Use of Lignosulfonate from Pulping Industrial Waste as a Potential Material for Proton Exchange Membrane in Fuel Cells

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Abstract
Bio-degradable natural materials, instead of synthetic polymers, for value-added applications have gained much attention due to the strong demand for green development. As a waste of pulp industry, converting lignosulfonate for various products has been a hot research topic in material field. Herein, a proton exchange membrane (PEM) for fuel cell is prepared by blending sulfonated poly(ether ether ketone) with lignosulfonate (LS) from pulping waste. The performance of as-prepared membrane is studied. The results indicate that the proton conductivity of the prepared membrane increases with the content of LS increasing in membrane. For as-prepared membrane containing 15% LS, the proton conductivity is remarkably higher than that of membrane fabricated by sulfonated poly(aryl ether ketone) at the same test conditions. Nevertheless, the physical strength decreases as the LS content increases. Comprehensively, the blending membrane containing 15% LS can satisfy the PEM application, which implies that LS should be a potential candidate for PEM application in a low temperature range.

Keywords Lignosulfonate · Pulping waste · Value-added products · Proton exchange membrane · Performance

Statement of Novelty
Blending sulfonated poly(aryl ether ketone) and lignosulfonate from pulping waste without further purification as a material for proton exchange membrane in fuel cell is a...
novel approach. Our results show that lignosulfonate can be used as potential candidate for PEM application.

Introduction

The unrestricted application of fossil fuels results in severe environmental problems such as global warming, energy shortage, toxic chemical pollution etc. One of the strategies to solve those problems is to find renewable energy sources to replace fossil fuels and mitigate environmental crisis.

Fuel cells are important new energy sources, and the proton exchange membrane fuel cell (PEMFC) has received extensive attention, which produces electric power from the fuel cell without discharging green house gases [1–5]. In a fuel cell system, proton exchange membrane (PEM) is a critical component providing proton pathways and preventing permeation of fuel [5–7]. An ideal PEM should meet the demands of low cost, low permeability, good chemical stability, favorable strength, and excellent proton conductivity [8–13]. The traditional membrane materials in PEMFC are perfluorosulfonic polymers like Dupont Nafion [14, 15]. These membranes show favorable performance in fuel cell, but their high cost, high fuel permeability and low proton conductivity have limited their application [16–20]. Sulfonated poly(ether ether ketone) (SPEEK) is well-known for PEM due to its excellent properties such as great thermal stability, low cost, easy preparation, hydrophilicity, stable chemical character, good mechanical strength and good proton conductivity [21–24]. Sulfonic groups (–SO₃H) in SPEEK play a critical role in transmitting hydron, and the amount of –SO₃H groups greatly affects the performance of PEM [25–28].

When used for membrane, polymers with high degree of sulfonation (DS) will lead to high water uptake (WU) and swelling ratio (SR), decreasing the physical strength [29, 30]. Polymer modification is considered as an effective strategy to improve the membrane properties [31]. Another approach is to blend different polymers to produce membrane with excellent properties [32, 33].

There are interests to develop natural polymer-based products, due to high demand for green/sustainable development. Lignin, as one of the main components in lignocellulosic biomass, is a renewable natural polymer. Every year, a huge amount of lignin is produced in the pulp industry, but only a small amount of it is converted to value-added products. Nowadays the conversion of lignin to value-added products has raised much interest among researchers.

Lignosulfonate (LS) is a by-product from the sulfite pulp manufacturing process [34]. Due to containing sulfonic acid group, which increases the activity and water solubility of lignin, LS can be applied in different fields, such as battery additive [35], concrete additive [36], dye dispersant [37], oil drilling additive [38], and adsorbent [39]. Sulfonic acid group can also effectively transmit hydron [25]. In this study, we envisaged and explored the possibility that LS from pulp industry was used as PEM. Therefore, a proton exchange membrane blending lignosulfonate from sulfite pulp plant and SPEEK was synthesized, and then applied as a hydron mediator in the fuel cell. The goal of this study was to identify value-added potential application of by-product (lignosulfonate) from pulp and paper industry.

Materials and Methods

Chemicals and Materials

Dimethyl sulfoxide (DMSO) was provided by Fuyu Chemical Co. Ltd. China. Poly(ether ether ketone) (PEEK) was purchased from Vigers company, Britain. Sulfuric acid was provided by Beijing chemical company, China. Calcium lignosulfonate (LS) was obtained from Shixian Double Deer Company, China. The LS was used directly without purification. Elemental analysis of LS was C: 39.5 wt%, H: 5.36 wt%, N: 0.12 wt%, S: 5.73 wt%.

Preparation of SPEEK

Preparation of SPEEK was conducted as following process similar to previous reports [40, 41]. 4 g of dried PEEK was relaxedly added into 100 mL sulfuric acid (98 wt%) with stirring at 50 °C for 5 h to prepare a homogeneous liquor. After that, the solution was gradually added into the chilled water under the agitation, and then settled overnight. The products were washed several times with deionized water until the pH was neutral. Then the products were dried at 60 °C in a vacuum drying oven for 24 h. The SPEEK (degree of sulfonation (DS), 59%, Titration method) was obtained.

Preparation of SPEEK/LS Composite Membrane

At first, the calcium lignosulfonate was treated with ion exchange resin to replace Ca²⁺ with H⁺ in lignosulfonate. The casting membrane solution was prepared according to following process. The SPEEKs were dissolved in DMSO (5 wt%) at room temperature. A calculated amount of LS was added to the polymer liquor with magnetic stirring for 16 h to form a homogeneous SPEEK/LS solution. The mass ratios of SPEEK to LS were 100/0, 100/5, 100/10, 100/15, and 100/20. Correspondingly, SP-LS-0, SP-LS-1, SP-LS-2, SP-LS-3, and SP-LS-4 were used as symbol for sample membrane, respectively. Afterward, the casting membrane solution was poured onto a clean glass plate to form membrane, followed by drying at 60 °C for 12 h in a vacuum oven. The dried membrane was cooled to room
temperature and immersed in sulfuric acid (1 mol L\(^{-1}\)) for 24 h to obtain active membrane. After that, the prepared membrane was washed with deionize water several times until neutral pH. The prepared membranes were stored in deionized water at room temperature for use. All the prepared membrane was about 50 μm of thickness.

**Characterizations**

Fourier transform infrared spectroscopy (FTIR, IRAffinity-1, Japan) was applied to characterize the chemical properties of membrane. Scanning electron microscope (SEM) (Evo 18, Germany) was employed to analyze the morphology of prepared membranes. Thermal stability was measured by a thermo-analytical instrument (PerkinElmer STA6000, USA) under the \( N_2 \) atmosphere. The samples were heated from 30 to 800 °C at a rate of 10 °C min\(^{-1}\).

**Performance Measurement**

**Water Uptake**

The water uptake (WU) of the synthesized samples was measured by gravimetric method. The prepared samples (2 cm × 1 cm) were dried in drying oven at 60 °C for 24 h and weighed. Then, the dried sample was immersed in deionized water at 20 °C, 40 °C, 60 °C and 80 °C for 16 h to reach saturation. After that, the wet membrane was fetched out, wiped with tissue paper, and weighed. The WU of prepared membrane was calculated as follow:

\[
W_{\text{uptake}} = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100\% 
\]

(1)

where \( w_{\text{wet}} \) and \( w_{\text{dry}} \) are the quality of the membrane after soaking for 16 h and the quality of dry membrane, respectively.

**Swelling Ratio**

The swelling ratio (SR) of membrane was calculated by determining the change of samples thickness under dry and wet conditions. The equation is as follow:

\[
\text{SR\%} = \frac{H_{\text{wet}} - H_{\text{dry}}}{H_{\text{dry}}} \times 100\% 
\]

(2)

where SR\% is swelling ratio, \( H_{\text{dry}} \) and \( H_{\text{wet}} \) are the thickness of membrane before and after immersing in the deionized water.

**Ion Exchange Capacity**

The ion exchange capacity (IEC) was measured with titration method. 1 × 1 cm\(^2\) of dried membrane was weighed then soaked in 1 mol L\(^{-1}\) of NaCl solution for 16 h. The immersing solution was titrated with 0.005 mol L\(^{-1}\) of NaOH. The IEC was calculated as following Eq. (3):

\[
\text{IEC (meq g}^{-1}\text{)} = \frac{M \times n}{G} 
\]

(3)

where \( G \) is the dried weight of prepared membrane, \( M \) and \( n \) are the volume (L) and the concentration (mol L\(^{-1}\)) of NaOH solution, respectively.

**Oxidative Stability**

The oxidative stability of membrane was determined by soaking the prepared membrane in reagent containing 2 ppm ferrous sulfate and 3 wt% H\(_2\)O\(_2\) aqueous solution, stirring at 80 °C for 1 h. The oxidative stability was calculated by the variation of mass [42].

**Mechanical Performance**

The mechanical properties of the fabricated membrane were determined with NWW-10 Universal Testing Machine at room temperature. The sample was cut into dimensions of 10 cm × 5 cm with 50 μm thickness.

**Proton Conductivity**

The proton conductivity of membrane was determined with an electrochemical workstation (CH1760E, Shanghai Huachen instrument, China) at a range from 10 Hz to 1 MHz of frequency. All samples were immersed in deionized water for 16 h before measurement. The result of proton conductivity (\( \sigma \)) was calculated as Eq. (4).

\[
\sigma = \frac{h}{BZ} 
\]

(4)

where \( B \) is the resistance resulted from the sample, \( h \) is the thickness between two platinum electrodes, and \( z \) is the area of sample.

All experiments were repeated three times and the average data was drawn from the calculation results using the collected data.
Results and Discussions

Characterization

The as-prepared membrane was characterized by FTIR spectra. As shown in Fig. 1, a wide peak at 3417–3448 cm⁻¹ is due to stretching of phenolic and aliphatic-OH groups of lignosulfonate [34]. The peak at 1139 cm⁻¹ and 1041 cm⁻¹ are ascribed to the asymmetric and symmetric stretch vibration absorption of S=O bonds of the lignosulfonate. The characteristic peak of the SPEEK membrane at 1647 cm⁻¹ is correlated to the vibration of C=O and the peaks at 1076 and 1010 cm⁻¹ belong to –SO₂H groups of SPEEK [4]. These characteristic peaks are also evident in SPEEK/LS membrane, supporting the conclusion that the SPEEK/LS membrane is successfully prepared.

The morphological analysis was conducted based on SEM technique. The surface images and cross-sectional images of the as-prepared samples are shown in Fig. 2. It is evident that significant differences were presented between images (a) and (b). The cross section of membrane prepared by SPEEK (without LS) keeps compact structure, which

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**Fig. 1** FTIR curves of samples

**Fig. 2** SEM images of as-prepared membrane: cross-sectional images of a SPEEK membrane (without LS), b SPEEK/LS membrane (SP-LS-3); surface images of c upper surface (SP-LS-3), and d bottom surface (SP-LS-3)
is rather homogeneous. Comparatively, for the composite membranes of SPEEK/LS (SP-LS-3), small LS particles are dispersed uniformly in the membrane, and the cross section has a dense structure with rough texture, without distinct separations of LS and SPEEK, implying a good compatibility of the two components. Figure 2c and d present a certain symmetric morphology between upper and bottom surface of blend membrane (SP-LS-3), indicating the good distribution of LS particles in membrane.

The thermal ability of samples was investigated by TGA. As shown in Fig. 3, all the samples exhibit a small weight loss below 100 °C because of desorption of water. Above 100 °C, the curve of LS weight loss demonstrates stages during the decomposition process. Within a range of temperature at 100–200 °C, the weight loss of LS is ascribed to carbon dioxide and volatilization of other products. The decomposition of LS between 200 and 400 °C can be attributable to the benzylic and phenolic hydroxyl groups in LS structure and sulfonation of the polymer [43, 44]. Degradation reactions of aromatic rings are responsible to the LS pyrolysis reaction at temperature more than 400 °C [43]. With the addition of SPEEK, the blend membranes demonstrate lower weight loss relative to LS, indicating an obvious enhancement in the thermal stability of the blend membrane due to the high thermal stability of SPEEK comparing with LS.

**Performance Measurement**

Water uptake (WU) has big impacts on dimensional stability, physical strength and proton conductivity of membrane. In general, the presence of water in membrane has a positive effect on the proton transports, and can improve the proton conductivity. Those shown in Figs. 4 and 5 are the results of the water uptake (WU) and swelling ratio (SR) of SPEEK/SL membrane as a function of testing temperature, respectively.

In Fig. 4, it is evident that the WU of membrane increase with temperature and LS content in the SPEEK/LS membrane. In Fig. 5, the same tendency is shown for SR. The reasons for these phenomenons is that the mobility of ionomer and the free volume for water absorption increase with an increase in temperature [45, 46]. Meanwhile, the strongly hydrophilic sulfonate groups existing in the prepared membrane, are responsible for the increased WU and SR.

IEC is a vital factor for the performance analysis of PEM, and directly related to the proton conductivity. The IEC results are presented in Table 1. It can be observed that IEC values are in the range of 1.39–2.20 meq g⁻¹, and the blend samples display higher IEC values comparing with the pure SPEEK membrane. And ICE values increase with
the increasing content of LS in composite membrane, which increase from 1.20 meq g⁻¹ of pure SPEEK membrane to 2.20 meq g⁻¹ of blend membrane containing 20% of LS. This result can be ascribed to the increase of –SO₃H groups in the samples, which facilitates the transmitting hydron across the membrane.

The oxidative stability was estimated by the remaining weight (RW, wt%) of blend membrane after treated with a Fenton’s reagent at 80 °C for 1 h. Table 1 exhibits the RW (%) of the sample membranes as a function of the LS content. It is found that the oxidative stability of sample membrane decrease with the increase in the LS content. At a 15% LS content (the SP-LS-3 sample), the RW (%) is 77.9%. The addition of more LS leads to more degradation under the testing condition.

The effect of LS addition to membranes on mechanical strength was summarized in Table 2. It can be seen that, with the adding content of LS increase from 5 to 20%, the tensile strength of blend sample decreases from 32.4 to 18.5 MPa, Young’s modulus decreases from 1.90 to 1.19 GPa, and elongation at break decreases from 10.17 to 6.49%, respectively. The drop of the mechanical strength attributes to the increase of the content of hydrophilic LS in blend membrane, which enhance water uptake, and weaken the hydrogen bonding between SPEEK and LS.

Proton conductivity is the one of the most important factor for PEM performance. Figure 6 shows the proton conductivities of prepared membrane at different temperature.

### Table 1 The IEC and remaining weight (RW) of prepared membrane

| Sample   | IEC (meq g⁻¹) | Thickness (μm) | RW (%)   |
|----------|---------------|----------------|----------|
| SP-LS-0  | 1.20 ± 0.32   | 49.0 ± 0.3     | 96.4 ± 2.5|
| SP-LS-1  | 1.39 ± 0.21   | 50.0 ± 1.2     | 93.8 ± 3.2|
| SP-LS-2  | 1.58 ± 0.42   | 50.2 ± 0.8     | 87.9 ± 2.8|
| SP-LS-3  | 1.94 ± 0.23   | 50.5 ± 1.0     | 77.9 ± 4.2|
| SP-LS-4  | 2.20 ± 0.18   | 51.0 ± 0.7     | Dissolving|

### Table 2 The mechanical properties of prepared membrane

| Samples  | Tensile strength (MPa) | Young’s modulus (GPa) | Elongation at break (%) |
|----------|------------------------|-----------------------|-------------------------|
| SP-LS-0  | 32.4 ± 1.3             | 1.90 ± 0.6            | 10.17 ± 1.8             |
| SP-LS-1  | 30.5 ± 2.1             | 1.73 ± 0.3            | 9.25 ± 2.4              |
| SP-LS-2  | 26.4 ± 3.5             | 1.64 ± 0.7            | 8.89 ± 1.2              |
| SP-LS-3  | 23.7 ± 1.8             | 1.41 ± 0.3            | 7.36 ± 0.8              |
| SP-LS-4  | 18.5 ± 2.4             | 1.19 ± 0.6            | 6.49 ± 1.7              |

0% SL to 0.08628 S cm⁻¹ for containing 20% LS at 20 °C. Similarly, the proton conductivity of prepared membrane increases with the temperature increasing. When the blend membrane contains 15% LS (SP-LS-3), the proton conductivity increases from 0.06369 to 0.24391 S cm⁻¹ at the range of 20–80 °C. Similar results were reported previously. For instance, Xing et al. [47] displayed that, at the range of 25–80 °C, the proton conductivities of membrane fabricated by sulfonated poly(aryl ether ketone) increased from 0.042 to 0.11 S cm⁻¹, which are deemed to meet the application of PEM in fuel cells.

Except for the membrane containing 20% LS, the proton conductivity of all PEM containing LS begins to decrease when the temperature is higher than 80 °C. The reason for this phenomenon may be that the LS begins to partially dissolve with the temperature increasing, so that the cross-sectional area of proton channel in PEM decreases and the resistance increases for proton transfer. For membrane containing 20% LS, the proton conductivity begins to decline as the temperature is higher than 60 °C, which may be on account of the dissolution and aggregation of higher concentration of hydrophilic LS in the membrane, simultaneously.

The prepared PEM demonstrates higher proton conductivity than other PEMs reported in the papers, as shown in Table 3. As discussed, the PEM obtained by blending SPEEK and LS, has larger water uptake, IEC and proton conductivity, lower oxidative stability and mechanical strength, both of which contribute to more hydrophilic lignosulfonate in the PEM prepared in this work, thus responsible for the characteristics mentioned above.

The synthetic route and proton transport in PEM are described in Fig. 7. Proton transmission needs pathway provided by water, and proton conductivity increases with the amount of water increasing in PEM [50]. In this work, high
proton conductivity attributes to the increasing of hydrophilic LS in blend membrane.

**Conclusions**

The lignosulfonate from sulfite paper industry waste was studied as part of the raw material for proton exchange membrane for PEMFC, and they were prepared by blending SPEEK and various amounts of LS. The results showed that LS significantly improve water uptake, swelling ratio, IEC and proton conductivity. The SO₃H-group is the main factor for increasing the proton conductivity of the composite membrane due to more proton carrier sites provided. Additionally, hydrophilic SO₃H-group accelerates the high degree of water uptake, which leads to proton conductivity increase. But high degree of water uptake decreases the dimensional stability and physical strength. Therefore, more amounts of LS are not suitable for use in PEM. Comprehensive, the prepared membrane containing 15% LS meets the need of proton membrane application. As a green and renewable biomass, lignosulfonate from pulp industry can be used as potential candidate for PEM application in a low temperature range as supported by this research work.

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