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An approach of balancing the ionic conductivity and mechanical properties of PVA based nanocomposite membrane for DMFC by various crosslinking agents with ionic liquid

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ABSTRACT

Nano composite membranes of polyvinyl alcohol (PVA) have been synthesized to investigate their applicability as a proton conducting membrane for direct methanol fuel cell. These membranes consist of PVA, sulfonated organic modified montmorillonite nanoclay (SMMt) and 1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide (BMIM TFSI) with different crosslinking agents such as sulfosuccinic acid (SSA), 4-sulfophthalic acid (SPA) and dodecanedioic acid (DDA). FTIR spectroscopy, scanning electron microscope (SEM) and thermogravimetric analysis (TGA) have been used to investigate the structure property relationship. The water uptake behavior of the membranes shows variation with the dosage of SMMt. The good dispersion of the nanoclay in the PVA matrix is detected by using ionic liquid. The improved tensile strength of the membrane comprising 3 wt% of SMMt is achieved. The proton conductivities of the membranes are dependant on the compositions and are in the range of 0.003–0.008 Scm^{-1} at room temperature and 100% relative humidity. A maximum proton conductivity of 0.017 Scm^{-1} has been obtained for the membrane comprising of 3 wt% SMMt at 80 °C. Furthermore, the peak power density of the direct methanol fuel cell fabricated with 3 wt% SMMt based membrane in 2 M methanol is 7.02 mW cm^{-2} at 70 °C.

Introduction

Today, fuel cells offer the prospect of a greener future to advance global energy resources, with environmental and economic benefits [1–4]. The success and progress of fuel cells depend in part on membrane material advancement. Many different routes are currently being employed to develop more economical polymer membranes [5,6]. Considerable effort has been dedicated to finding membrane less expensive than Nafion® [7,8]. The challenge is to produce a cheaper material that can satisfy the requirements for use in a direct methanol

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fuel cell (DMFC). Some sacrifice in material lifetime and mechanical properties may be acceptable, provided the cost factors are commercially realistic. In view of the importance of an inexpensive material, the prospect of poly(vinyl alcohol) (PVA) based membranes in a DMFC is attractive due to cost and environmental considerations, and, in addition, provides the ability to tune the proton conductivity and methanol crossover properties [9–12].

The hybrid composite membrane materials using PVA as a polymer matrix have been investigated for DMFCs application [13–17]. Maiti et al. prepared a polymer electrolyte membrane for DMFC application using sulfonic acid functionalized multiwalled carbon nanotubes (MWCNT) and fluorine functionalized montmorrilonite nanoclay (MMt) into the PVA matrix to increase the sulfonic acid content with hydrophobic fluorinated surface of the membrane [13]. Yang et al. [14] suggested a high performance poly (vinyl alcohol)/titanium oxide nanotubes/poly (styrene sulfonic acid) (PVA/nt-TiO_2/PSSA) proton-conducting composite membrane prepared by a solution casting method. Kim et al. [15] synthesized PVA/poly(-styrene sulfonic acid-co-maleic acid) (PSSA_MA)/clay hybrid membranes containing sulfonic acid and carboxylic acid groups which showed the lower methanol permeability. Tripathi et al. [16] prepared novel modified chitosan (NCBC)-silica-PVA nanocomposite membranes with varied NCBC-silica content and cross-linking density for achieving highly proton conductive and stable polyelectrolyte membranes. Cho et al. [17] introduced sulfonated mesoporous benzene-silicas into a poly (vinyl alcohol) (PVA) polymer matrix. The morphology and the pore size of mesoporous benzene-silica materials related with interface in the mixed membrane system are crucial factors to control the transport property of methanol and the proton conductivity.

In the past few decades, nanoclay (MMt) [18–20] was studied intensively as typical nano fillers to incorporate into polymer matrices. The dispersion of nanoclay in polymer can result in a reduction of moisture absorption, thermal stability, barrier properties and flammability as well as significant enhancements of modulus, strength and hence the overall performance of nanocomposite [21,22]. Furthermore, clay is inexpensive relative to traditional reinforcing materials and is environmentally benign. Despite these advantages of MMt, there is a lack of compatibility with polymers, consequently requires surface modification or pretreatment. MMt has been treated with mineral acids [23–25] to improve its compatibility as well as the conductivity of the polymer electrolyte membrane.

Because of its water solubility, PVA must be crosslinked to transform into rigid and mechanically strong insoluble polymer. Also, it does not contain any proton conduction moiety in its backbone. Therefore, it is chosen to use multifunctional molecules containing both sulfonic acid and carboxylic acid groups for serving as both proton conducting as well as crosslinking agent. Sulfosuccnic acid (SSA), sulfophthalic acid (SPA), poly(styrene sulfonic acid-co-maleic acid) (PSSA_MA) are generally employed both as a chemical crosslinking agent and as a donor of hydrophilic $-SO_3H$ for PVA based polymer electrolyte membrane [26,27,15]. Glutaraldehyde and poly(-acrylic acid) etc. are also utilized as non sulfonated crosslinking agents for PVA based membrane [28]. Both sulfosuccnic acid as a first crosslinking agent and glutaraldehyde as a second crosslinking agent have been used to form an inter crosslinked dense structure as well as a hydrophobic protective layer of PVA based membrane [29].

In this paper, we have presented a chemical crosslinking strategy to increase the sulfonic acid content and mechanical stability of PVA based membrane by incorporating three different types of crosslinking agents. Our main aim is to prepare the membrane with good mechanical properties. At the same time it should provide good ionic conductivies to be useful in direct methanol fuel cell. So there is a trade off between ionic conductivities and mechanical strength. Sulfosuccinic acid (SSA) crosslinker provides main source of proton conduction and major crosslinking agent to make the membrane effective in our present investigation. In addition, there are two other crooslinking agents. One is 4-sulfophthalic acid (SPA) and another one is dodecanedioic acid (DDA). SPA contains benzene ring moiety with sulfonic acid group that will not only supply ionic conductions but also contribute stability of the membrane. On the other hand, DDA with its long alkyl chain has the ability to deliver flexibility of the membrane.

With a view to achieving better dispersion of MMt particle into PVA polymer, ionic liquid (IL) has been mixed with PVA polymer. The earlier study shows that, when ILs are incorporated into polymer matrix, it plays multiple role like enhancing ionic conductivity of polymer electrolyte membrane, improving thermal, mechanical stability and unit cell performance of membrane [30,31].

In this work, a polymer electrolyte membrane consisting of PVA, crosslinkers, sulfonated MMt, and 1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide (BMIM TFSI) has been prepared by simple solution casting method.

Experimental

Materials

Polyvinyl alcohol (molecular weight of 31,000–50,000 g/mole, +99% hydrolysis), sulfosuccinic acid (SSA) (70 wt% in water), 4-sulfophthalic acid (SPA), dodecanedioic acid (DDA), 1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide (BMIM TFSI) and montmorillonite K10 (MMt) were purchased from Aldrich Company (Korea). All other chemicals used are of reagent grade.

Sulfonation of MMt

The sulfonation of montmorillonite (SMMt) was carried out according to the previous literature report [32]. First, the dispersion of MMt (1 g) in 200 ml ethanol was done by stirring at room temperature for 3 h. Then, (3-Aminopropyl)triethoxysilane (APS) (1.25 ml) was dropwise added into the mixture. The mixture was refluxed at 80 °C for 24 h. The SiMMt was filtered and washed with deionized water. After that, the mixture of SiMMt, WSC (1.28 g) and 4-sulfophthalic acid (2.75 ml) in distilled water was stirred at room temperature for 24 h. The product was filtered, washed with deionized water, and dried in vacuum at 60 °C for overnight [32] (Scheme 1).