



Full Length Article

Effect of aminated nanocrystal cellulose on proton conductivity and dimensional stability of proton exchange membranes



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ARTICLE INFO

Keywords:

Nanocrystal cellulose

Poly(ether ketone)s

Nanocomposite

Proton exchange membranes

ABSTRACT

A functionalized nanocrystal cellulose bearing amino and sulfonic acid groups (Am-sNCC) is prepared through a two-step chemical modification of microcrystal cellulose powders, first by sulfonic acid and then by a 3-trimethoxysilyl propyl ethylenediamine. The structure of Am-sNCC is characterized by Fourier Transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). A sulfonated poly(ether ether ketone) (Ph-SPEEKK) is synthesized via the direct sulfonation of a high-molecular-weight phenylated polymeric precursor under a mild reaction condition. The nanocomposite membranes composed of the Ph-SPEEKK matrix and the Am-sNCC additive are successfully prepared by a solution casting method. The properties related to their application for proton exchange membranes are carefully evaluated. The nanocomposite membranes containing Am-sNCC, which served as a performance-enhancing component to form hydrogen bonding networks with the Ph-SPEEKK matrix, exhibited much improved dimensional stability, higher water absorption capacities, higher proton conductivity, better mechanical and fuel cell properties than the Ph-SPEEKK membrane.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are among the most promising energy conversion devices because of their rich sources, high efficiency, and convenient transportation [1–4]. Du Pont's Nafion, which is a perfluorinated sulfonic acid polymer, is a good proton conductor for hydrated membranes [4,5]. However, Nafion membranes suffer from inevitable water control and poor conductivity at elevated temperatures, insufficient resistance to methanol crossover, and high cost [6–8]. Therefore, several low-cost alternative materials with high performance have been developed as potential polymer exchange membranes (PEMs) for research. Among the various PEMs, aromatic poly(ether ketone)s (PEKs) have attracted significant attention because of the overall combination of their physical, chemical and mechanical properties and costs [9,10]. Liu et al. [11] investigated various sulfonated PAEKs that were obtained via a mild sulfonation method and

found Ph-SPEEKK and Me-SPEEKK that contain rigid phenyl-ketone-phenyl-ketone-phenyl moieties, which exhibited low methanol permeability values. The proton conductivity of Me-SPEEKK and Ph-SPEEKK was much higher than that of Nafion 117 at 100 °C. However, these sulfonated polyaromatics still have technical barriers that need to be solved to replace Nafion [12–14]. A remarkable problem that exists in non-Nafion membranes is their swollen and even solubility in water when the content of sulfonic acid group reaches a certain level, which hinders their application in fuel cells [15].

Continuous efforts have been exerted to improve the performance of polyaromatic-type PEMs. Cross-linking is an efficient method to enhance the mechanical strength and suppress the excess swellings of PEMs, especially under hot and humid circumstances. Na et al. [16] prepared a series of covalent-ionically cross-linked membranes through the reaction between sulfonated poly(arylene ether ketone) containing carboxylic acid groups (C-SPEEK) and poly(ether ether ketone)

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<https://doi.org/10.1016/j.apsusc.2018.10.063>

Received 7 September 2018; Received in revised form 4 October 2018; Accepted 8 October 2018

Available online 10 October 2018

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containing amino groups. Compared to pristine C-SPEEK, the cross-linked blend membranes showed higher mechanical strength, lower methanol permeability, and less water swelling because of the cross-linked structures. Unfortunately, the cross-linked membranes showed lower proton conductivity because of the interaction between the amino and sulfonic groups, which inevitably sacrificed the number of free sulfonic groups. One of the objectives for the cross-linked membranes is to construct systems that have improved proton conductivity and better dimensional stability. Lee et al. [17] reported several membranes cross-linked by the click reaction between the sulfonated poly(arylene ether sulfone) containing azidomethyl groups and the cross-linkers containing azido and sulfonic acid groups. The cross-linked membranes showed better physical and chemical stabilities and higher proton conductivity than the linear sulfonated poly(arylene ether sulfone) membrane. Kim et al. [18] prepared sulfonated PAEK membranes covalent-ionically cross-linked by 2,2'-benzidine disulfonic acid.

The membranes with low degree of sulfonation (DS) exhibited better toughness and flexibility than Nafion. However, the mechanical properties of the membranes with high DSs were undesirable. Several nano-sized materials, such as SiO₂ and carbon nanotube, have been introduced into a polymeric matrix to prepare nanocomposite materials with enhanced performance for proton exchange membranes [19,20].

Nanocrystal cellulose (NCC) has been gaining increasing interest because of its biodegradability, renewability, hydrophilicity, non-toxicity and excellent mechanical properties (modulus as high as 145 GPa and tensile strength as high as 7500 MPa) [21–24]. Three basic approaches to obtain NCC from cellulose materials, which can be mainly summarized as acid hydrolysis, mechanical treatments, and enzymatic hydrolysis, have been reported in the literature [25]. Significant effort has been focused on the production of nanocomposites with nanocellulose as reinforcement. Favier et al. [26] prepared first poly(styrene-co-butyl acrylate)-based nanocomposites with NCC as reinforcing nanofillers. Angles et al. [27] obtained nanocomposite materials using glycerol plasticized starch as the matrix and a colloidal suspension of cellulose whiskers as the reinforcing phase.

However, several obstacles to the successful use of NCC still exist, such as agglomeration in processing, lack of commercial availability, and low yield production [28–30]. Furthermore, using NCC in systems that are not polarized and water-based is difficult due to the strong hydrogen bond between hydroxyl groups and NCC's polarity [31]. NCC modification is an effective and simple approach to avoid these drawbacks. The presence of hydroxyl groups on the NCC surface allows further modification to improve its hydrophilicity [32]. Several studies on surface modifications have been reported in the literatures to improve the dispersion in the polymeric matrix. These modifications include (i) covalent grafting of single molecules (acetylation, silylation, succinic anhydride, and coupling with isocyanate derivate); (ii) covalent grafting of polymer chains; and (iii) molecule adsorption on NCC surfaces (surface active agent, for example) [33]. Lin et al. [34] prepared acetylated cellulose nanocrystals (ACN), which exhibited a decrease in surface polarity caused by the reactions with the hydroxyl groups on the surface of the cellulose nanocrystals and the acetic anhydride. The prepared ACN exhibited improved dispersion in tetrahydrofuran (THF), dichloromethane, toluene, DMF, and acetone.

NCC can be the “performance-enhancing” filler for sulfonated polymers because of its hydrophilic nature and the possibility of chemical modification. The hydroxyl groups on NCC could interact with the sulfonic groups on the sulfonated polymers through hydrogen bond, and thus, NCC can act as a cross-linker in the matrix to reinforce membrane performance. Furthermore, the hydroxyl groups can also interact with the water molecules through hydrogen bond, NCC therefore can also act as a water absorber. On the other hand, the amino groups could also act as a ‘bridge’ between sulfonic acid groups of SPEEK to promote proton transfer as illustrated by Jiang [35]. The proton conductivity of the membranes was thus improved significantly.

Therefore, the aminated NCC are supposed to be a good method for enhancing the properties of SPEEK membranes.

In this study, the aminated NCC bearing –OH, –NH₂ and –SO₃H groups (Am-sNCC) was prepared, and Ph-SPEEK was synthesized as a matrix. Furthermore, a series of covalent cross-linked membranes containing 0–8% of aminated NCC was successfully obtained by solution casting. The –NH₂ on the Am-sNCC and the –SO₃H groups on the Ph-SPEEK interacted more strongly than the sole hydrogen bond between the –OH and –SO₃H groups. The water uptake, thermal and dimensional stability, proton conductivity, mechanical and fuel cell properties of the composite membranes were investigated to evaluate their potential as PEMs for fuel cell applications.

2. Experimental

2.1. Materials

Cellulose microcrystalline powder (20 μm), 2,5-Dihydroxybiphenyl hydroquinone and N-[3-(trimethoxysilyl)propyl]ethylenediamine were supplied by Sigma-Aldrich. 1,4-Bis(4-fluorobenzoyl)benzene was supplied from Jilin University, China. Sulfuric acid (95–98%), hydrochloric acid (HCl, 37%), and toluene were purchased from Beijing Chemical Reagent, China. Potassium carbonate (K₂CO₃) was supplied by Beijing Chemical Reagent, and dried at 110 °C in vacuo for 12 h prior to use. Tetramethylene sulfone (TMS) and Dimethyl sulfoxide (DMSO) were purchased from Tianjin Chemical Reagent, China. All other organic solvents were obtained from commercial sources and didn't do other special treatment.

2.2. Preparation of sulfonated nanocrystal cellulose (sNCC)

Sulfonated nanocrystal cellulose (sNCC) was extracted from microcrystalline cellulose (MCC). Colloidal sNCC suspension in water was prepared by following procedure described in the literature [36,37]. Briefly, MCC powder (5.0 g, 20 μm) were subjected to hydrolysis with H₂SO₄ solution (64%, 43.7 ml) at 45 °C under continuous stirring. The reaction was quenched by adding 500 ml of deionized water. The reaction mixture was washed with deionized water using multiple centrifugations and dialyzed for several days until pH reached a constant value. The newly generated suspension was freeze-dried for 24 h to obtain sulfonated nanocrystal cellulose (sNCC).

2.3. Preparation of amino functionalized sNCC

The above obtained sNCC (0.12 g) was placed in ethanol (95%, 15 ml) containing 0.15 ml of N-[3-(trimethoxysilyl)propyl]ethylenediamine. The pH value of the mixture was adjusted to 5.0 by adding acetic acid. After stirring for 4 h at 40 °C, the product was washed with distilled water and ethanol respectively. Finally, the product, coded as Am1-sNCC, was freeze-dried for 24 h. The product named as Am3-sNCC was obtained using the same procedure except that the content of silane coupling agent was adjusted to 0.45 ml instead of 0.15 ml.

2.4. Synthesis of sulfonated poly(ether ether ketone ketone)

Sulfonated poly(ether ether ketone ketone) (Ph-SPEEK) was synthesized applying the same method as shown in Reference [36]. The details are as following. 2-Phenylhydroquinone (0.02 mol, 3.839 g), 0.02 mol (6.446 g) of 1,4-bis (4-fluorobenzoyl), 3 g of potassium carbonate, 40 ml of sulfolane and 12 ml of toluene were combined in a dry 100 ml three-necked flask under nitrogen protection. The mixture was kept stirring for approximately 3 h at 140 °C in order to remove the generated water through azeotropic distillation, and the toluene was also removed. Subsequently, the temperature was raised slowly to 180 °C and maintained it for 6 h. The viscous solution was poured into 800 ml of deionized water with constant stirring. Subsequently, the

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