand for energy globally. Among the various fuel cell technologies [6,7], a new kind of fuel cell using the alkaline anion exchange membrane has became a promising candidate, which has attracted extensive interest owing to its numerous advantages, such as the intrinsic restraint of methanol crossover [8,9], the inherently faster kinetics of the oxygen reduction reaction [10], the expanded selection window of metal electrocatalysts including conventional noble metal Pt with the addition of non-noble and low-cost metals such as Ag or Ni (thus contributing directly to lower costs [11–13]), and ease of water management [14]. In alkaline anion exchange membrane fuel cells (AAEMFCs), the alkaline anion exchange membrane (AAEM) is the core component, which is used to transport the OH^- ions produced at the cathode to the anode. Unlike the well-established proton exchange membranes, most of the conventional and commercial AAEMs are used in other applications, mainly for electrodialysis. Currently, there is growing interest in developing AAEM research for fuel cells.

AAEMs can be prepared in several ways: (1) polymer blended with alkali, (2) pyridinium base type polymer, (3) radiation-grafting, quaternization and alkalization of polymer matrix, and (4) chloromethylation, quaternization and alkalization of polymer [15]. Of these, the fourth way of preparing AAEMs is more conventional and advantageous. Chloromethylation and quaternization are two key reactions that determine the ultimate ionic conductivity of the membrane. However, the chloromethylation reaction is not easy to handle; the reaction efficiency, with commonly used chloromethyl methyl ether and bis-chloromethyl ether, is high, but the reagent is highly toxic and carcinogenic thus its use is restricted since the 1970s [16,17]. In addition, the quaternization may be incomplete, leading to low ionic conductivity. Till now, some promising AAEMs have been prepared successfully. Such as, with chloromethyl methyl ether as the chlromethylating reagent and concentrated sulfuric acid as the solvent, chloromethylated poly(phthalazinone ether ketone) could be prepared from poly(phthalazinone ether ketone), and then from it to obtain quaternized poly(phthalazinone ether ketone) anion exchange membranes [18]. Using an appropriate quaternization approach could significantly improve the ionic conductivity and optimize the conductivity of the membrane even though the functional chloromethyl groups attached to the polymer are limited [13]. As about the high temperature AAEMs, the excellent temperature durable quaternary ammonium polyetherketone hydroxide membranes have been developed for alkaline fuel cells operating at elevated temperatures via chloromethylation, quaternization and alkalinization method [19]. With polysulfone-based material, alkaline anion exchange membranes of high ionic conductivities have been obtained too by adding a chloromethyl pendant group to the polysulfone at different reaction times and temperatures followed by reacting the chloromethyl group with different amines to form

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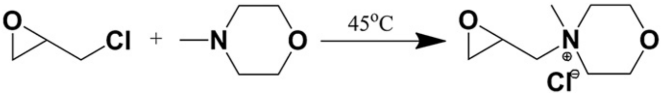

Fig. 1. Synthetic reaction route for the preparation of MGMC.

different quaternary ammonium pendant groups which acted as the counterion for hydroxide anion [20]. Furthermore, although encouraging progress has been made, improved ionic conductivity and thermal stability are still two major issues for AAEM.

For this study, researchers chose poly(vinyl alcohol) as a starter material. Its outstanding features are: low cost, good film-forming ability, chemical stability and availability of cross-linking sites that can be used to obtain cross-linked membranes by means of chemical reactions, which could suppress water swelling and improve thermal stability. To avoid the use of toxic materials and simplify the AAEM preparation procedure, a new way to prepare novel anion exchange membranes based on PVA is presented. Through quaternization using self-made 4-methyl-4-glycidylmorpholin-4-ium chloride as a functional reagent, aliphatic morpholine ring units, which acted as the fixed charged groups, were grafted directly onto the backbone of PVA matrix by a one-step procedure. The cross-linking reaction was innovatively conducted with bisphenol-A epoxy resin. The AAEMs thus developed were evaluated for AAEMFC applications.

2. Experimental

2.1. Materials

PVA, degree of polymerization: 1750, and degree of hydrolysis: 98–99%, was supplied by Sinopharm Chemical Reagent Co., Ltd. of China. N-methylmorpholine (MML) and epichlorohydrin (ECH) were purchased from Aladdin Reagent Co. Diglycidyl ether of bisphenol A, as a cross-linking agent (DGEBA, epoxy value 0.41–0.47) was purchased from Yueyang Petrochemical Co. of China. Sodium hydride (70 wt.% powder in mineral oil) was purchased from Tianjin Guangfu Fine Chemical Research Institute of China. Dimethyl sulfoxide (DMSO, Kermel Chemical Co.), acetonitrile (Sinopharm Chemical Reagent Co. Ltd. of China) and anhydrous ether (Shanghai Malu Chemical Co. of China), AR grade, were dried over 4Å molecular sieves prior to use. PVA was dried at 80 °C in a vacuum for 24 h. Other reagents were used as received.

2.2. Preparation of the AAEM

2.2.1. Synthesis of 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC)

The procedure for synthesizing 4-methyl-4-glycidylmorpholin-4-ium chloride has been fully described in Xia et al. [21]. The reaction route is shown in Fig. 1, and the product was identified as MGMC. To a dried 250 ml three-necked flask MML (0.36 mol) and ECH (0.432 mol) were dissolved in 10 ml of acetonitrile under nitrogen flow to form a homogeneous solution. The molar ratio of ECH to MML was 1.2:1. After stirring for half an hour at room temperature, the mixture was heated at 45 °C for 55 h. At last the resulting white solid was filtered, washed thoroughly with anhydrous ether, and dried at 55 °C under vacuum.

2.2.2. Synthesis of quaternized poly(vinyl alcohol) (QPVA)

A series of QPVA were synthesized by grafting the MGMC to the OH-PVA at the feed ratios by mole of MGMC/OH-PVA = 1:1, 1.1:1, 1.2:1, 1.3:1, 1.4:1 respectively, and the purified product were designated as QPVA-100%, QPVA-110%, QPVA-120%, QPVA-130%, and QPVA-140%. A typical procedure is described as follows using the QPVA-100% as an example.

The quaternization of PVA was carried out by the following method: to a completely dried 250 ml of three-necked flask, which was equipped with a magnetic stir bar, a reflux condenser and a nitrogen inlet/outlet, 1.76 g (40 mmol) PVA and 160 ml dry DMSO were charged under N_2 flow. The solution was heated at 80 °C until completely dissolved. After cooling to room temperature, 1.65 g (48 mmol) of sodium hydride was added over 1 h followed by addition of 7.75 g MGMC (40 mmol), and the reaction was performed at 40 °C for 15 h under stirring. Ultimately it was terminated with water, and the polymer solution was poured into a mixture of ice and water and precipitated in anhydrous ethanol successively to remove unreacted materials and solvent. The fiber-like precipitate was collected by filtration, thoroughly rinsed with anhydrous ethanol until at neutral pH, then dried at 60 °C for at least 24 h in vacuum to yield an off-yellow solid QPVA. The chemical reaction equation for QPVA synthesis is shown in Fig. 2.

2.2.3. Synthesis of cross-linked and quaternized poly(vinyl alcohol) membranes

The cross-linked QPVA/DGEBA membranes were obtained by casting. To prepare 0.11 g/ml solution, the cross-linker DGEBA was dissolved in DMSO. The QPVA solution was prepared by dissolving 0.4 g of the purified QPVA in 25 ml DMSO at 60 °C under continuous stirring, until a homogeneous solution was obtained. To this solution, different amounts of DGEBA solution (as shown in Table 1) were mixed with QPVA under further stirring at room temperature for 12 h and statically deaerated. The resulting homogeneous mixtures were cast on Teflon plates and dried in an air oven at 50 °C for 4 h and 80 °C for 15 h. Then the dried membranes were peeled off the Teflon plates, further dried at 120 °C for 10 h to remove traces of solvent and the DGEBA laterally cross-linked with the QPVA. The chemical reaction equation for cross-linked and quaternized poly(vinyl alcohol) (CLQPVA) synthesis is shown in Fig. 3.

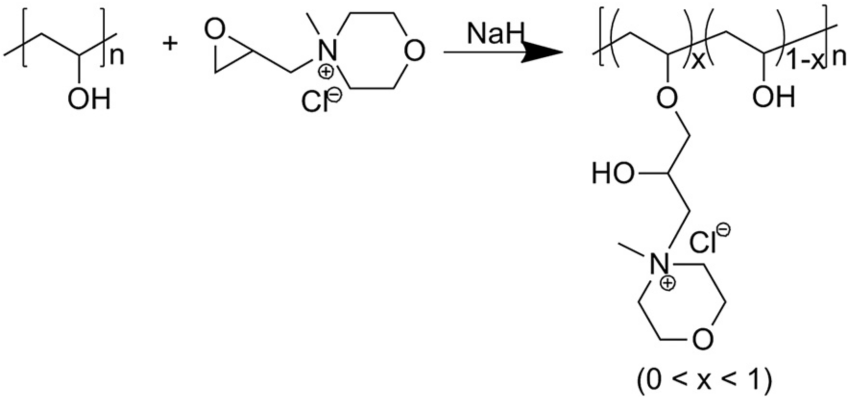

Fig. 2. Synthetic reaction route for the preparation of QPVA.

2.2.4. Alkalization

The CLQPVA membranes were immersed in 2 M KOH solution at room temperature for 48 h to alkalize the membranes, and convert