



Embedding phosphoric acid-doped cellulose nanofibers into sulfonated poly(ether sulfone) for proton exchange membrane



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HIGHLIGHTS

- Cellulose nanofibers (CNFs) were successfully fabricated by ESB process.
- CNFs were embedded into SPES as PEMs for DMFC.
- Phosphoric acid doped nanofibers were used to increase proton conductivity.
- Nanofibers SPES membranes show enhanced WU, thermal and dimensional stability.

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ABSTRACT

Optimization of chemical composition and topography is vital to obtain high-performance proton exchange membranes (PEMs). In this work, cellulose nanofibers were incorporated with phosphoric acid and embedded into the sulfonated poly(ether sulfone) (SPES) matrix to develop PEMs with improved proton conductivity by building proton transfer channels and providing additional proton transport sites. The morphology and chemical structure of the nanofibers doped with different phosphoric acid concentrations and the performance of the composite PEMs were characterized by multi-technics. The results showed that the thermal stability, water swelling ratio (SR) and proton conductivity of the composite membrane were improved in the phosphoric acid-doped cellulose nanofibers. The maximum conductivity (0.154 S/cm, 80 °C, 100 RH) was reached for composite membranes with cellulose nanofibers doped with 0.25 mol/L phosphoric acid. Hence, composite membranes containing proton-conducting cellulose nanofibers could be used to develop novel PEMs for fuel cells.

1. Introduction

Fuel cells transform chemical energy into electric energy and can be used in portable electronic devices and automobile power plants because of their unique characteristics, such as high efficiency, high-energy density, and quick start-up [1,2]. Proton exchange membranes (PEM) are the core component of fuel cells [3] and can directly influence the performance, cost, and application prospects of the cells. Perfluorosulfonic acid PEMs, such as Nafion® series, showing high proton conductivity, high chemical stability, and satisfactory mechanical properties, which is already widely used in fuel cells [4]. However, the high methanol permeability [5] and cost [6] limited the practical application of Nafion in PEM fuel cells. In this regard, scholars have focused on developing new alternative materials to Nafion. Recently

developed hydrocarbon polymers include sulfonated polyimides, sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(ether sulfone) (SPES), and sulfonated polybenzimidazole (SPBI), which are characterized by low cost, high conductivity, and high methanol resistance [7] and used to prepare PEMs. However, the high degree of sulfonation in these polymers causes membrane swelling and poor dimensional stability and mechanical properties; the low degree of sulfonation in the membrane exhibits low proton conductivity. In this regard, sulfonated polymers must be modified to improve restriction on ion accumulation area and increase the proton conductivity [8]. Thus, modifications of sulfonated polymers to improve accumulation area and increase the proton conductivity become important.

Continuous proton-conducting structural domain and channels, which are formed in PEMs, can effectively increase the proton

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conductivity in proton transport mechanism [9]. Scholars have focused on using amphoteric sites with characteristics of proton donor and acceptor as the carrier of proton transfer in PEMs. Phosphoric acid groups ($-\text{PO}_3\text{H}_2$) not only show excellent advantages in proton gain and losses and water retention capacity but also possess low proton transfer barriers. When $-\text{PO}_3\text{H}_2$ is used as proton donor, it can dissociate automatically and form high-concentration inherent proton flaws; when it is used as proton acceptor, it can promote high migration rates of excessive or inadequate protons [10]. High-concentration liquid phosphoric acid may also show relatively high conductivity due to structural diffusion [11]. Therefore, introducing $-\text{PO}_3\text{H}_2$ as the locus of proton transmission has become a new strategy for modifying PEMs [12]. He et al. [13] prepared doped membranes cross-linked with polybenzimidazole (PBI) and phosphoric acid; the as-prepared membranes exhibited excellent mechanical strength and dimensional stability but had limited practical application because of the high phosphoric acid permeation. Wei et al. [14] grafted phosphoric acid functionalized siloxane onto a PBI membrane by using a cross-linking agent; the cross-linked membrane showed excellent thermal stability and mechanical properties. Under 20 °C–160 °C anhydrous conditions, the proton conductivity of the cross-linked membrane increased by one order of magnitude. Binsu et al. [15] modified chitosan by using phosphoric acid and combined it with poly(vinylalcohol) to prepare composite membranes with different mixing ratios. Extensive characterization confirmed the successful introduction of phosphoric acid groups into the composite membrane. The composite membrane showed equivalent proton transfer quantity and conductivity to the Nafion 117 membrane but lower methanol resistance and higher selective value. Cao et al. [16] prepared a composite membrane by using sulfonated poly(ether ether ketone)/phosphorylated titanium dioxide ball (SPEEK/PHT) through template method. According to the experimental study, the addition of PHTs increased the water-retaining property of the composite membrane and improved the proton conductivity at the additional proton transfer loci at the organic–inorganic interface. At 70 °C and 100% relative humidity (RH), the highest proton conductivity was 0.228 S cm^{-1} .

Recently, constructing proton-conducting channels by using nanofibers has gained increasing attention because nanofibers can be used as proton transfer loci to establish an ordered pathway and increase the performance of the PEM. Carolin Klose et al. [17] filled proton-conducting sulfonated poly(ether ketone)(SPEK) nanofiber as reinforcement into the Nafion membrane and performed the chemical and mechanical stress test. The result confirmed the reinforcement effect of SPEK nanofiber and indicated that the fuel cell added with SPEK nanofiber composite membrane achieved 30% higher power density (2.04 W/cm^2) compared with membrane (1.57 W/cm^2) enhanced with chemically inert nanofiber poly(vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP). In our previous studies, PEMs containing carbon nanofibers, SPEEK, bio-functionalized PVDF and SPES were prepared by solution blowing method and the achieved composite PEMs showed improved mechanical properties, methanol diffusion resistance, and proton conductivity [18–21].

In this study, a composite membrane was prepared by introducing phosphoric acid-doped cellulose nanofiber into the membrane matrix (P-Cell/SPES) and considering the proton transfer characteristics of phosphoric acid groups and the order of nanofiber. P-Cell/SPES membranes were prepared from nanofibers impregnated with different concentrations of phosphoric acid. The structure and properties of the composite membranes were investigated.

2. Materials and methods

2.1. Materials

The test materials included cellulose acetate (CA), Mn ~ 30000 and DS = 2.45 (Shanghai Sigma Reagent Co., Ltd), sulfonated poly(ether

sulfone) (PES) (Changchun Application Chemical Institute), H_3PO_4 (Aladdin Chemical Reagent Co., Ltd), absolute ethyl alcohol (Tianjin Fengchuan Chemical Reagent Co., Ltd), and NaOH, N,N-Dimethylacetamide (DMAC) and N,N-dimethylformamide (DMF) (Tianjin Kemiou Chemical Reagent Co., Ltd). All reagents were analytically pure.

2.2. Preparation of cellulose nanofibers

Cellulose nanofibers were fabricated by processing of CA nanofibers under alkali conditions. CA nanofibers were prepared by electrostatic induction-assisted solution blowing (ESB). CA was dissolved in acetone and DMAc of 2:1 (volume ratio) to get a 17 wt.% polymer concentration solution for spinning. ESB process is similar to our previous report [22]. A copper circular induction electrode (diameter, 20 mm) was located 5 mm below the spinning nozzle. An aluminous plate was placed under a polyporous belt for collector. Voltage was applied on the circular electrode to form an electrostatic field. ESB process is briefly described as follows: the polymer solution is poured into the injector pump and adjusted at a constant feeding speed of 20 ml/h. As soon as the polymer solution stream is pressed out from the nozzle, it is extremely drawn by the high-speed airflow from the coaxial outlet and electrostatic force. Nanofibers were formed and deposited on the belt by evaporating the solvents. The spinning parameters is as follows: induction voltage of 15 kV, air pressure of 0.1 MPa, collect distance of 40 cm. The nanofibers were dried in vacuum at 60 °C for 12 h to eliminate the solvent.

At room temperature, the prepared CA membrane was hydrolyzed in 0.05 M NaOH/EtOH solution for 24 h. The membrane was then rinsed completely by deionized water and dried in vacuum at 60 °C for 24 h to obtain cellulose nanofiber membrane.

2.3. Phosphoric acid doping of cellulose nanofiber

An appropriate amount of phosphoric acid and distilled water was collected to prepare different concentrations (0.1, 0.15, 0.2, and 0.25 mol/L) of phosphoric acid solutions. The hydrolyzed cellulose membrane was cut into 3×3 pieces, which were impregnated into different concentrations of phosphoric acid solutions for 72 h. The processed membranes were placed in DMF to remove residual phosphoric acid on the surface. The membranes were then dried in vacuum at 50 °C for 10 h to obtain cellulose nanofiber membranes modified with different concentrations of phosphoric acid. The samples were denoted as P-Cell-0.1M, P-Cell-0.15M, P-Cell-0.2M, and P-Cell-0.25M.

2.4. Preparation of P-cell/SPES composite PEMs

SPES solid particles were synthesized using a previously reported method [23]. SPES solution with 15% polymer was prepared by dissolving SPES into DMF. The P-Cell membrane was impregnated into the SPES solution to prepare composite membrane. The composite membrane was kept static for a certain period, impregnated in deionized water for 12 h, and freeze dried for 10 h to obtain P-cell/SPES composite membrane. Pure SPES membrane was prepared by the same method for comparison. The impregnated P-cell nanofiber content was 5% (mass fraction) of the composite membrane, and the error was controlled within $\pm 2\%$. The prepared P-Cell/SPES composite membrane was placed between two smooth steel plates and processed by a thermocompressor for approximately 15 s at 165 °C/0.5 MPa to obtain a membrane with compact, smooth, and uniform structure. The composite PEMs were denoted as P-Cell/SPES-0.1M, P-Cell/SPES-0.15M, P-Cell/SPES-0.2M, and P-Cell/SPES-0.25M. The average thickness of the nanofiber composite PEM was controlled within 85–120 μm .

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