Solid State Ionics 282 (2015) 18–25

Contents lists available at ScienceDirect

Solid State Ionics

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

Dyeing polyvinyl alcohol membrane with low-temperature reactive dye X-2R as a new type of proton-exchange membrane for fuel cells

Tianchi Zhou [a,b], Feifei Song [c], Xuemei He [b], Kongliang Xie [a,*]

[a] College of Chemistry, Chemical Engineering and Biotechnology, Donghua University,2999 Ren'min North Road, Shanghai 201620, China
[b] YanCheng Institute of Technology, 9 Ying'bing Road, Yancheng 224003, China
[c] College of Environmental Science and Engineering, Donghua University, 2999 Ren'min North Road, Shanghai 201620, China

ARTICLE INFO

Article history:
Received 6 April 2015
Received in revised form 19 July 2015
Accepted 18 September 2015
Available online 6 October 2015

Keywords:
Membrane
Reactive dyes
Conductivity
Thermal stability
Dyeing process

ABSTRACT

In this work, a new type of proton-exchange membranes constructed by poly(vinyl alcohol) and X-type reactive dyes (X-2R) had been successfully prepared and comprehensively investigated in depth. FT-IR and SEM were used for chemical and structural characterization of these membranes. The membranes' H^+ conductivity and water uptake were studied using AC impedance technique and the method of weighing, respectively. The effects of different thicknesses of the membranes were emphatically studied. Considering all properties, the optimal thickness of the PVA/X-2R membrane was 45 μm, and the resulting membrane exhibited high proton conductivity 0.0519 S cm^{-1} at room temperature with the water uptake reaching 1.57 g g^{-1}, which afforded a power density of 48.9 mW cm^{-2} at 127.4 mA cm^{-2} and open-circuit voltage (OCV) of 893.1 mV. The PVA/X-2R membrane remained about 75.2 wt% of the originals up to 30 h in Fenton's reagent (3%H_2O_2(V/V), 2 ppm $FeSO_4$), which showed the high oxidative stability. Thermal analysis also showed that the PVA/X-2R membranes exhibited the significant improvement of thermal stability.

1. Introduction

Proton-exchange membrane (PEM) fuel cell is one of the most promising green power sources for electronic products. As the key component in PEM fuel cell, the development of PEM is always an attention hotspot researched by many scholars. Perfluorinated proton-exchange membranes, such as Nafion, are the most widespread type of polymeric membranes used for PEM fuel cells. However, one great weakness of these membranes is their high production costs due to the difficulty to synthesize perfluorinated macromolecule. Furthermore, organofluorine compounds have been found to be the dominant factor of some potential environmental problems. In recent decade, more and more non-fluorinated membrane materials with relatively low cost and the required electrochemical characteristics have been explored. These membranes are constructed mainly from organic hydrocarbon polymers with the sulfonic acid groups directly attached to the main chain, or carrying short pendant side chains with terminal sulfonic acid units. At present, polyimide [1–3], polybenzimidazole [4–7], poly(aromatic ether) [8–10], and polybenzoxazole [11–14] are the most main research objects. However, some obstacles such as hydrolysis stability, still high price, relatively low proton conductivity, and poor durability have been difficult to resolve.

In our previously work, a series of conductive films applied on fuel cells had been successfully prepared by blending and solution cast technique, using poly(vinyl alcohol) (PVA) as material [15–18]. PVA is a polyhydroxy polymer (Fig. 1a) and possesses many excellent characteristics such as easy preparation, biodegradability, good film-forming capacity and stability, low cost, hydrophilic properties, and a high density of reactive chemical functions [19,20]. Hence, in this work, we still used PVA as the membrane's matrix and chose anionic dye Reactive Red Violet X-2R (X-2R) (Fig. 1b) (chemical name: sodium 5-((4,6-dichloro-1,3,5-triazin-2-yl)amino)-4- hydroxy-3-((4-methoxyphenyl)diazenyl)naphthalene-2,7-disulfonate) as a proton conductor. X-2R is an economic reactive dye mainly used in the dyeing and printing of cellulose fibers. As shown in Fig. 2, nucleophilic substitution reaction can take place between the dichlorotriazine groups of X-2R and the −OH groups of PVA at low temperature. By the conventional dyeing processes, X-2R can be firmly fixed on the PVA matrix owing to the formed covalent bonding. Considering the sodium sulfonate groups in X-2R, it should be feasible to apply these membranes to proton-exchange membrane fuel cells. However, since both PVA and X-2R are hydrophilic matters, a major research objective is how to adjust the membrane's water uptake to balance the conductive performance and mechanical performance. Chemical cross-linking PVA by glutaraldehyde (GA) is a highly versatile method to solve this problem by adjusting the cross-linking density of the membranes prepared [21–27]. Compared with the blending technique we adopted in the past work [15–18], the dyeing process used in this work possesses

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* Corresponding author. Tel.:+86 18951550608.
E-mail address: 120413181@qq.com (K. Xie).

http://dx.doi.org/10.1016/j.ssi.2015.09.013
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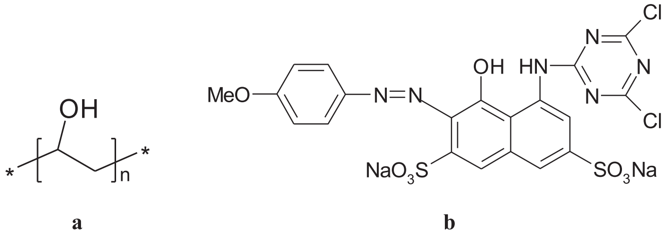

Fig. 1. Chemical structure of polyvinyl alcohol (a) and reactive dye X-2R (b).

some special advantages, especially the improved flexibility and toughness. The PVA/X-2R membrane is post-functionality, that is, the polymer is solidified to prepare the matrix membrane before the functional steps, and then the proton conductive component X-2R dyes PVA membrane to form various bonding forces. Thus, it can effectively avoid the poor compatibility in the blending system. Furthermore, we can adopt some chemical agents to help X-2R dye fix on the PVA membrane, and these agents can be easily removed by washing the membrane several times. This is difficult for the blending system to achieve, so it is also an extremely promising approach to prepare polymer electrolyte membranes for fuel cells.

Based on the above conception, in this article, a series of cost-effective membranes based on PVA had been prepared first, and then these membranes were modified by Reactive Red Violet dye X-2R using dyeing techniques. The membranes prepared were studied by using infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) to analyze their chemical structure and morphological microstructure. Thermo gravimetric analysis (TGA) was adopted to study the thermal stability. The membrane characteristics, including H^+ conductivity (σ), water uptakes (WU), ion exchange capacity(IEC), mechanical properties, and oxidative stability, were discussed to evaluate their application performances. Finally, these membranes were used to fabricate membrane electrode assemblies (MEAs) for actual H_2/O_2 single fuel cells.

2. Experimental

2.1. Materials and membrane preparation

The matrix membrane was synthesized by solution-casting technology. In this method, PVA (99% hydrolyzed, average molecular weight Mw = 86,000–89,000; Aldrich) was dissolved in water with continuous stirring to make a 6% transparent solution at 80 °C. The obtained solution was cast onto a plastic Petri dish and evaporated slowly at room temperature for 3 days to form the matrix membrane. Then the membrane was soaked in a dye bath containing the concentration of X-2R (analytical pure, kindly provided by Wujiang Taoyuan Dyestuff Co., Ltd., China) 10 g/L at a liquor ratio of 1:50. The temperature of the dye bath was warmed up to 30 °C before one-half 25 g/L sodium chloride was added with stirring. After 30 min, another one-half 25 g/L sodium chloride was added, and the dyeing temperature was kept on 30 °C for 30 min. Then the dyeing temperature was gradually increased to 50 °C before 20 g/L sodium carbonate was added to fix the dye onto PVA membrane, and the fixing process was continued for 60 min. Finally, the treated sample was washed with water (5 g/L soap flakes at 40 °C) and then thoroughly rinsed in tap water before they were dried naturally. The whole dyeing process was shown in Fig. 3.

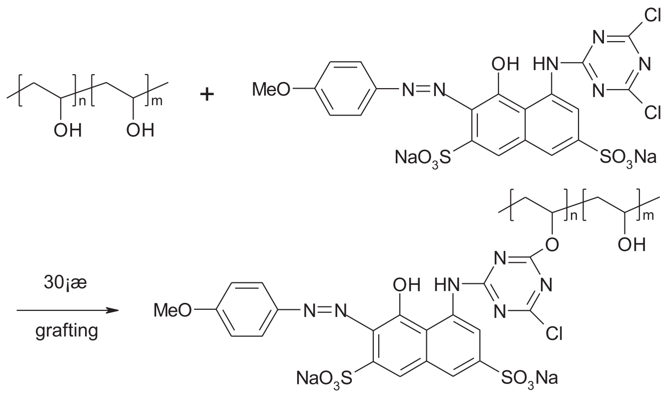

Fig. 2. The reaction equation of the modified PVA by X-2R.

To enhance the mechanical properties and reduce swelling property of the membrane, the dyed membrane was immersed in a solution consisting of 10 wt.% glutaraldehyde (GA) and several drops of HCl in acetone at 30 °C for 30 min to form cross-linked structure. Cross-linking can be formed because of the reaction between the —OH of PVA and the —CHO of GA due to the catalysis of acid, and the dye molecules can be maintained in the membrane via multiple interactive forces between molecules (Fig. 4). Then the membrane was soaked in a 1.0 M HCl solution to convert the SO_3Na form into the SO_3H form. Before the use, the membrane was washed with deionized (DI) water several times to remove excess HCl and finally dried naturally. Flat membranes were obtained with a thickness of about several tens of micrometers (20–130 μm) measured by a micrometer.

2.2. Characterization of PVA/X-2R membranes

Fourier-transform infrared spectra were recorded on an FT-IR-4200 spectrometer (Shimadzu, Japan). Samples in the form of thin films were sandwiched between two KBr plates and placed in the cell to be measured. Air was employed as a background reference.

A Quanta 200 scanning electron microscope analyzer (FEI, USA) was employed to observe the surface and cross profile morphology of the membranes. Prior to observations, the membrane samples were fractured in liquid nitrogen and sputtered with gold, then examined at 2000 and 10,000 magnifications.

Thermogravimetric analysis of the membrane was performed using an STA449C apparatus (Netzsch, Germany). Samples of about 10 mg were loaded into an alumina pan and then heated from 30 °C to 650 °C at a rate of 10 °C min^{-1} under air atmosphere. The vacant alumina pan was used as a reference throughout the whole experiment.

Tensile strength (MPa) and elongation at break (%) were measured on a universal material testing machine (H5K-S, Hounsfield) under ambient condition (room temperature, ~65% relative humidity) at a speed of 12 mm min^{-1} with a 5000 N sensor loaded. The mean value was obtained from at least five strip samples with the size of 1 × 5 cm.

2.3. The ion exchange capacity

The ion exchange capacity (IEC, mEq g^{-1}) of the PVA/X-2R membranes was determined by titration method. Square pieces of the membranes were set in 20 mL of a 1 M NaCl solution at room temperature for

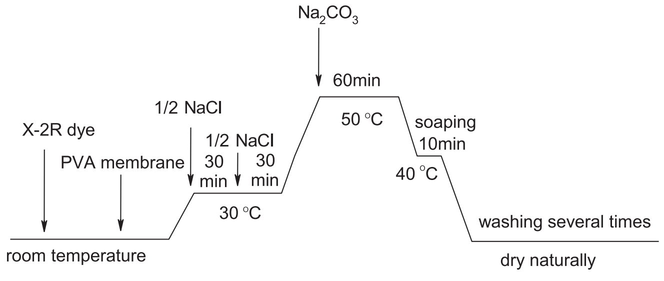

Fig. 3. The curve of the dyeing process for the pristine PVA membrane.