



Self-assembly prepared anion exchange membranes with high alkaline stability and organic solvent resistance



Jifu Zheng^a, Qifeng Zhang^a, Huidong Qian^b, Boxin Xue^{a,c}, Shenghai Li^a, Suobo Zhang^{a,d,*}

^a Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

^c University of Chinese Academy of Sciences, Beijing 100039, China

^d Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), China

ARTICLE INFO

Article history:

Received 20 July 2016

Received in revised form

12 September 2016

Accepted 16 September 2016

Available online 16 September 2016

Keywords:

Self-assembly

Anion exchange membranes

Stable alkaline

Organic solvent resistance

ABSTRACT

A self-assembly strategy has been developed for the synthesis of anion-exchange membranes (AEMs) with high alkaline stability. Cardo poly(aryl ether sulfone ketone)s with pendent tertiary amine groups were grafted with alkyl siloxane to form a polymer with cation quaternary ammonium groups. This polymer produced a zwitterionic polymer via partially hydrolysis of the alkyl siloxane in weak basic medium. The flexible and transparent zwitterionic polymer membranes possessing a Si-O-Si cross-linked network were prepared via the sol-gel polycondensation reaction and a self-assembly process. The homogeneous and continuous Si-O-Si cross-linked network inhibited membrane swelling and improved the mechanical properties and thermochemical stability. The membrane showed alkaline stability in 1 M NaOH aqueous solution at 60 °C for 600 h and solvent resistance in polar aprotic solvents (DMAc, NMP, and DMSO) at 60 °C for 30 days.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, alkaline polymer electrolyte fuel cells (APEFCs) have shown numerous advantages over traditional proton exchange membrane fuel cells due to the favorable kinetics of oxygen reduction in high pH conditions and reduced dependence on noble metal catalysts [1–4]. Alkaline anion-exchange membranes (AEMs) are the key component of APEFCs. To date, the development of high-performance AEMs with high ionic conductivity and selective permeability has become an area of intense research, and the poor chemical stability of AEMs under device-relevant high pH conditions and elevated temperatures has become a significant barrier in the development of APEFCs [5–8]. A number of approaches have been studied to improve the stability of AEMs including the incorporation of stable ion groups in the polymer membranes [9–15], and the use of an inert polymer backbone stabilized by electron donating or sterically bulky groups [16–20]. Due to these methods AEMs usually possess high ionic conductivity with increased ionic exchange capacity (IEC) values, however there are still disadvantages such as decreased selective ionic permeability, high water uptake and swelling ratio, and the

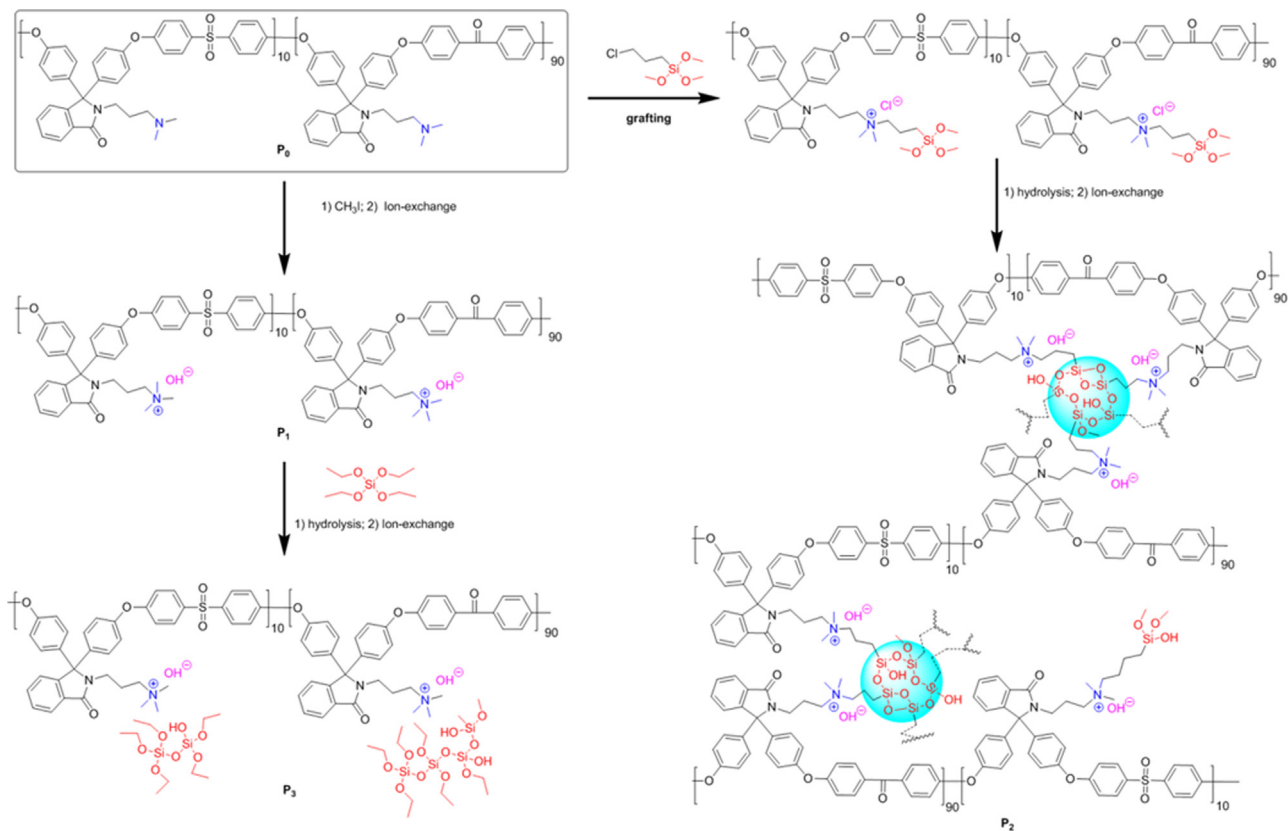
loss of mechanical performance caused by good solubility in water [19].

It is well known AEMs must possess good dimensional stability to ensure continuous and stable operation of APEFCs undergoing repeated thermal cycles. Therefore controlling the water uptake and swelling of AEMs is critical to increase the ionic conductivity and maintain mechanical strength. Commonly adopted methods to resist membrane swelling include block copolymers, cross-linked membranes (including covalent, ionic, and mixed), and blending or nano-composite membranes (including inorganic and inorganic-organic hybrids) [21–26]. Among these, cross-linked membranes exhibit high ionic conductivity and selective permeability by nontraditional length-scale parameter analysis. Despite the desirability of these effects, the IEC values of cross-linked polymer membranes have been shown to decrease [8].

Mesoporous silica materials with high specific surface area, tunable pore size, and rich morphology have received considerable attention as potential electrolyte membrane materials [27–29]. The cross-linked, porous inorganic structures of these materials can impart their mechanical and structural durability to inhibit membrane swelling in hydrated states. Moreover, high densities of ionic groups with organic moieties can be formed in the mesopores via ionic group self-assembly on the silica surface, which promotes ion conductivity to increase. However, because of their inherent insolubility and infusibility, silica materials are difficult to process. Additionally, poor distributions of amorphous silica

* Corresponding author at: Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

E-mail address: sbzhang@ciac.ac.cn (S. Zhang).



Scheme 1. The methodology for the formation of P₁–P₃ membrane.

nanoparticles and weak interfacial contacts between amorphous silica nanoparticles and the polymer matrix can result in defects and reduce membrane performance [29]. Consequently, improving the compatibility between the silica nanoparticles and the polymer matrix is critical to increase the comprehensive performance and durability of the polymer electrolyte membranes.

When silica species are prepared under basic conditions, rich SiO⁻ groups exist on the surface of Si-O-Si cross-linked networks, which allow positively charged quaternary ammonium group (GA) species to self-assemble due to strong electrostatic forces [30]. If the GA groups of the AEMs are covalently linked with alkyl siloxane, zwitterionic polymers can be produced under alkaline hydrolysis conditions. This allows for further self-assembly via strong electrostatic forces between the positive and negative moieties to form the membrane. In this way, silica species can uniformly disperse in the polymer matrix and the interfacial compatibility between silica species and the polymer matrix can improve. Additionally, high densities of ionic groups on the Si-O-Si cross-linked network surface can be obtained.

Based on the above, a novel self-assembly strategy for the preparation of AEMs with high alkaline stability was developed. Cardo poly(aryl ether sulfone ketone)s with pendent tertiary amine groups were initially grafted with alkyl siloxane to obtain a polymer with the cationic quaternary ammonium groups. Zwitterionic polymer was then produced via partial hydrolysis of alkyl siloxane in weak basic medium. The solution of zwitterionic polymer was then treated by solvent evaporation to afford novel AEMs with Si-O-Si cross-linked networks. The synthesis, characterization, morphology, ionic conductivity, and alkaline stability of new AEMs are investigated and comparison with the hydrophobic segment copolymers is discussed.

2. Experimental section

2.1. Materials

3-Chloropropyltrimethoxysilane was purchased from Alfa Aesar. *N,N*-Dimethylacetamide (DMAc) was dried with CaH₂ and distilled under reduced pressure before use. Tertiary amine and terminal quaternary ammonium copolymers (P₀ and P₁, respectively) were synthesized according to previously described procedures [31].

2.2. Measurements

Solid-state NMR spectra were obtained on a Bruker AV400 spectrometer. FT-IR spectra were acquired on a Bio-Rad Digilab Division FTS-80 IR spectrometer. Thermo gravimetric analyses (TGA) were obtained under nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer from 50 °C to 800 °C at 10 °C min⁻¹. The thermal transitions of the copolymers were investigated by 01db-Metravib DMA+450 in the OH⁻ form. Tensile measurements were conducted with an Instron-1211 at a speed of 1 mm min⁻¹ at room temperature and ambient humidity conditions. Wide-angle X-ray diffraction (WAXD) measurements were collected on a Rigaku Max 2500 V PC X-ray diffractometer with Cu K α radiation at a wavelength of 1.54 Å (40 kV, 200 mA) and a scan rate of 5° min⁻¹ from 10° to 50°. SAXS experiments were performed using a Nano STAR-U (BRUKER AXS INC.) with Cu K α radiation ($\lambda=0.154$ nm). The generator was operated at 40 kV and 650 μ A. Two-dimensional SAXS patterns were obtained using a HI-STAR detector. The sample to detector distances were LSD=1074 mm. The effective scattering vector q ($q=\frac{4\pi}{\lambda} \sin \theta$, where 2θ is the scattering angle) at this distance ranged from 0.044 to 2.0 nm⁻¹. The surface of the membrane was examined by X-ray

Download English Version:

<https://daneshyari.com/en/article/4989363>

Download Persian Version:

<https://daneshyari.com/article/4989363>

[Daneshyari.com](https://daneshyari.com)