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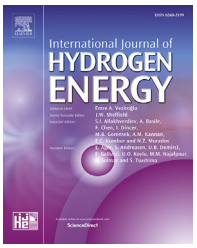

Proton conducting composite membranes from crosslinked poly(vinyl alcohol) and poly(styrene sulfonic acid)-functionalized silica nanoparticles

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ABSTRACT

Proton conducting membranes based on crosslinked poly(vinyl alcohol) (PVA) and poly (styrene sulfonic acid)-functionalized silica particles (PSSA-Si) were reported. Two-step crosslinking process involving sulfosuccinic acid (SSA) and glutaraldehyde as crosslinking agents was conducted to provide additional proton source and to enhance hydrolytic and mechanical stabilities. PSSA-Si was synthesized from vinyltrimethoxysilane via Stöber method, followed by radical polymerization of sodium 4-vinylbenzenesulfonate on the silica particle. The obtained PSSA-Si was characterized by thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). The effects of PSSA-Si loading (0, 2.5, 5, and 10%) and PSSA content in PSSA-Si (2, 5, 8, and 12%) on membrane properties including surface morphology, water vapor absorption, water uptake, ion exchange capacity, mechanical and oxidative stabilities, and proton conductivity were investigated and discussed. Proton conductivities of these composite membranes were found to increase with PSSA-Si loading and PSSA content. Promising proton conductivities of ~0.072 S/cm were obtained from PVA-8%PSSA-Si-10 and PVA-12%PSSA-Si-10 membranes, having PSSA-Si loading of 10%, and PSSA contents of 8%, and 12%, respectively. In addition, these membranes showed good hydrolytic and oxidative stabilities with high storage moduli.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been considered as promising alternative energy sources for automotive and portable electronic devices due to their high energy density, high conversion efficiency, quick start up and shut down time, and nonpolluting properties [1,2]. Polymer electrolyte membrane (PEM) is the key component in

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PEMFCs. One of the most successfully commercialized PEMs is Nafion®, perfluorinated sulfonic acid membrane, as it provides high proton conductivity and electrochemical stability. However, its widespread usage is limited by the high production cost and low mechanical strength under hydrated condition [3,4].

Poly (styrene sulfonic acid) (PSSA) is of great interest as candidate for PEM because of its relatively high proton conductivity and low cost. Nevertheless, its poor hydrolytic stability is the main drawback as proton transport mechanism, namely vehicular mechanism, relies on the presence of water [5]. Attempts to overcome hydrolytic instability issue of hydrophilic polymers for uses as PEMs include copolymerization [6–8], blending with other polymers such as poly (vinyl alcohol) (PVA) [9], poly (vinyl chloride) [10], and sulfonated poly (ether ether ketone) (sPEEK) [11], and functionalization onto inorganic materials [12–14]. Several functionalized inorganic materials have been reported. Functionalized graphene oxide nanosheets (FGOs) bearing polymer brushes provided almost 7-fold enhancement of proton conductivity to chitosan membrane [15]. Incorporation of PSSA-functionalized multi-walled carbon nanotubes (PSSA–MWCNTs) into sPEEK matrix demonstrated improvement in mechanical and thermal properties, and ionic conductivity [16]. Poly (sulfonic acid)-grafted silica nanoparticles (PSA-*g*-SN) were shown to enhance several properties including mechanical properties and proton conductivity of pristine PVA membrane [17]. The highest proton conductivity of 10.4 mS/cm was achieved at 5% nanoparticle loading. Recently, PSSA-functionalized silica nanoparticles have been incorporated into sulfonated poly (arylene ether sulfone) membrane [18]. The addition of these nanoparticles was found to enhance dimensional and mechanical stabilities along with proton conductivity of the membrane.

Among PEM polymer matrices, PVA has attracted much attention due to its film forming ability, good mechanical and chemical stabilities, high hydrophilic property, and low cost [19,20]. Proton conduction property of PVA has been introduced by chemical modification, and blending or compositing with proton conducting materials [21–23]. Crosslinked PVA-sulfosuccinic acid-glutaraldehyde membranes demonstrated encouraging proton conductivity of 5.3×10^{-3} S/cm at room temperature [24]. Moreover, the double-crosslinking process offered membranes with high water resistance.

In this work, composite membranes comprising crosslinked PVA and PSSA-functionalized silica particles (PSSA-Si) were prepared and evaluated as proton conducting membranes. Sulfosuccinic acid (SSA) was chosen to serve as a proton source and crosslinking agent. In addition, glutaraldehyde was also used as the second crosslinking agent to lower water uptake and to provide strength. The aim of the introduction of PSSA-Si to PVA network was to increase sulfonic acid content while maintaining hydrolytic and mechanical stabilities. The effects of PSSA-Si loading and PSSA amount in PSSA-Si on membrane properties including surface morphology, water vapor absorption, water uptake, ion exchange capacity, mechanical and oxidative stabilities, and proton conductivity were investigated.

Experimental

Materials

Vinyltrimethoxysilane (VTMS, 98%), 2,2′-azobis (2-methylpropionitrile) solution (AIBN, 0.2 M in toluene), sodium 4-vinylbenzenesulfonate (SSANa, ≥90%), poly (vinyl alcohol) (PVA, M_w 130,000, >99%), and sulfosuccinic acid solution (70% wt. in H_2O) were purchased from Sigma-Aldrich. Dimethylacetamide (DMAc, analytical grade) and ethanol (99.9%) were supplied from RCI Labscan. Ammonia solution (NH_4OH, 30%) and calcium chloride ($CaCl_2$, 92%) were obtained from Carlo Erba. Glutaraldehyde (25% aqueous solution) and sodium chloride (NaCl, 99.9%) were purchased from Loba Chemie, and Ajax Finechem, respectively. Dialysis tube with a molecular weight cutoff of 12,000 to 14,000 was purchased from Cellu Sep. All chemicals were used as received.

Synthesis of vinyl-functionalized silica particles (vinyl-Si)

In a slight modification of a literature preparation [18], silica particles having vinyl groups (vinyl-Si) were synthesized as follows: VTMS (5.0 mL) was added to 250 mL of deionized (DI) water. The mixture was stirred until a transparent solution was obtained. NH_4OH (0.25 mL) was added, and the solution was stirred at room temperature for 12 h. The resulting solid was obtained by centrifugation and later washed thoroughly with water and ethanol.

Synthesis of PSSA-functionalized silica particles (PSSA-Si)

PSSA-functionalized silica particles (PSSA-Si) were synthesized via conventional free radical polymerization of vinyl-Si and SSANa initiated with AIBN (14 mol% of SSANa) [18]. The polymerization was carried out in DMAc at 60 °C for 24 h. The weight ratio of SSANa to vinyl-Si was 5:1. After polymerization, the mixture was centrifuged. The obtained solid was washed several times with water and ethanol, and then soaked in 0.1 N HCl for 24 h to exchange proton from PSSANa to PSSA. The solid was washed thoroughly with water and dialyzed against water to remove residual HCl. The final product was centrifuged and later heated at 80 °C overnight. Four different PSSA-Si particles were obtained by varying SSANa amount and polymerization time, and were named according to the amount of PSSA in PSSA-Si particles as determined by TGA as x%PSSA-Si where x was the amount of PSSA in PSSA-Si particles.

Preparation of composite membranes

Aqueous 5 wt% PVA solution was prepared by dissolving PVA in DI water at 70 °C with constant stirring for 8 h. The solution was cooled to room temperature prior to addition of SSA at PVA:SSA molar ratio of 1:0.25. The solution was stirred at 70 °C for 6 h. The solution was poured into a petridish and later heated at 40 °C for 72 h to induce crosslinking reaction. The resulting membrane was peeled off and then soaked in 0.5 M glutaraldehyde solution for 1 h. The membrane was heated at

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