



Dual cross-linked organic-inorganic hybrid polymer electrolyte membranes based on quaternized poly(ether ether ketone) and (3-aminopropyl)triethoxysilane



Na Zhang, Baolong Wang, Chengji Zhao*, Yurong Zhang, Fanzhe Bu, Ying Cui, Xuefeng Li, Hui Na*

Alan G MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

HIGHLIGHTS

- The dual cross-linked organic-inorganic hybrid membranes were prepared.
- The pores were formed in surfaces and interior of membranes by cross-linker.
- Both the pores and Si–OH groups contributed to improving proton conductivity.
- The connective phosphoric acid clusters could improve proton conductivity.

ARTICLE INFO

Article history:

Received 17 September 2014
Received in revised form
12 November 2014
Accepted 15 November 2014
Available online 17 November 2014

Keywords:

Quaternized poly(ether ether ketone)
High temperature proton exchange
membrane
Fuel cell
Phosphoric acid

ABSTRACT

Quaternized poly(ether ether ketone)s (QPEEKs) are synthesized to absorb phosphoric acid (PA) and used as high temperature proton exchange membranes (HTPEMs). In order to improve their oxidative and mechanical stability without sacrificing proton conductivities, a series of dual cross-linked organic-inorganic hybrid membranes are prepared using (3-aminopropyl)triethoxysilane (APTES) as a cross-linker. The amine of APTES reacts with two benzyl bromide groups to build the primary cross-linking network. The Si–O–Si network generated by the hydrolysis of triethoxysilane in APTES is the secondary cross-linking network. The dual cross-linking hybrid networks improve the mechanical and oxidative stability of PA doped membranes. They can endure up to 15.3 h in 3 wt.% H₂O₂, 4 ppm Fe²⁺ Fenton solution at 80 °C. During the hydrolysis of triethoxysilane, the release of small molecules (H₂O and C₂H₅OH) forms many pores in surfaces and interior of membranes. These pores and the resulted Si–OH groups corporately enhance the PA absorbing ability and proton conductivity. The highest proton conductivity is 61.7 mS cm⁻¹ for PA-QPEEK-10%APTES at 200 °C under anhydrous condition. These membranes show great potential to be used in HTPEM fuel cell.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

With the shortening of energy and worsening of environment around the world, the clean and high effective energy has been a hot spot for a long period. The proton exchange membrane fuel cell (PEMFC) is able to convert the chemical energy (in H₂, CH₃OH or C₂H₅OH) into electric energy directly with low pollution [1]. Therefore, it has been widely used in the fields of aerospace, electric generation, electric vehicle and portable power sources. The proton

exchange membrane is the core of a PEMFC and its development has always been one of research hotspots in this field. At present, perfluorosulfonic membranes, represented by Nafion[®] (DuPont), are the mainly commercial PEM. Due to the perfluorinated polymer chain and hydrophilic-hydrophobic phase separation structure, Nafion[®] shows excellent chemical stability and high proton conductivity at high levels of hydration. However, it has an operating temperature limitation of about 80 °C. Firstly, Nafion[®] has a glass transition temperature of 110–115 °C, so operation at high temperature would result in the loss of mechanical strength [2–4]. Secondly, Nafion[®] suffers a great loss of proton conductivity above 100 °C due to the quick loss of water from the membrane. Although there are many researches focusing on the enhancement of water

* Corresponding authors.

E-mail addresses: zhaochengji@jlu.edu.cn (C. Zhao), huina@jlu.edu.cn (H. Na).

retention in Nafion[®] membrane, for example, Nafion[®]/silicon oxide hybrid membrane, there has been no significant improvement in proton conductivity at elevated temperatures [5–7]. These drawbacks have restricted the further use of Nafion[®] in high temperature fuel cells. However, operating a PEMFC at high temperature (here, the high temperature is usually 100–200 °C) has many advantages, such as enhanced electrochemical kinetics, simplified water and heat management, utilization of non-platinum catalyst and higher CO-rich reformed hydrogen [8–11]. Therefore, it is necessary to develop alternative polymer electrolyte membrane with high proton conductivity at elevated temperatures.

Polybenzimidazole (PBI) is a kind of high performance polymer that exhibits high mechanical performance at high temperatures up to 300 °C. Phosphoric acid (PA) doped PBI membrane with outstanding high temperature performance is one of the most widely studied materials for high temperature proton exchange membrane (HTPEM). In this system, PA acts as the acceptor and donor of protons and builds the hydrogen bond network for proton transport [12,13]. High PA doping level always leads to high proton conductivity, but accompanying by the decrease of mechanical stability. So, the parent PBI polymer must possess high molecular weight to ensure the tensile strength of PA doped membrane. However, PBI with high molecular weight always shows poor solubility in common solvents, such as dimethyl sulfoxide and *N*-methyl-2-pyrrolidone, resulting in poor processability for membrane casting. Alternative parent polymers studied as the HTPEMs are poly(arylene ether ketone/sulfone)s owing to their great thermal stability and high tensile strength [11,14–19]. Usually, they are functionalized by quaternary ammonium groups, which can tether PA molecules by acid–base interaction. The quaternized polymers based on poly(arylene ether ketone/sulfone)s are much cheaper than PBI. And the amount of quaternary ammonium groups, which determines the PA doping level, is controllable. It makes much easier to control the PA doping level by controlling the concentration of quaternary ammonium groups.

The cross-linking method has been extensively investigated to improve the tensile strength, thermal and oxidative stability of materials in many fields including HTPEM. In general, cross-linking would result in the decrease of proton conductivity owing to the formation of dense cross-linking network structure, while only some special cross-linkers can improve the proton conductivity.

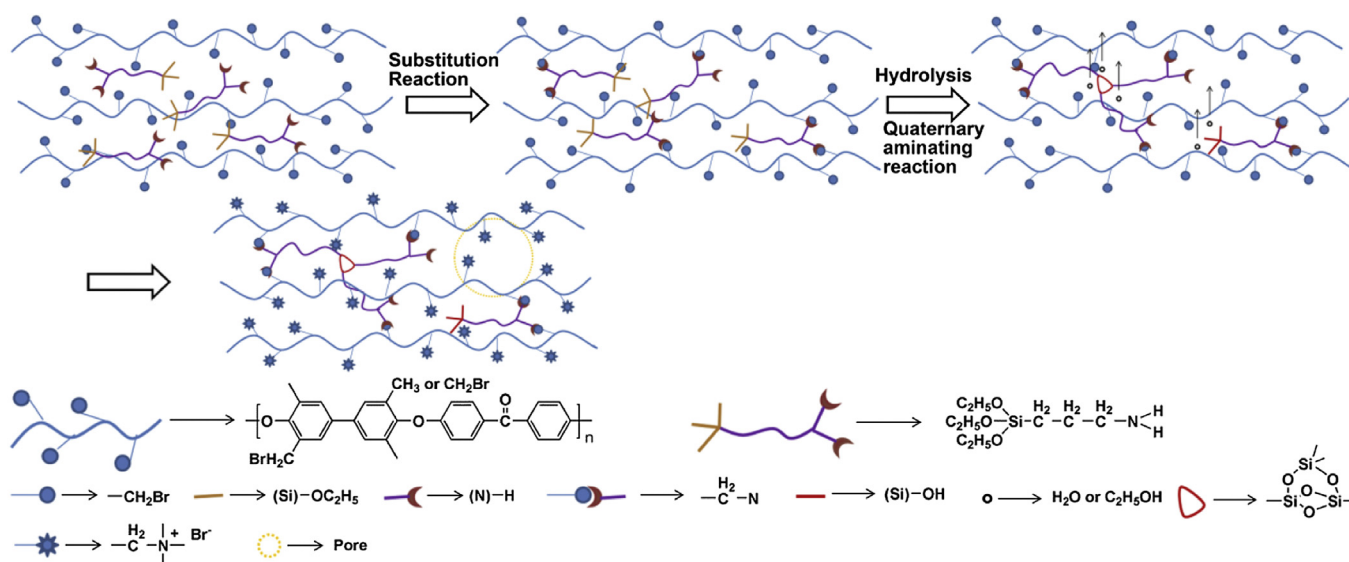
Kallitsis's group prepared cross-linked aromatic polyethers bearing polar pyridine units along the main chain, using the bisazide [20] and bistetrazole [21] as the cross-linkers, respectively. They obtained the increased T_g , improved proton conductivity and fuel cell performance. In our previous work, the cross-linked PBI membranes using a silane coupling agent, γ -(2,3-epoxypropoxy)propyltrimethoxysilane, as the cross-linker were prepared. The cross-linked membranes exhibited improved tensile strength and enhanced proton conductivities due to the introduction of silane-cross-linking structure [22].

In this work, we prepare a series of dual cross-linked poly(ether ether ketone) (PEEK) membranes using another silane coupling agent, (3-aminopropyl)triethoxysilane (APTES), as the cross-linker. The amine group ($-\text{NH}_2$) of APTES reacts with two benzyl bromide groups ($-\text{CH}_2\text{Br}$) of bromomethylated poly(ether ether ketone) (BrPEEK) to form the primary cross-linking network. After being hydrolyzed, the triethoxysilane of APTES produces the secondary Si–O–Si network; thus, the dual cross-linked organic-inorganic hybrid membranes are obtained. The residual benzyl bromide groups in the cross-linked membranes are then ammoniated by trimethylamine to obtain the cross-linked quaternized poly(ether ether ketone) (QPEEK) membranes. It is interesting to find that many pores are formed by the release of small molecules during the hydrolysis of APTES (Scheme 1). These pores are beneficial for PA absorbing because of the capillarity effect [2,23–26]. As we reported previously, the Si–OH groups in the cross-linked network contributed to increasing PA doping level through electrostatic interaction, thus resulting in higher proton conductivity at elevated temperatures [22]. In this work, the obtained Si–OH groups and pores are expected to together improve the PA doping level and proton conductivity. Meanwhile, the mechanical properties and oxidative stability are also improved because of the introduction of dual cross-linking structure.

2. Experimental

2.1. Materials

3,3',5,5'-Tetramethyl-4,4'-bisphenol (TMBP) and 4,4'-difluorobenzophenone (DFBP) were obtained from Shanghai Jiachen Chemical Company. Potassium carbonate, *N*-methyl-2-pyrrolidone



Scheme 1. The preparation process of the QPEEK-x%APTES membrane.

Download English Version:

<https://daneshyari.com/en/article/7734140>

Download Persian Version:

<https://daneshyari.com/article/7734140>

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