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Perfluorinated sulfonic acid ionomer/poly(*N*-vinylpyrrolidone) nanofiber membranes: Electrospinning fabrication, water stability, and metal ion removal applications

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ABSTRACT

Perfluorinated sulfonic acid ionomer/poly(*N*-vinylpyrrolidone) (PFSA/PVP) fibrous membranes with varying compositions were prepared by electrospinning. The morphology, physicochemical structure and water stability of these membranes were investigated by SEM, XRD, and FTIR. The crosslinking agent 4,4′-diazostilbene-2,2′-disulfonic acid disodium salt (DAS) was added to the spinning solutions, and its effect on electrospinning behavior and PFSA/PVP membrane morphology was investigated. Thermal annealing of the DAS-containing PFSA/PVP fibrous membranes resulted in improved water stability due to PVP crosslinking. The adsorption properties of the nanofiber membranes were measured by the ability to remove Cu^{2+} and Ca^{2+} ions from water. Nanofiber membranes with higher surface area provide more exposed functional groups and thus better ion removal capability. These functional PFSA/PVP nanofiber membranes show applicability in water treatment and may find potential applications in sensors and drug delivery or as components of the catalytic layer of proton-exchange membrane fuel cells.

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1. Introduction

Perfluorinated sulfonic acid (PFSA) ionomer consists of a fluorocarbon backbone with pendant sulfonates. This special chemical structure imparts PFSA membranes with unique mechanical, chemical and thermal stability, superb selectivity and efficient cation transport [1]. This functional polymer can be used in such diverse areas as sensing [2], metal ion recovery [3], drug release [4], polymeric catalysis [5,6], and proton exchange membrane fuel cells [7,8]. Many efforts have been made to optimize their structure for performance. Chen found that at least 13% of the exchange sites are isolated by the fluorocarbon cage and thus are inaccessible for ion exchange within the recast PFSA film; this value exceeds 25% in molten extrusion films [9]. For many applications, fabrication of PFSA into nanoscale architectures with high surface area and increased functional site accessibility improves its work efficiency [10,11]. For example, PFSA/silica nanocomposite membranes with high surface area exhibit greater than 100 times higher catalytic activity than that of pure PFSA-dense membrane [11].

Electrospinning has proven to be a simple, versatile, and cost-effective method for producing polymeric fibrous non-woven membranes with high aspect ratio, large specific surface area and flexibility in surface functionality. For functional polymers, such unique microstructure affords many more exposed functional sites in an interconnected three-dimensional network. Many functional polymers with applications in energy storage, environmental engineering [15,16], biotechnology [17–19], health care, defense and security have been successfully electrospun from solution into nanofiber membranes [12–14].

It is expected that PFSA can be fabricated into nanofibers through electrospinning to improve performance. However, under mild conditions, PFSA is poorly soluble in most common solvents. PFSA chains can be dissolved in special solvent mixtures under high pressure and elevated temperature but aggregate into micellar structures when cooled to room temperature. Such aggregation results in insufficient polymer chain entanglement in PFSA solutions, rendering them unsuitable for electrospinning [20]. Carrier polymers are PFSA-compatible molecules that are used to break up aggregate formation and thereby enhance chain entanglement in the complex polyelectrolyte solution. Generally, polyacrylic acid (PAA) [20], poly(vinyl alcohol) (PVA) [21], poly ethylene oxide (PEO) [22–24], and poly(*N*-vinylpyrrolidone) (PVP) [25,26] are utilized as carrier polymers.

Zhu and co-workers [25] fabricated electrospun Nafion/PVP nanowires for use in micro fuel cells whose performance was several orders of magnitude higher than that of traditional fuel cell power sources. However, the PVP content was as high as 67.2 wt% with respect to the total polymer weight. Nafion/PVP electrospun fibers prepared by Bajon et al. [26] have an even higher

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PVP content of 75 wt%. Such high PVP content reduces the water stability and, thus, the long-time performance of the resulting devices. The architecture of non-woven electrospun fibrous membranes with high PVP content can be destroyed by water exposure, although such formulations should be avoided when membranes with large specific surface area and high porosity are required. To the best of our knowledge, the water stability of PFSA/PVP nanofiber membranes has not been reported.

In the present paper, electrospun PFSA/PVP nanofiber membranes were prepared. The choice of PVP as the carrier polymer is based on its good compatibility and efficient acid–base interaction with PFSA and its facile crosslinking using 4,4′-diazostilbene-2,2′-disulfonic acid disodium salt (DAS) through thermal treatment. The PFSA/PVP system is thus electrospinnable, and the resulting nanofiber membrane maintains its structure well throughout the thermal annealing. The physicochemical properties of the composite fibrous membranes with varying PVP content were examined by SEM, XRD, and FTIR techniques. The PVP chains interfered with the crystallization of PFSA molecules, resulting in a decrease in swell stability. Furthermore, PVP molecules without chemical crosslinking tend to gradually dissolve, leading to the deterioration of fibrous structure. The effect of DAS on the electrospinning behavior of PFSA/PVP was investigated. Thermal treatment of the resultant DAS-doped PFSA/PVP fibrous membranes greatly improved their water stability. The ability of such water-stable, fibrous, porous PFSA/PVP fibrous membranes to remove metal ions from aqueous solution was evaluated and compared to cast membranes. Nanofiber membranes showed higher adsorption capacity than cast membranes due to more accessible sites for ion exchange. Such functional PFSA/PVP nanofiber membranes may find application in sensors and drug release, or in the catalytic layers of proton exchange membrane fuel cells, where high surface area and porous structure are desired.

2. Materials and methods

2.1. Materials

PFSA ionomer in pellets and powders was provided by Dongyue Shenzhou New Materials Company Ltd., China. PVP (MW = 1300,000) was purchased from Alfa and utilized without further treatment. *N*,*N*-dimethylformamide (DMF, 99%) was obtained from Sinopharm Chemical Reagent Co., Ltd. (China) and used as received.

2.2. Preparation of PFSA/PVP and PFSA/PVP-DAS nanofiber membranes

Transparent PFSA/PVP solutions were prepared by dissolving PFSA and PVP powders in DMF and stirring at room temperature for 12 h. The solutions were *degassed* with a 350W SK5200H ultrasonicator for 10 min *before* spinning. PFSA/PVP nanofibers were prepared using a laboratory electrospinning apparatus. Briefly, the electrospinning solution, added to a 3-mL syringe, was delivered into a blunted medical needle spinneret (OD 0.89 mm, ID 0.60 mm) through a Teflon tube using a KD-200 syringe pump. A high voltage power supply was used to charge the spinning drop by directly clamping one electrode to the metal needle spinneret and another to an aluminum-foil-covered lab rack. The tip-to-collector distance was 15 cm. The humidity in the chamber was reduced to approximately 40% using a *dehumidifier*. Other operating parameters in the chamber are as follows: voltage 10 kV, flow rate 0.1–0.3 mL h^{-1}, and ambient temperature.

The preparation of PFSA/PVP-DAS nanofiber membranes is similar to that of PFSA/PVP. The spinning solutions were prepared by adding DAS (0.4, 0.8, 1.2, or 1.6 wt% with respect to the total polymer weight) to the PFSA/PVP (92/8 by weight) solution to a total polymer concentration of 43 wt%. The solutions were stored or electrospun in the dark before crosslinking treatment.

2.3. Crosslinking of electrospun nanofibers

Thermal treatment or UV-irradiation of DAS produces nitrogen (N_2) and highly reactive nitrene intermediates [27] that further reacts with PVP in the absence of oxygen (Scheme 1), resulting in cross-linked networks.

The spun DAS-doped PFSA/PVP (92/8 by weight) nanofiber membranes were placed in a vacuum oven for 24 h to remove the residual DMF, heated to 150 °C for 1 h, and then at 200 °C for 1 h. Thermal annealing promoted the chemical crosslinking of PVP and physical crosslinking of PFSA. The dry nanofiber membrane was light-yellow in color.

2.4. Characterization

Morphological observation of the samples were performed on a JSM-7401F (JEOL Ltd., Japan) SEM under low vacuum. The samples were sputter-coated with a thin layer of gold before SEM experiments. The average diameter of the nanofibers was determined by measuring 50 fibers using Image J software.

FTIR measurements were conducted and collected in the 4000–650 cm^{-1} range at a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum 100 spectrometer. X-ray diffraction measurements were conducted on a Rigaku D/max-2500B2/PCX system. The radiation source (Cu Kα X-ray) was operated at 40 kV and 200 mA at room temperature, with a scanning angle range of 5–50° (2θ) and a scanning velocity of 4° min^{-1}.

Steady viscosity measurements of the PFSA/PVP-DAS solutions were conducted in a control stress rheometer (RS600-Haake) using a cone-plate sensor system with a diameter of 60 mm and 1° angle at 26 °C.

2.5. Adsorption kinetics and equilibrium experiments

The ion exchange capacity of the materials was determined as follows: the sample was equilibrated with 1.0 N hydrochloric acid and then rinsed with deionized water to remove the adsorbed acid. The acidified sample ($-SO_3-H$) was equilibrated in a NaCl solution (0.5 N) for 4 h. The amount of hydrogen ions released from the membrane by ion exchange with sodium ions was determined by titration with a standard NaOH solution.

Batch adsorption experiments of Cu^{2+} and Ca^{2+} onto PFSA/PVP (92/8 by weight) nanofiber membranes were conducted. The samples were dried under vacuum at 80 °C for 16 h. They were next equilibrated in 10 mL aqueous solutions of 600 mg L^{-1} metal ions with magnetic stirring at 600 rpm for 2 h. The pH was adjusted to 5 with HNO_3 or NaOH at the beginning of each experiment. At definite time intervals, aliquot samples (0.1 mL) were removed from the remaining solution and diluted to determine the residual concentration of metal ions in the solution using an atomic absorption (Hitachi Z-5000 Polarized Zeeman) spectrophotometer.

The amount of metal ions adsorbed per unit mass of membrane q was calculated using

$$q = \frac{\sum_{i=1}^{n}(c_{i-1} - c_i)(V_0 - (i-1)V_s)}{m \times 1000} \tag{1}$$

where q is the amount of adsorption (mg g^{-1}), and C_0 and C_i are the concentration of initial solution and ith sample, respectively (mg L^{-1}). V_0 and V_S are the initial and sampled volumes of the solution (mL), respectively, and m is the mass of dry adsorbent used (g).

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