



Sulfonated poly(arylene ether nitrile)s containing cross-linkable nitrile groups for proton exchange membranes

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ABSTRACT

In order to solve the problem of high methanol crossover for direct methanol fuel cells, a series of cross-linkable sulfonated poly(arylene ether nitrile)s with pendent nitrile groups as cross-linkable groups have been synthesized through direct condensation polymerization. As far as we know, there are no detailed reports connected with nitrile groups being used as cross-linkable groups. The chemical structures of the sulfonated poly(arylene ether nitrile)s were confirmed by Fourier transform infrared (FT-IR) spectroscopy. The introduction of cross-linking network structure caused significant enhancement in thermal property and dimensional stability. Meanwhile, methanol permeability, swelling ratio and water uptake of the membranes substantially decreased after cross-linking. For instance, the water uptake and swelling ratio of SPEN-CN-70 are 1985.3% and 157% at 80 °C, while those of CSPEN-CN-70 decrease to 64.9% and 16.9%, respectively. The SPEN-CN membranes showed the methanol permeability range from 0.838×10^{-7} to $8.24 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, while the CSPEN-CN membranes showed the lower permeability range from 0.156×10^{-7} to $1.64 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively. Most importantly, after cross-linking, CSPEN-CN-60 showed the highest selectivity of $5.37 \times 10^5 \text{ S cm}^{-3}$, which was 11.9 times higher than that of Nafion 117. Although the conductivity of the CSPEN-CN was lower than that of the SPEN-CN, the higher selectivity makes the CSPEN-CN as potential candidate for applications in fuel cells.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted increasing attention as alternative energy resources for stationary, automobile, and mobile devices due to relative high energy, high efficiency and environmental friendliness [1–3]. The most important component in a fuel cell is polymer electrolyte membrane (PEM), since it can transfer protons from anodes to cathodes and avoid cross leaking of fuel gas/methanol between the electrodes [4,5]. Only those with such tough criteria as physic-chemical stability, high proton conductivity, thermal durability, low permeability and low-cost can be chosen as PEM [6,7]. Till now, the investigation of PEM materials has been mainly focused on Nafion, due to its high proton conductivity, good mechanical property and excellent chemical stability ($< 80 \text{ }^\circ\text{C}$). Nevertheless, Nafion is quite expensive due to its synthesize-difficulties. Besides, it possesses undesirable properties such as poor water management capability, poor thermal properties, that limited operation temperature ($< 80 \text{ }^\circ\text{C}$) and relatively high methanol permeability [8–11]. In order to mitigate these problems, many researchers devote themselves to develop effective alternatives to replace traditional PEM materials. Especially, materials

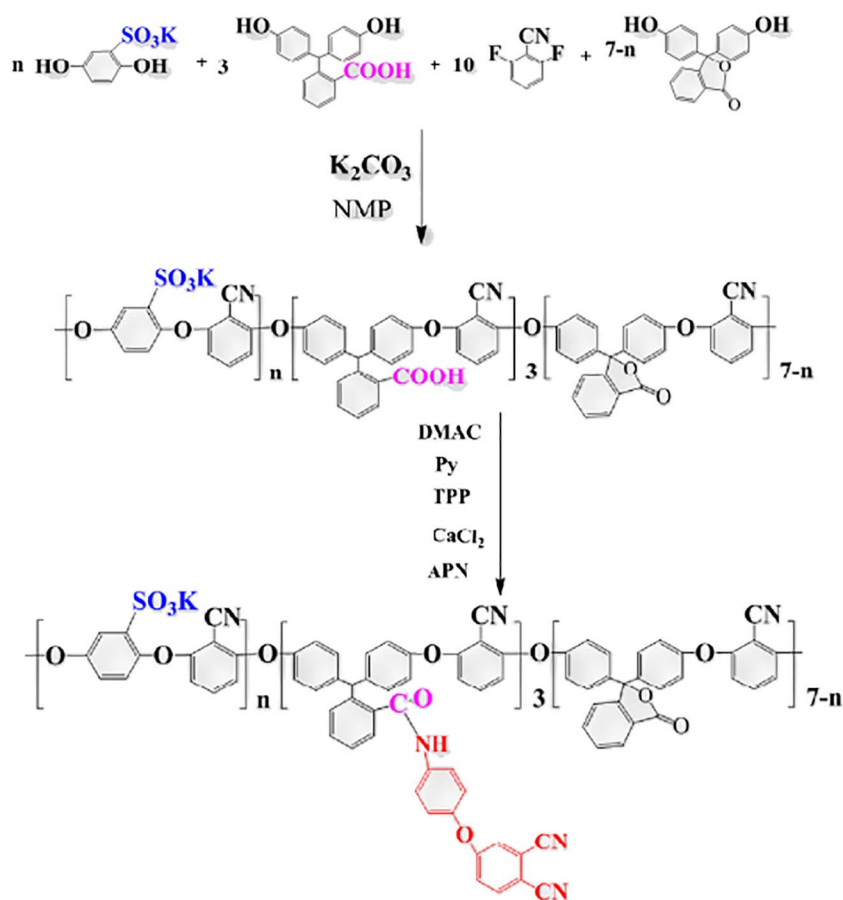
based on high performance polymers with aromatic main chain have been a candidate. These materials include sulfonated poly(arylene ether)s [12,13], sulfonated polyimide [14,15], sulfonated polybenzimidazoles [16,17] and so on, which possess high proton-conductivity, good thermal-stability, low-cost and proper methanol-permeability.

Among alternative membrane materials, sulfonated poly(arylene ether nitrile)s (SPENs) have been research hotspots since the water uptake and swelling have been reduced owing to the nitrile groups on SPENs [18–20]. Moreover, it is reported that the nitrile groups on the polymer main chains can promote adhesion between polymers and electrodes in the preparation of MEAs [19]. Thus, SPENs has the potential to be a good candidate as polymer electrolyte membrane.

Proton conductivity of SPENs increased as the degree of sulfonation increases. However, as the sulfonation degree reaches a high level, the membranes tend to swell in the environment with high humidity and increasing temperature. Consequentially, the mechanical properties of the membranes tend to decrease and the mal-function rate of the membranes under FC conditions may increase. Furthermore, it leads to a high crossover of methanol permeability along the large hydrophilic

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Fig. 1. Synthesis and preparation of SPEN-CN-x ($x = 50, 60, 70$).

channels. SPENs with higher proton conductivity than that of perfluorinated ionomer membranes have been prepared in our lab. Whereas, high methanol-permeability and swelling ratio of the SPENs might limit further applications [18]. In order to solve these problems, there is a considerable amount of research that has been done by many research groups. It's proved that cross-linking is an easy method to obtain enhanced mechanical properties, to decrease membrane swelling degree and reduces the methanol-permeability of cross-linked sulfonated polymer membranes significantly. Cross-linking reaction is the most common method in improving polymer performance. However, cross-linked membranes normally show decreased conductivity compared to that of the homologous pristine ones, owing to two factors: 1) sulfonic acid groups will be eliminated, resulting in decrease of the proton conductivity of the membrane. 2) the introduction of cross-linker may dilute the sulfonic acid groups, which resulted in the reduction of proton conductivity. To our knowledge, few reports are focused on covalently cross-linking ionomer membranes without elimination of sulfonic acid groups [21–23].

In this work, novel SPENs containing nitrile cross-linkable moieties were synthesized by direct polymerization to prepare new self-cross-linked and net-structured PEMs. To our knowledge, there are still no detail reports containing nitrile cross-linkable moieties as cross-linked groups. In present work, the nitrile groups can undergo crosslinking reaction in the presence of the main chain to form a much denser network structure and the sulfonic acid group act as a benign solid catalyst. Typically, crosslinking (nitrile trimerization) is accomplished by application of heat, typically to a temperature of 160 °C or more, in the presence of suitable initiators or catalysts. Suitable initiators or catalysts may include ammonia, ammonium compounds, fluorinated carboxylates, Lewis acids, and the like. In this work, it is easier for the crosslinking reaction to take place since the *o*-SO₃H can act as a catalyst. Since the sulfonic acid group is not involved in the crosslinking

reaction and no additional crosslinking agent are introduced, the proton conductivity of those cross-linked membranes does not decrease severely. At the same time, water uptake, swelling ratio and methanol permeability of the cross-linked membranes decreased obviously. As a result, SPENs have been expected to be a good candidate to be used as PEMs in direct methanol fuel cells.

2. Experimental

2.1. Materials

DFBN and SHQ were purchased from Aldrich. Phenolphthalein, sodium hydroxide (NaOH; AR), and zinc were supplied by Chengdu Haihong Chemicals. *N,N*-Dimethylacetamide [DMAC; (AR)], *N*-methyl pyrrolidone (NMP; AR), potassium carbonate (K₂CO₃; AR), hydrochloric acid, sodium chloride (NaCl; AR), pyridine (Py), toluene (AR), triphenyl phosphite (TPP), and anhydrous calcium chloride (CaCl₂) were obtained from Tianjin BODI chemicals. The 4-nitrophthalonitrile (99%) was obtained from Alpha chemicals (Dezhou). All of the materials were used without further purification. The synthesis of PPL and 3-(3-aminophenoxy)phthalonitrile (3-APN) were implemented according to the literature [24,25].

2.2. Synthesis of sulfonated poly(arylene ether nitrile) copolymers

The synthesis of SPEN was performed in accordance with a procedure described by previous reports [26]. A typical procedure to synthesize SPEN was as follows: A 250 ml three-neck round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a Dean-Stark trap, was charged with DFBN (0.15 mol, 20.85 g), SHQ (0.09 mol, 20.25 g), PPL (0.045 mol, 14.4 g), PP (0.015 mol, 4.77 g) and K₂CO₃ (28 g) were mixed in the flask with 75 mL NMP and 25 mL toluene. The

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