ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–14

Available online at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/he

Mussel-inspired strategy towards functionalized reduced graphene oxide-crosslinked polysulfone-based anion exchange membranes with enhanced properties

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ARTICLE INFO

Article history:
Received 9 June 2018
Received in revised form
16 July 2018
Accepted 24 July 2018
Available online xxx

Keywords:
Cosslinked anion exchange membranes
Polysulfone
Reduced GO
Mussel-inspired
Properties

ABSTRACT

Chemical crosslinking is regard as an effective method to balance the ionic conductivity and dimensional stability of anion exchange membranes (AEMs). In this work, a series of crosslinked AEM composite membranes based on polydopamine-functionalized reduced graphene oxide (PDArGO) were constructed from quaternized polysulfone (QPSU) with amino groups via mussel-inspired chemistry strategy. On the one hand, as the dopant, the hydrogen bonding interaction between PDArGO and a large number of amino groups on the side chains of QPSU can enhance the water uptake of the membranes and has a positive influence on the ionic conductivity of composite membranes. On the other hand, PDArGO also acts as the crosslinker, which can form a micro-crosslinked structure with the amino groups on the side chains of the polymer through the Michael addition/schiff base reactions. Under the combined influence of the above two factors, the crosslinked composite AEMs exhibited special delightful properties. In general, the crosslinking reaction will lead to the decrease of the ionic conductivity of the membranes, but as for the membranes prepared by us, the ionic conductivity had been improved to some extent. Especially, the QPSU-1.5%-PDArGO exhibited 57% improvement in the hydroxide conductivity than that of pure QPSU membrane and reached the highest value of 61 mS cm^{-1} at 80 °C. Besides, the crosslinked membranes also exhibited strong dimensional stability, good mechanical strength, comparable alkaline stability and improved methanol permeability.

Introduction

With the deterioration of the environment, people's demand for high quality and clean energy is becoming more and more intense. Fuel cells, a kind of clean and efficient energy conversion devices, have been considered as an effective energy substitute [1,2]. As a key component of proton exchange membrane fuel cells (PEMFCs), proton exchange membranes (PEMs) have been extensively studied. The Nafion membrane with excellent properties developed by DuPont is one of the most widely used proton exchange membranes (PEMs) at present. However, there are still many problems need to be solved, such as high cost, environmental pollution, high fuel permeability, and the strong dependence on noble metal catalysts (Pt). Alkaline anion exchange membrane fuel cells (AAEMFCs) using anion exchange membranes (AEMs) as the

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https://doi.org/10.1016/j.ijhydene.2018.07.153
0360-3199/

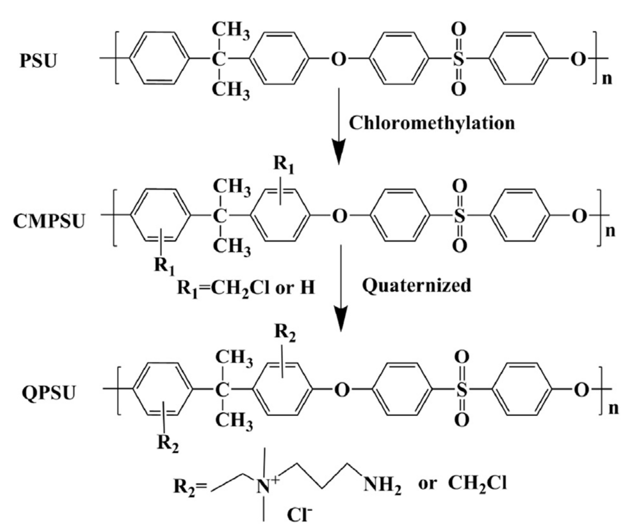
Please cite this article in press as: Miao L, et al., Mussel-inspired strategy towards functionalized reduced graphene oxide-crosslinked polysulfone-based anion exchange membranes with enhanced properties, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.07.153

ion-conducting membrane are a good substitute for PEMFCs due to their higher oxygen reduction kinetics, the employ of non-noble metal catalysts and the reverse transmission direction of hydroxide ions which has a positive impact on the reduction of fuel leakage [3–6].

As we know, the performance of AEMs can directly affect the efficiency of alkaline fuel cells (AFC). However, current commercial AEMs generally have the shortcoming of low ionic conductivity due to lower mobility of hydroxide ions compared to protons. So it is necessary to introduce more ionic conductive groups into the AEMs to increase ion exchange capacity (IEC), and improve their anion conductivity. But it may lead to another negative effect that the AEMs with high IECs usually possess excessive swelling and poor dimensional stability. So far, many strategies including crosslinking [7–17], various kinds of polymerization [18–23] and organic-inorganic hybrid methods [24] have been used to develop different structural AEMs with improved properties. As an important modification method, crosslinking is expected to enhance mechanical strength, dimensional stability and other properties of composite membranes. Meanwhile, it also can get rid of the conductivity-swelling dilemma to a certain extent. In the early stage, the researchers constructed a simple crosslinking structure mainly through the reaction between halogen and the aromatic ring [25,26]. This way is very simple and doesn't require extra crosslinking agents and catalysts, but it will obviously reduce the ionic conductivity of the membranes. In the following studies, researchers have put forward many other novel and effective crosslinking measures for AEMs. Xu et al. prepared the crosslinked AEMs through disulfide bonds which can be recycled. The obtained cross-linked membranes showed enhanced mechanical properties and excellent dimensional stability over the pure membrane [16]. A unique terminal crosslinking reaction was discovered by Lee et al. and was used to prepare AEMs. The obtained XE-Imd70 membrane displayed excellent electrochemical performance (107 mS cm^{-1} at 80 °C, 202 mA cm^{-2} at 0.6 V and a maximum power density of 196.1 mW cm^{-2}). Moreover, the crosslinked membranes also presented improved chemical stability and durability [14]. Hickner and his co-worker successfully synthesized a series of crosslinked AEMs based on poly(2,6-dimethylphenylene oxide) (PPO) by introducing a hydrophilic, long chain cross-linker into the polymer networks. The crosslinked membranes gained improved comprehensive properties [7]. In addition to the above mentioned methods, there are still several typical cross-linking methods, such as ion crosslinking [10], click chemistry crosslinking [27], nucleophilic substitution reactions [28], a single step amination and alkalization procudure [29,30], etc.

Another effective way to prepare AEMs is to introduce inorganic dopants into polymers. This so-called organic-inorganic hybrid method can also improve the properties of AEMs. The dopants used by the researchers are divided into the following categories: SiO_2 [31,32], ZrO_2 [33,34], montmorillonite [35], TiO_2 [36,37], polyhedral oligomeric silsesquioxane (POSS) [38,39], GO [40–44] and so on. As a new type of materials, graphene oxide (GO) provides numerous possibilities for applications due to their unique and superior mechanical, electrical and physical properties. In addition, it is worth noting that the surface of GO contains a large number of oxygen-containing functional groups, which will provide feasibility for the surface modification. Our group has done some work on this aspect. For examples, the quaternized graphenes (QGs) were introduced into quaternized polysulfone to prepare a series of hybrid anion exchange membranes with excellent comprehensive properties [43]. A reversible addition fragmentation chain transfer (RAFT) polymerization was chosen to fabricate quaternized polymer brush-functionalized graphenes (QPbGs). After incorporating the QPbGs into the polysulfone matrix, we found that the ionic conductivity of composite membranes increased with the increase of the doping content and reached the maximum value of 56 mS cm^{-1} at 80 °C. At the same time, the stability, methanol permeability and water uptake of AEMs were all improved [44]. What's more, our group also developed the crosslinked hybrid membranes with high stability by azide-assisted nitrene addition reaction between the rGO and azido modified quaternized polysulfone. The resulted crosslinked hybrid membranes exhibited obvious improved properties such as alkaline stability, oxidation stability, and methanol permeability [15].

Recently, many researchers have paid high attention to the mussel-inspired chemistry for it's simple operation process and omnipotency [45–48]. Dopamine, a simple organic small molecule, has been regarded as an important component of adhesives. It could form polydopamine (PDA) through self-polymerization under undersuitable conditions, e.g. under a tris buffer of pH = 8.5. In addition, polydopamine admits the Michael addition/schiff base reactions with polymer molecules containing thiol or amino groups [49–51]. In this work, we have developed a facile and effective method to fabricate reduced GO-crosslinked polysulfone-based AEMs based on mussel-inspired chemistry which combines the advantages of hybridization and crosslinking (Scheme 1). Polydopamine modified rGO (PDArGO) was used as dopant and crosslinking agent. As we expected, the crosslinked membranes exhibited strong dimensional stability, good mechanical strength, comparable alkaline stability and improved methanol permeability. It is surprising that the ionic conductivity of the



Scheme 1 – Preparation process of QPSU.