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Fabrication and performances of solid superacid embedded chitosan hybrid membranes for direct methanol fuel cell

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ABSTRACT

This study reports the fabrication and performances of hybrid proton-conducting membranes by dispersing nanosized solid superacid inorganic fillers, TiO_2–SO_4^{2-} ($STiO_2$), into chitosan (CS) matrix. Fourier transform infrared spectra demonstrate intermolecular interactions between $STiO_2$ and chitosan segmental chains. High resolution scanning electron microscope characterization reveals an essentially homogeneous dispersion of the solid superacid fillers within chitosan matrix. The incorporation of the superacid fillers leads to a reduced fractional free volume (*FFV*) of the hybrid membranes as confirmed by positron annihilation lifetime spectroscopy (PALS) analysis. This reduced *FFV* and more tortuous pathway significantly enhance the methanol diffusion resistance through the membranes, resulting in a decreased methanol crossover. Under identical conditions, compared with TiO_2 embedded membranes, the $STiO_2$-filled hybrid membranes exhibit simultaneously improved methanol barrier and proton transport properties due to the enhanced interfacial interaction and proton conductive ability. Moreover, compared with Nafion 117 membrane, all the $STiO_2$-filled hybrid membranes display much lower methanol crossover whereas the proton conductivity of the membranes remains high enough for DMFC applications. Meanwhile, due to the interfacial interactions between $STiO_2$ and chitosan chains, the hybrid membranes exhibit an enhanced mechanical strength and adequate thermal stability as verified by mechanical strength characterization and thermogravimetric analysis.

1. Introduction

Referred as the next generation materials, hybrid materials have been widely used in the fields of molecular recognition, biomimetics, molecular sieve, catalytic materials, membrane materials, etc. Recently, organic–inorganic hybrid membranes have been proposed as promising electrolytes for direct methanol fuel cell (DMFC) application. The rationale for incorporating the inorganic additives is manifold: (1) improving thermal, mechanical, and chemical stabilities by intrinsic organic–inorganic interfacial interactions [1,2]; (2) reducing methanol crossover through blocking methanol transport path and/or suppressing membrane swelling [3–5]; (3) enhancing proton conductivity by constructing new proton transport pathway and/or by improving water retention property of the membranes, especially, at high temperatures [6,7].

Among numerous inorganic materials, solid superacids have triggered increasing attention because of their fine hygroscopic and proton conductive properties as well as good mechanical property when incorporated into polymers, which are advantageous for high performance proton exchange membrane. To date, the commonly-utilized solid superacids can be categorized into metal oxide supported sulfate (M_xO_y–SO_4^{2-}), heteropoly acid (HPA) and zeolite solid superacid [8–12]. Navarra et al. developed a high temperature superacid zirconia-doped Nafion composite membrane, and the presence of superacid promoted the hydration degree and acidity, which in turn reflected in enhanced proton conductivity (1.5×10^{-2} S cm^{-1}) compared with plain Nafion (3.0×10^{-6} S cm^{-1}) at 140 °C and low relative humidity [8]. Cui et al. prepared a series of cithosan-heteropoly acids (phosphomolybdic acid, phosphotungstic acid and silicotungstic acid) hybrid membranes. They found that incorporating HPA improved both the methanol barrier and proton conductive properties [10]. Kim et al. incorporated MCM-41 supported heteropoly acid and tungstophosphoric acid (TPA) into Nafion matrix. The resulting hybrid membranes displayed higher proton selectivity and thus better DMFC performance [12].

It is well known that the solid superacid TiO_2–SO_4^{2-} ($STiO_2$) has an acid strength stronger than that of 100% H_2SO_4 due to the presence of the promoted oxide of Lewis and Brønsted acidic sites at the surface [13–15]. Strong Lewis acidity could be attributed to the existence of unsaturated Ti^{4+} cations which bear a high electron accepting ability. It has also been proposed that the O atom in the S=O bond in SO_4^{2-} exerts pronounced inductive effects on S atom, leading to the increase of electrostatic field of Ti. As

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for the Brønsted acidity, it could be assumed that the protonated titanium hydroxyls are rendered more acidic owing to the charge withdrawing effect of the adjacent sulfate group. In virtue of its strong acidity, TiO_2–$SO_4{}^{2-}$ has been widely utilized as an acid catalyst in isomerization, cracking, alkylation, acylation, esterification, etc. To our knowledge, TiO_2–$SO_4{}^{2-}$ has scarcely been exploited as an active inorganic filler in hybrid proton exchange membranes till now. Recently, Wu et al. have evaluated the performances of Nafion composite membranes embedded by TiO_2–$SO_4{}^{2-}$ and noted that in DMFC single cell performance test, the composite membrane with 6% TiO_2–$SO_4{}^{2-}$ content achieved similar performance at 1 M methanol feed, and a higher performance at 5 M methanol feed compared with pure Nafion membrane [16]. They also observed that the methanol crossover first decreased and then gradually increased with the filler content, in particular, these membranes displayed obvious methanol crossover (above $2.7 \times 10^{-6}\,cm^2\,s^{-1}$). Furthermore, the influence of the solid superacid particle on physicochemical properties of the composite membranes was seldom investigated. These have prompted us to extend the investigation of such inorganic material in hybrid proton exchange membrane.

In this study, chitosan (CS) was employed as a promising polymeric matrix for DMFC application considering its low cost, desirable alcohol barrier property and proton conductivity as well as adequate thermal stability after crosslinking [17–19]. Meanwhile, nanosized solid superacid TiO_2–$SO_4{}^{2-}$, prepared via chemical adsorption, was chosen as inorganic filler embedded into chitosan matrix to fabricate a series of hybrid proton exchange membranes for the first time. The objective was to systematically investigate the influence exerted by TiO_2–$SO_4{}^{2-}$ on the physicochemical properties of membrane including mechanical strength, thermal stability, microstructure, crystallization and free volume characteristics, along with the water uptake, swelling, methanol permeability and proton conductivity of the membrane.

2. Experimental

2.1. Materials and chemicals

TiO_2 powder with 12 nm average particle diameter was supplied by zhuerna High-Tech Powder Material Co. (Shanghai, China). Chitosan (CS) with a degree of deacetylation of 91% was purchased from Golden-Shell Biochemical Co. (Zhejiang, China) and used as received. Acetic acid, sulfuric acid and methanol were of analytical grade and supplied from Tianjin. All the reagents were commercially available and used without any further purification. De-ionized water was used in all experiments.

2.2. Preparation of TiO_2–$SO_4{}^{2-}$

The TiO_2 nanoparticles were sulfated by chemical absorption according to the procedure in the literatures [20,21]. TiO_2 powder (10 g) was dispersed into 100 mL of 1 M H_2SO_4 aqueous solution under stirring for 4 h, then was filtrated, washed and dried in vacuum at 40 °C. Thereafter, the resultant powder was calcined at 450 °C for 4 h, and the white TiO_2–$SO_4{}^{2-}$ solid superacid powder was thus obtained.

2.3. Fabrication of the membranes

Chitosan (1.5 g) was dissolved in 40 mL of 2 wt.% acetic acid aqueous solution under stirring at 80 °C. Simultaneously, certain amount of TiO_2 or TiO_2–$SO_4{}^{2-}$ powder was dispersed into 35 mL of 2 wt.% acetic acid aqueous solution with ultrasonic treatment for 30 min. These two parts of solution were then mixed and stirred vigorously at 80 °C for another 2 h. After degasification, the resulting homogenous solution was cast onto a clear glass plate and dried at 25 °C. The membrane was afterwards immersed and cross-linked in 2 M H_2SO_4 for 24 h and then extensively rinsed with de-ionized water to remove residual H_2SO_4. Finally the hybrid membrane was dried under vacuum at 25 °C for 48 h. The resulting membranes were designated as CS/TiO_2-X or CS/STiO_2-X representing TiO_2 or TiO_2–$SO_4{}^{2-}$ as the fillers, where X (X = 5, 10, 15, 20, 25 or 30) was the weight ratio of the inorganic filler to chitosan. Control CS membrane was fabricated in exactly the same way as above without incorporating inorganic filler and designated as CS. It should be pointed that membrane thickness was in range of 60–70 μm.

2.4. Characterization

The morphology of the TiO_2 before and after sulfation was characterized by transmission electron microscopy (TEM, Tecnai G2 20 S-TWIN). The cross-section of the membranes was observed using field emission scanning electron microscope (FESEM, Nanosem 430) operated at 5 kV after being freeze-fractured in liquid nitrogen and then sputtered with gold. The crystalline structure of the membranes was investigated with a RigakuD/max2500 v/Pc X-ray diffractometer (XRD, CuK 40 Kv, 200 mV, 2° min^{-1}) in the range 3–60°. The peak position was extracted with MDIjade5 software. The Brunauer–Emmett–Teller (BET) surface area of the powder sample was determined by nitrogen adsorption on a ASAP 2020 nitrogen adsorption apparatus.

The elemental composition of the solid superacid particles was characterized by X-ray photoelectron spectroscopy (XPS) using a PHI 1600 spectrometer with an Mg Kα radiation for excitation. Fourier transform infrared spectra (FTIR, 4000–400 cm^{-1}) of the fillers and membranes were recorded on a Nicolet MAGNA-IR 560 instrument. The thermogravimetric analysis (TGA, Perkin-Elmer Pyris) data of the membranes were obtained from 30 to 700 °C using a heating rate of 10 °C min^{-1} at nitrogen atmosphere. The mechanical strength of the membranes was carried out by using 350 AX overall drawing Testometric. The membranes were cut into 1.0 × 5.0 cm for each sample and then examined with a 10 mm min^{-1} scan rate at room temperature.

Positron annihilation lifetime spectroscopy (PALS) experiment was performed by using an EG&G ORTEC fast–fast coincidence system (resolution 201 ps) at room temperature. The resource of ^{22}Na (5×10^5 Bq) was sandwiched between two pieces of sample, each of which with an overall thickness of about 1.0 mm. The integral statistics for each spectrum was more than 2×10^6 coincidences. In this technique, assuming that o-Ps was localized in a spherical potential well surrounded by an electron layer of thickness Δr equal to 0.1656 nm, the radius of free volume cavity (r) is obtained from pick-off annihilation lifetime (τ) of o-Ps in the free volume elements by a semiempirical equation [22,23]:

$$\tau = \frac{1}{2}\left[1 - \frac{\gamma}{\gamma + \Delta\gamma} + \left(\frac{1}{2\pi}\right)\sin\left(\frac{2\pi\gamma}{\gamma + \Delta\gamma}\right)\right]^{-1} \quad (1)$$

The volume of the equivalent sphere can be calculated by Eq. (2):

$$V_f = \frac{4\pi}{3}\gamma^3 \quad (2)$$

Further, the fractional free volume (*FFV*) may be estimated from Eq. (3):

$$FFV = V_{f_3} I_3 \quad (3)$$

where V_f and I are free volume of the sphere and intensity of o-Ps, respectively.