Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Power Sources 145 (2005) 292–297
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

Lignin-based membranes for electrolyte transference

Xiao Zhang [a], Juana Benavente [b], Ricard Garcia-Valls [a,*]

[a] *Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain*
[b] *Department of Applied Fisics, Faculty of Science, University of Málaga, Málaga, Spain*

Accepted 7 February 2005
Available online 1 June 2005

Abstract

Homogeneous PSf-LS membranes are formed by incorporating Lignosulfonate (LS) into the Polysulfone (PSf) network. LS obtained from sulfite pulping process contains sulfonic acid groups that will act as proton transport media. PSf-LS membranes were characterized by reflectance Infrared and scanning electron microscopy. LS showed significant influence on membrane morphology. Higher LS concentration caused a decrease in macrovoid formation and induced larger pores. Precipitation temperature was investigated as influencing parameter. Proton fluxes through PSf-LS membranes were measured by transport experiments. Impedance analysis confirmed that PSf-LS membranes possess ion conductivity. The selected PSf-LS membranes exhibited high selectivity for proton over methanol, which indicates their potential applicability in direct methanol fuel cell (DMFC).

Keywords: Lignosulfonate; Polymer blends; Membrane morphology; Proton conductivity; Selectivity

1. Introduction

As an alternative energy source, polymer electrolyte membrane fuel cell (PEMFC) has developed quickly since 1980s. Hydrogen fuel cell powered electric buses are already running in Canada and USA. A Japanese company has declaimed that in 2005 they are going to put into market a new type mobile phone powered by direct methanol fuel cell (DMFC). Recently, China is backing up this global event and shows its potential in the PEMFC market.

The most important part of PEMFC is the proton transport membrane. At present, there are only few commercial membranes to meet the market, i.e. Nafion® by Du Pont. Nafion is a perfluorosulfonic acid (PFSA)-based polymer. This membrane is still quite expensive. It is commonly used in hydrogen fuel cell. Nafion shows a high methanol cross-over, which limits its application in DMFC due to its consequent lowering of the efficiency, one of the factors in fuel cell implementation. Under this scenario, materials for proton transport membrane have been developed quickly. Many of them are sulfonated polymers and their blends. For example, sulfonated PSf, sulfonated PEEK, sulfonated polyimide among others. Sulfonation provides sulfonic acid groups in the polymer main chain, which improves the proton transport. Usually the sulfonation degree determines the proton transport of the membrane, high sulfonation degree results in high proton transport [1,2]. On the other hand, high sulfonation degree also increases methanol transport since methanol can be transported by electro-osmotic drag and diffusion [3]. Therefore, an optimized sulfonation degree is crucial to control the membrane property.

Instead of modifying polymers by a sulfonation process, our approach to the problem is the application of lignosulfonate (LS) in the preparation of a proton transport membrane. LS is an amorphous, polyphenolic, high cross-linked polymer containing sulfonic acid groups. Its molecular structure is showed in Fig. 1. LS is a by-product of sulfite pulping. Annually a huge amount of LS is produced all around

* Corresponding author. Tel.: +34 977 55 96 11; fax: +34 977 55 85 44.
E-mail address: ricard.garcia@urv.net (R. Garcia-Valls).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.02.052

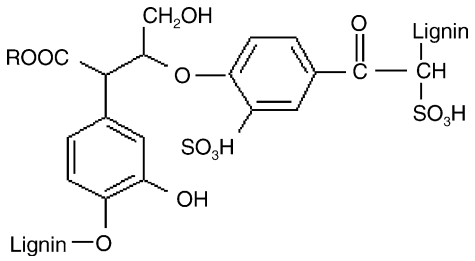

Fig. 1. Molecular structure of LS.

the world. It has application as additive [4], surfactant [5]. LS has also been reported as a component in polymer blends and showed bioactive and biocompatibility [6]. Moreover, LS has applications in blends with thermoplastics [7]. Although LS research is getting more attention, most of LS is incinerated as a waste and it is still a significant environmental burden.

Incorporating LS into PSf matrix to produce membrane provides membrane with proton-affiliated functional groups. The preparation procedure of the membrane can be simple and industry compatible. The membrane price would easily be lower than the commercially available at present. This new exploration of LS application could be of significant improvement from both the economical and environmental point of view.

2. Experimental

2.1. Preparation of PSf-LS membranes

PSf (M_w 35,000) was purchased from Aldrich and LS (7000 g mol^{-1}) was provided by Lignotech. The casting solution was prepared by dissolving LS and 15 wt.% PSf in *N*,*N*-dimethylformamide (DMF) at 35 °C. Then the coating machine spread the casting solution onto a glass surface in a controlled thickness film. The wet film was precipitated in water bath immediately.

We obtained series of PSf-LS membranes (PSf-LS1, PSf-LS2, PSf-LS3) by changing the LS concentration in the casting solution (1, 2 and 3 wt.%, respectively) and the temperature of the water bath.

The obtained membranes were light yellow color. After precipitation, they were kept in distilled water for a week and were daily rinsed before use.

2.2. Membrane characterization

PSf-LS membranes were characterized by reflectance infrared (Bruker-Tensor 27) to demonstrate the incorporation of LS in the membrane.

Cross-section images of PSf blank and PSf-LS membranes were obtained by scanning electron microscopy (SEM, JEOL JSM-6400). The membrane morphologies present in the SEM pictures were analyzed by software IFME® [8].

2.3. Transport experiments

In our research, we are using flux (J mol cm^{-2} s^{-1}) to evaluate the membrane ability for proton and methanol transport. The transport cell includes two compartments, which are separated by the tested membrane [9]. In the case of proton transport, the initial feed was 1.0 M HCl aqueous solution and the stripping was 1.0 M NaCl aqueous solution. The pH value of stripping was measured every 2 s by a Crison Compact Titrator. In the case of methanol transport, the initial feed was 1.0 M methanol aqueous solution and stripping was deionized water. The methanol in the stripping was detected versus time by HPLC (Agilent 1100), using a XDB-C8 column.

Eq. (1) describes permeability coefficient (p, cm^3 cm^{-2} s^{-1}) [10]:

$$-\ln\frac{C_f}{C_0} = \frac{Ap}{V_f}t \tag{1}$$

where C_0 (mol l^{-1}) is the initial concentration of feed, C_f (mol l^{-1}) is the feed concentration calculated through the stripping solution at time t (s). V_f is the feed volume (ml) and A the actual membrane area (cm^2). From Eq. (1) we observe the linear relationship between $-\ln(C_f/C_0)$ and time. The slope of the corresponding plot determines the value of p.

Under steady-state condition, proton and methanol flux were calculated by Fick's First Law:

$$J = \frac{P\Delta C}{l} \tag{2}$$

where, l (cm) is the membrane thickness. ΔC is the concentration difference between the initial feed and the final stripping. In our condition, C_0 is much greater than the final stripping concentration, so we consider $\Delta C \approx C_0$.

P is the permeability (cm^2 s^{-1}), which is defined as:

$$P = pl \tag{3}$$

Then the flux is related to the permeability coefficient:

$$J = pC_0 \tag{4}$$

Selectivity α of proton over methanol is a comprehensive evaluation of membranes and is calculated by Eq. (5):

$$\alpha = \frac{J_{H^+}}{J_{Methanol}} \tag{5}$$

2.4. Impedance spectroscopy

In order to check that the results from transport experiments reflected the intrinsic conductivity of tested membranes, we also measured proton conductivity of some selected hydrated membranes by using impedance spectrometry (Solartron 1260). The cell has two compartments with volume of 10 cm^3 each, the electrode used was Ag/AgCl. Membranes were examined at maximum voltage of 10 mV with the contact solution of 0.1 M NaCl.