Preparation and properties of direct methanol fuel cell membranes by embedding sulfonic titania into sulfonated poly(arylene ether nitrile)s

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Abstract. In order to improve the performance of DMFCs, sulfonic Titania have been synthesized and incorporated sulfonated poly (arylene ether nitrile) s to fabricate hybrid membranes with enhanced proton conductivity and methanol resistance. The introduction of particle content caused significant improvement in thermal property, methanol permeability, proton conductivity and dimensional stability. For instance, SPEN-5 wt% showed the highest selectivity of 5.05×105 S s cm-3, which was more than 10 times higher than that of Nafion 117. All the results make the hybrid membranes as potential candidate for applications in fuel cells.

1. Introduction

Recently, direct methanol fuel cells (DMFC) has been attracted more and more attention as renewable energy for automobile, stationary, and mobile devices thanks to their high efficiency in energy conversion, long lifetime and low pollution [1-3]. Polymer electrolyte membrane (PEM) act as the most important component since it can transfer protons and avoid high permeability of methanol [4, 5]. In past decades, the perfluoro sulfonic acid (PFSA) membrane has greatly contributed to fuel cell technologies due to its good physicochemical stability and excellent proton conductivity [6]. However, these membranes possess a number of shortcomings such as limited operating temperature, high cost, and high methanol permeability. To overcome these limitations, numerous alternative electrolyte membranes possessing reinforced a superior properties and controllable structure for DMFC are greatly being developed. Sulfated aromatic polymers have been chosen as alternatives to Nation, such as suffocated poly(Arlene ether nitrile)s (SPEN), suffocated poly(Arlene ether ketone) (SPAEK), and suffocated poly(ether sulfonic), which can meet the following requirements: low cost, high mechanical and chemical stability, and low methanol crossover [7-11]. Among these materials, SPEN has been considered as one of the most potential electrolyte membranes thanks to its excellent chemical stability, high mechanical strength, low cost and excellent methanol resistant [12].

However, the performance the SPEN membrane is connecting with the ionic exchange capacity (IEC) level. The low proton conductivity makes the SPEN not fulfil for widely applications in DMFC at a low IEC level. With the increasing the degree of suffocation of the SPEN membrane, it displays high proton conductivity as well as sacrificing other properties such as: mechanical strength and dimensional stability, especially methanol permeation. Thus, methods such as ionic, physical cross-
linking, and chemical, especially fabricating hybrid membranes have been used to improve the proton conductivity while benefit of higher mechanical strength and dimensional stability, and lower methanol crossover.

Herein, in this work, we synthesized a novel type of suffocated titanic and embedded it into SPENs to prepare hybrid electrolyte membranes. The as-synthesized suffocated titanic and the SPENs-TiO2-SO3H hybrid membranes were measured by TGA and SEM. The effects of TiO2-SO3H incorporation on membrane properties, including proton conductivity, thermal stability, water uptake, swelling and methanol permeability, were extensively investigated.

2. Experimental section

2.1. Preparation of SENs-TiO2-SO3H hybrid membranes

SPENs-TiO2-SO3H hybrid membranes could be got by the solution casting method. SPENs were dissolved into hot DMF solvent and then stirred to form a transparent SPEN solution. With that different ratio of TiO2-SO3H (0, 3.0, 5.0, 10.0 and 15.0 wt. %) were added into the SPEN solution and then ultrasonic for 1 h under a nitrogen atmosphere. After that the SPENs-TiO2-SO3H solution was casted onto a clean glass plate and dried at 80, 100, 120 and 160°C for 2 h, respectively. Finally, the as-prepared films were cooled to room temperature.

2.2. Characteristic

The fractured and surface morphology of SPENs-TiO2-SO3H membranes were observed by a scanning electron microscopic (SEM, JSM6490LV, and Japan). Thermo gravimetric (TGA) were carried out on a TGA-Q50 (TA Instruments) at a heating rate of 20°C min⁻¹.

3. Results and Discussion

![Figure 1](image)

**Figure 1.** SEM images of TiO2 (a), TiO2-SO3H (b), the surface (c) and the cross-sections (d) of SPENs-TiO2-SO3H hybrid membranes.

Fig. 1 a and b show the morphology of the TiO2 and TiO2-SO3H, as clearly observed that morphologically identical and monodispersed TiO2-SO3H with size of 35–55 nm were successfully prepared. Compared with pure TiO2, there is no obvious change in the size and shape of TiO2-SO3H particles. SEM was used to observe the internal microstructure of the film and the dispersion of TiO2-SO3H as shown in Fig. 1 c and d. TiO2-SO3H homogenously dispersed in in SPENs without obvious agglomeration and sedimentation. The uniform dispersion of the particles could be ascribed to the electrostatic repulsion between the TiO2-SO3H with the modified sulfonic acid groups on the titania surface and the strong SPEN–TiO2-SO3H interfacial interactions. The good compatibility between the polymer and the inorganic filler are benefit to improve the membrane performance.
Figure 2. (a) TGA curves, (b) Water uptake, (c) Swelling ratio of SPEN–TiO2-SO3H-x.

Thermal stability of the hybrid membrane samples were investigated by TGA thermograms in Fig. 2a. All the membranes were first heated to 150°C and remained 5 mins to evaporate of the residual solvent and water. The first rapid weight loss is -SO3H group degradation; and the second weight loss region may be attributed to the degradation of main chain of SPENs. Figure 5 b and c shows the water uptake and swelling ratio of membranes at different test temperature. Both the extent of swelling and the water uptake of the SPEN–TiO2-SO3H membranes and pure SPENs increased with the increasing of temperature. Meanwhile, the water uptake and swelling ratio of hybrid membranes exhibited increased first and then decreased with the increasing content of TiO2-SO3H compared to pristine membrane. This was because extra more hydrophilic groups in the TiO2-SO3H could absorb more water. However, higher interaction formed between TiO2-SO3H and the SPEN, which restricted the free volume of polymer lead to lower water absorption.

Figure 3. (a) Proton conductivity, (b) Methanol permeability (c) Selectivity of SPEN–TiO2-SO3H-x

The proton conductivity of the PEM materials is the key performance of fuel is determined by the. The proton conductivities of all SPEN–TiO2-SO3H membranes and SPEN were measured at different temperatures and 100% RH as shown in Figure 3a. The proton conductivities of all membranes increased with increasing the temperature, indicating a thermally activated process. It can be observed that the proton conductivities of SPEN–TiO2-SO3H membranes increased first and then decreased with the incorporation of TiO2-SO3H increasing. As inferred from Figure 3a, SPENs-TiO2-SO3H-5% exhibited the highest proton conductivity among these SPEN–TiO2-SO3H membranes, which can be ascribed to the following two aspects: i) extra sulfonic acid groups grafted on the TiO2-SO3H rendered more facile hopping sites for proton conduction; ii) sulfonic acid groups coupled with water molecules in the hybrid membranes might form additional pathway for proton conduction. After the incorporation of the TiO2-SO3H more 5%, too much TiO2-SO3H led the polymer matrix became more compact, leading to decreased proton conductivity. Methanol permeability of membranes is another important parameter the performance of PEM, as the data are shown in Figure 3b. It can be
inferred that all SPEN–TiO2-SO3H membranes exhibited are all lower than that of the SPEN. This may be ascribed to the TiO2-SO3H led the SPEN matrix became more compact, leading lower methanol. Selectivity is a standard to evaluate the practical application property of PEMs, which is defined as the ratio of proton conductivity to methanol permeability, as shown in Figure 3c. TiO2-SO3H makes the SPEN–TiO2-SO3H membranes become more compact to improve the methanol resistance. For instance, SPENs-TiO2-SO3H-5% exhibited the highest selectivity of $5.05 \times 10^5$ S·s·cm$^{-3}$, which was more than 10 times higher than that of Nafion 117. All the results indicated that the SPEN–TiO2-SO3H membranes could be used as the alternative electrolyte membranes for applications in fuel cells.

4. Conclusion
In this study, high-performance alternative electrolyte membranes were prepared by incorporating TiO2-SO3H into SPEN. The extra sulfonic acid groups of the TiO2-SO3H rendered more facile hopping sites for constructing consecutive proton transfer channels. Furthermore, the barrier effect of TiO2-SO3H significantly reduced the methanol permeability of the SPEN–TiO2-SO3H membranes. It could be believed that the SPEN–TiO2-SO3H membranes could be used as the alternative electrolyte membranes for applications in fuel cells.

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