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Preparation, characterization and properties of polymer electrolyte nanocomposite membranes containing silica nanoparticles modified via surface-initiated atom transfer radical polymerization

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ABSTRACT

Hydrophilic sulfonated monomers including styrene sulfonic acid sodium salt (SSA) and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) were grafted onto a brominated silica nanoparticle (BSN) as a macroinitiator via surface-initiated atom transfer radical polymerization (SI-ATRP) at pH of about 10 in the presence of CuBr/bipyridine as a catalyst/ligand system and water/methanol (3/1 v/v) mixture as a solvent at 25 °C for 24 h. To synthesize BSN macroinitiator, silica nanoparticle (SN) was first modified with 3-aminopropyltriethoxy silane and then brominated via reacting with 2-bromopropionyl bromide in the triethylamine/THF solution. Modified SNs were characterized by FTIR spectroscopy and thermogravimetric analysis (TGA). Grafting percentage of the monomers onto the SNs was calculated from TGA thermograms to be 30.6%, 47.6% (for the initial AMPS concentration of 0.8 and 2.0 M, respectively) for PAMPS and 28.1% (for the initial SSA concentration of 1.2 M) for PSSA. The PVA-based nanocomposite membranes containing various amounts of the pristine and modified SNs were prepared by solution casting and then cross-linked at 40 °C for 15 min in an acetone solution containing 0.5 M glutaraldehyde and 0.12 vol% HCl. SEM photograph and X-ray mapping of the cross-sectional view of the membranes showed that pristine and modified SNs have homogeneously dispersed at a nanometric scale in the PVA matrix. It was found that ion exchange capacity, water uptake (WU) and proton conductivity of the PVA-based membranes increase by increasing the SN, especially sulfonated polymer-modified SN, loading up to 10 wt%. It was found that proton conductivity of the nanocomposite membranes increases by increasing the grafting percentage of the sulfonated monomer onto SNs. Moreover, for similar grafting percentage of the monomers onto SNs, higher WU and proton conductivity was observed for a membrane containing SN modified with the PAMPS chains. Results showed that both hydrophilic nature and grafting efficiency of the sulfonated hydrophilic monomers can play an important role in the proton conductivity of the PVA-based membranes. Tensile modulus and tensile strength of the PVA-based membranes enhanced by adding modified

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SNs to the PVA matrix. Methanol uptake and permeability of the PVA-based polymer electrolyte membranes were also decreased by adding SNs to the PVA matrix.

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Introduction

Fuel cells (FCs) have received more attentions due to their high energy density and low emission of the pollutants [1–3]. Among the other fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have attracted considerable attentions due to their convenient operating temperature range of 60–120 °C and using air as an oxidant [4–6].

The basic function of the PEM is to avoid a direct contact between the fuel and oxidant and to provide a proton conductive medium. Therefore, PEM can be considered to be heart of the fuel cells. Perfluorinated sulfonated ionomer membrane, for example Nafion developed by DuPont, shows proton conductivity as high as about 100 mScm⁻¹ at a fully hydrate state with good mechanical property and thermal stability [1,2]. Hence, it has frequently been used as a PEM in the fuel cell applications. However, this membrane shows its excellent performance only at a temperature below 90 °C and high relative humidity (RH) with the hydrogen as a fuel [1–6]. Moreover, application of Nafion in the fuel cells such as electrical vehicles and portable devices is limited due to the high production cost and significant decrease of the proton conductivity at high temperatures. In addition, an essential drawback of the perfluorinated ionomer is its high methanol permeability of about 10⁻⁶ cm² s⁻¹, which drastically reduces its performance in the direct methanol fuel cells (DMFCs) [1–6].

Poly(vinyl alcohol) (PVA) has good chemical, thermal and mechanical stability. Because of the film forming ability, high hydrophilic behavior and low methanol permeability, PVA has been used as a PEM [10,11]. However, PVA-based membranes suffer from their solubility in water, where mechanical strength of the membrane reduces and the methanol cross-over increases. High density of the functional hydroxyl groups onto PVA allow its chemical cross-linking with aldehydes such as glutaraldehyde under acidic conditions [7–9]. Therefore, degree of the swelling can be controlled and limited via partially cross-linking [8].

In comparison with Nafion, proton conductivity of the PVA-based membranes is poor because the PVA itself does not have any negative charged ions such as carboxylic and sulfonic acid groups. In other words, there are no functional groups able to exchange protons in the PVA. However, PVA membranes can be used as a PEM in the fuel cell applications providing that the negative ions are held within their structure [6]. To increase proton conductivity, PVA-based membranes have been prepared by adding strong acids such as phosphomolybdic [10], phosphotungstic acids (PWA) [12], polystyrene sulfonic acid [13], poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) [14] and sulfonic acid

tethered poly(methyl vinyl ether-alt-maleic anhydride) copolymer [15].

Using hybrid polymer/inorganic (nano)composites is another approach to improve properties of the membranes. Adding inorganic (nano)particles such as alumina, titanium oxide, silica, zirconia or clay to a polymer matrix [16] and preparing membranes such as of PVA/SiO₂-PWA composite [17], PVA/sulfonated SBA-15 [18], PVA/montmorillonite [19], Nafion/[(ZrO₂)·(HfO₂)_{0.25}], Nafion/[(SiO₂)·(HfO₂)_{0.28}] [20,21] and Nafion/fluoroalkylated silica [22] has been lead to improved mechanical properties (via acting as a reinforcing agent) of the membrane and decreased methanol cross-over [16]. Proton conduction has been observed to be dependent on the size of the particles (nano or micro), their surface properties (acidic or basic) and their functionality [16,23,24]. It has not completely been understood that whether the inorganic (nano)particle actively participates in the proton conduction by enhancing ion dissociation or by providing desirable pathways for the ions along the polymer/inorganic interfaces [24,25]. Moreover, proton conduction in the presence of nanoparticles seems to be complex and additional effects such as interactions between the polymer and nanoparticle can also act at the same time [20–22].

Various controlled radical polymerization (CRP) methods have successfully been used to graft polymers onto the functionalized inorganic nanoparticles. These methods allow us to synthesize polymers with well controlled molecular weight and narrow molecular weight distribution. Among the other CRP methods, atom transfer radical polymerization (ATRP) is a promising CRP technique due to its tolerant to the functional groups and impurities and hence wide range of the monomers can be polymerized by this technique in organic or aqueous phases. Surface-initiated ATRP (SI-ATRP) is an ATRP technique to be used for chemical modification of the organic or inorganic surface. This promising polymerization has been applied to grow polymer brushes onto inorganic nanoparticles such as silica [26,27]. Various halogenated reagents are easily available which can be used to modify surface of the nanoparticles where halogenated nanoparticles can then be used as a (macro)initiator in the SI-ATRP reactions.

In the present study, a crosslinking agent containing aldehyde group, i.e. glutaraldehyde (GA), is used for PVA crosslinking which is expected to limit water swelling and to increase mechanical properties of the PVA membrane. Negative charge (sulfonic acid) is introduced into the PVA-based membranes by chemical modification of the silica nanoparticles (SNs) with polymers containing sulfonic acid groups, i.e. poly(styrene sulfonic acid) (PSSA) or poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS), via SI-ATRP. The objective of this study is to investigate effect of the sulfonated polymer-grafted SNs loading on the transport properties, such

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