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

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Abstract

A polymer membrane as a proton exchange membrane (PEM) used in fuel cell is prepared by blending lignosulfonate (LS) from sulfite pulp industrial waste with sulphonated poly (ether ether ketone) (SPEEK). Different contents of LS ranging from 0 to 20% (w/w) were blended with SPEEK to measure the influence of LS content on performance of membrane. The results indicated that the proton conductivity of the prepared membrane was increased with the content of LS 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 decreased as the LS content increased. Comprehensively, the blending membrane containing 15% LS can satisfy the PEM application, which implies LS as a potential candidate for PEM application in a low temperature range.

Statement Of Novelty

Lignosulfonate from pulping waste 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 as energy results in severe environmental problems such as global warming, energy shortage, toxic chemical pollution etc. One of the approaches to those problems is to find sources of renewable energy alternative to fossil fuels. Simultaneously, clean production could satisfy the demand to mitigate environmental crisis.

As a significant new source of energy, the fuel cell has attracted extensive attention because it generates electric power from the fuel cell without emission of greenhouse gases [1–5]. In a fuel cell, proton exchange membrane (PEM) plays a vital role by providing hydron pathways and prevents permeation of fuel [1, 6–7]. A good 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 used as PEM are perfluorosulfonic polymers like Dupont Nafion [14–15]. These membranes demonstrate favorable performance in fuel cell. But their high cost, high fuel permeability and low proton conductivity have restricted their application [16–20]. Sulphonated poly (ether ether ketone) (SPEEK) is a good polymer as PEM due to its low cost, stable chemical character and good mechanical strength [21–24]. Sulfonic groups ($-\text{SO}_3\text{H}$) in SPEEK play a critical role in transmitting hydron [25], and the amount of $-\text{SO}_3\text{H}$ groups greatly affects the performance of PEM [26–28].

Polymers with high degree of sulfonation (DS) will result in high water uptake(WU) and swelling ratio(SR), and then decrease the physical strength because of the high hydrophilic characteristic of sulfonic groups. Polymer modification is considered as an effective strategy for improvement of the membrane

performances [29]. Another approach is to blend different polymers to fabricate membrane with excellent properties. [30–31].

There are interests to develop natural renewable polymer-based products due to high demand for green/sustainable development. Lignin, as one of the main components in lignocellulosic materials, is a natural and renewable polymer. Annually, high amounts of lignin is produced in the pulp mills, but a small percentage of it is reused. Nowadays the conversion of lignin into value-added products has raised much interest among researchers.

Lignosulfonate (LS) is a by-product from the sulfite pulp manufacturing process [32]. LS contains sulfonic acid group, which increases the activity and water solubility of lignin. LS can be applied in different fields, such as battery additive [33], concrete additive [34], dye dispersant [35], oil drilling additive [36], adsorbent [37]. Sulfonic acid group can also effectively transmit hydron [25]. In this work, we synthesized a proton exchange membrane by blending lignosulfonate from sulfite pulp mill and sulphonated poly (ether ether ketone), which was then applied as a hydron mediator in fuel cell. The purpose of this work is to identify value-added potential application of by-product (lignosulfonate) from pulp and paper industry.

Material And Methods

Chemicals and materials

Dimethyl sulfoxide (DMSO) was provided by fuyu chemical Co. Ltd. China. Poly (ether ether ketone) (PEEK) was provided by Vigers company, Britain. Sulfuric acid was provided by Beijing chemical company, China. Calcium lignosulfonate (LS) was obtained from Shixian Double Deer Company, China.

Preparation of SPEEK

Preparation of SPEEK was conducted following process similar to previous reports [38–39]. 4g PEEK was slowly added into 100ml sulfuric acid (98 wt%) and was stirred at 50°C for 5h to prepare a homogeneous liquor.

The liquor was added into the chilled water with agitation, and then settled overnight. The deionized water was used to wash products till neutral pH. After that, a vacuum drying oven was used to dry the products at 60°C for 24h. The SPEEK with 59% of DS (Titration method) was obtained.

Preparation of SPEEK / LS composite membrane

At first, the calcium lignosulfonate was treated with ion exchange resin to replace Ca^{2+} with H^+ in lignosulfonate. The casting membrane solution was prepared according to following process. The SPEEKs were dissolved in DMSO (5 wt%) at ambient temperature. A pre-determined content of LS was poured into each polymer liquor with magnetic agitation for 16h to form a homogeneous SPEEK/ LS solution. The mass ratios of SPEEK to LS were 100/0, 100/5, 100/10, 100/15, 100/20. Correspondingly,

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SP-LS-0, SP-LS-1, SP-LS-2, SP-LS-3, SP-LS-4 were used as symbol for sample membrane, respectively. Afterward, the casting membrane solution was poured on a glass sheet to form membrane. Then, a vacuum drying oven was used for drying the prepared membrane at 60 °C for 12h. The dried membranes were cooled to room temperature and immersed in sulfuric acid (1mol L⁻¹) for 24h to obtain active membrane. After that, the prepared membrane was washed by deionize water several times till neutral pH. The prepared membranes were stored in deionized water for next application. All prepared membrane was about 50 μm of thickness.

Characterizations

Fourier transform infrared (FTIR, IRAffinity-1, Japan) characterization was applied for analyzing the chemical properties of membrane. The morphological characteristics of prepared samples were determined using Scanning Electron Microscope (SEM) (Evo 18, Germany).

Performance measurement

Water uptake

The water uptakes (WU) of synthesized samples were measured using gravimetric method. The prepared samples (2cm×1cm) were dried with a drying oven at 60°C for 24h, then measured their dry weight. Subsequently, the dried samples were dipped in deionized water at 20°C, 40°C, 60°C and 80°C for 16h until the membranes reach saturation. Then, the wet membranes were taken out and removed the surface moisture of sample by filter paper and determined wet mass. The WU of prepared membrane was obtained by Eq. (1):

$$w_{uptake} = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100\%$$

1

Where w_{dry} is the mass of the dry membrane and w_{wet} is the mass of membrane after 16h soaking, respectively.

Swelling ratio

The swelling ratio (SR) of membrane was measured through the change of samples thickness of dry and wet state. The equation is as follow:

$$SR\% = \frac{H_{wet} - H_{dry}}{H_{dry}} \times 100\%$$

2

Where SR% is swelling ratio, H_{dry} is the thickness of dry sample, H_{wet} is the thickness of wet sample, respectively.

Ion exchange capacity

The ion exchange capacity (IEC) was detected with titration method. $1 \times 1 \text{ cm}^2$ of dried membranes were weighted and then dipped into NaCl solution (1 mol L^{-1}) for 16h. 0.005 mol L^{-1} NaOH was used to titrate the immersing solution. The IEC data was obtained based on the Eq. (3):

$$\text{IEC} \left(\text{meqg}^{-1} \right) = \frac{M \times n}{G}$$

3

Where G is the dried mass of prepared membrane. n is the concentration (mol L^{-1}) of NaOH, and M is the volume (L) of NaOH solution.

Oxidative stability

The oxidative stability of membrane was determined by soaking the prepared membrane in reagent containing 2 ppm ferrous sulfate and 3wt% H_2O_2 aqueous solution, stirring at 80°C for 1h. The results were calculated by the variation of mass [40].

Mechanical performance

The mechanical performances of the fabricated membrane were determined with NWW-10 Universal Testing Machine at ambient temperature. The prepared membranes were cut into dimensions of $10 \text{ cm} \times 5 \text{ cm}$ with $50 \mu\text{m}$ thickness.

2.5.6 Proton conductivity

The proton conductivity of membrane was determined with an electrochemical workstation (CH1760E, Shanghai Huachen instrument, China) with 10Hz to 1M Hz of frequency. Before determination, all prepared samples were dipped in deionized water and lasted for 16h. The results were obtained 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.

Results And Discussions

Characterization

Chemical component of as-prepared membrane was analyzed by FTIR spectroscopy. The results are presented in Fig. 1. In Fig. 1, it is noticed that an emerged peak at $3417\text{--}3448\text{ cm}^{-1}$ is correlated with the phenolic and aliphatic-OH groups of lignosulfonate [32]. The S = O bonds in the lignosulfonate is corresponded to the absorption of peaks observed at 1139 cm^{-1} and 1041 cm^{-1} . The bond of C = O is responsible for the characteristic peak at 1647 cm^{-1} , the peak of samples at 1076 and 1010 cm^{-1} relate to $\text{--SO}_3\text{H}$ groups of SPEEK [4]. These characteristic peaks also appear in SPEEK/LS membrane, supporting the conclusion that the SPEEK/LS membrane is fabricated successfully.

The morphological analysis was conducted by SEM technique. The cross-sectional images of the SPEEK/LS samples are exhibited in Fig. 2. It is evident that significant differences were presented between images (a) and (b). The transection of membrane prepared by SPEEK (without LS) keeps compact structure, which is rather homogeneous. Comparatively, for the composite membranes of SPEEK/LS (10% LS content), the cross section has a dense structure with rough texture, without distinct separations of LS and SPEEK, implying a good compatibility of the two.

Performance measurement

Water uptake (WU) significantly affects the shape stability, physical strength and proton conductivity of membrane. In general, the water existing in membrane has an advantageous effect on the hydron transmission and can improve the proton conductivity. Figure 3 and Fig. 4 exhibit the water uptake (WU) and swelling ratio (SR) of SPEEK/SL membrane at various temperature, respectively.

In Fig. 3, it is demonstrated that WU of membrane increase with temperature and LS amount in the SPEEK/LS membrane. In Fig. 4, the same phenomenon is shown for SR. The strongly hydrophilic sulfonate groups existing in the prepared membrane, are responsible for the increased WU and SR.

Ion Exchange Capacity (IEC) is a vital factor for the performance of PEM, and it is directly related to the content of proton exchangeable groups of membranes. Table 1 presents the IEC results of membrane. It can be shown that the blend sample displays higher IEC values comparing with the pure SPEEK membrane. And ICE values increase with the increasing LS content, which increase from the 1.20 meq g^{-1} of pure SPEEK membrane to 2.20 meq g^{-1} of blend membrane with 20% LS. This result can be ascribed to the increase of $\text{--SO}_3\text{H}$ groups in the samples, which facilitate the transmitting hydron across the membrane.

The remaining weight (RW, wt%) is employed to estimate the oxidation stability of prepared samples after dealing with a Fenton's chemicals at 80°C for 1h. Table 1 exhibits the RW (%) of the samples as a function of the LS amount containing in membrane. It was noticed that the oxidative stability of sample decreased as the LS content increase. At a 15% LS content (the SP-LS-3 sample), the RW (%) is 86.3%.

The addition of more LS leads to rapid degradation of the SPEEK/LS membrane under the testing condition.

Table1. The IEC and remaining weight (RW) of prepared membrane

Sample	IEC (mmol g ⁻¹)	Thickness (μm)	RW (%)
SP-LS-0	1.20	49.0	96.4
SP-LS-1	1.39	50.0	93.8
SP-LS-2	1.58	50.2	87.9
SP-LS-3	1.94	50.5	77.9
SP-LS-4	2.20	51.0	—

Mechanical property of membranes has a remarkable impact on performance of PEM. The influence of LS addition to blend membrane on mechanical strength is summarized in Table 2. The results demonstrate that the tensile strength (TS) of blend sample decreases following the increase of LS amount. The drop of the mechanical strength attributes to the increase of hydrophilic LS in blend membrane, which enhance water uptake and, weaken the hydrogen bonding between SPEEK and LS. In addition, the SP-LS-3 membrane shows the Tensile stress of 23.7MPa, which exceed that of the Nafion 117 presented in paper (less than 20MPa) [4]. Young’s modulus decreases from 1.73 to 1.19 GPa with the increase of LS content from 5 to 20%. Likewise, elongation at break decreases from 9.25 to 6.49% in the range of 5–20% LS content.

Table2. The mechanical properties of prepared membrane

Samples	Tensile strength (MPa)	Young’s modulus (GPa)	Elongation at break (%)
SP-LS-0	32.4	1.90	10.17
SP-LS-1	30.5	1.73	9.25
SP-LS-2	26.4	1.64	8.89
SP-LS-3	23.7	1.41	7.36
SP-LS-4	18.5	1.19	6.49

For PEM performance, proton conductivity is a vital factor for PEM performance evaluation. The results on proton conductivity of sample are exhibited in Fig. 5. The proton conductivity of samples demonstrates a remarkable increase as LS content increase in Fig. 5. For instance, the proton conductivity of samples increases from $0.00586 \text{ S cm}^{-1}$ for containing 0% SL to $0.08628 \text{ S cm}^{-1}$ for containing 20% at 20°C . Similarly, the proton conductivity of prepared samples increases as temperature increase. When the blend membrane at 15% LS (SP-LS-3), the proton conductivity increase from $0.06369 \text{ S cm}^{-1}$ to $0.24391 \text{ S cm}^{-1}$ at the range of $20\text{--}80^{\circ}\text{C}$, as presented in Fig. 5. Similar results were reported previously. For instance, Xing et al [41] displayed that, at the range of $25\text{--}80^{\circ}\text{C}$, the proton conductivities of membrane fabricated by sulfonated poly (aryl ether ketone) increased from 0.042 S cm^{-1} to 0.11 S cm^{-1} , which are deemed to satisfy the application of PEM in fuel cell.

The proton transport in PEM is described in Fig. 6. Proton transmission needs pathway provided by water, and proton conductivity increases with the amount of water increasing in PEM [42]. In this work, high proton conductivity attributes to the increasing of hydrophilic LS in blend membrane.

Conclusions

The lignosulfonate from sulfite paper mill waste is successfully applied in proton membrane through blending with SPEEK. The SO_3H - group is the main factor for increasing the proton conductivity of the composite membrane due to more proton carrier sites provided. Additionally, hydrophilic SO_3H - group accelerates the high degree of water uptake, which leads to proton conductivity increase. But high degree water uptake decreases the dimensional stability and physical strength. Comprehensively, the prepared membrane containing 15% LS meets the need of proton membrane application. As a green and renewable biomass, lignosulfonate can be used as potential candidate for PEM application in a low temperature range as supported by this research work.

Declarations

All manuscripts must contain the following sections under the heading 'Declarations'.

If any of the sections are not relevant to your manuscript, please include the heading and write 'Not applicable' for that section.

To be used for all articles, including articles with biological applications

Funding (information that explains whether and by whom the research was supported)

Not applicable

Conflicts of interest/Competing interests (include appropriate disclosures)

Not applicable

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Availability of data and material (data transparency)

Not applicable

Code availability (software application or custom code)

Not applicable

Authors' contributions (optional: please review the submission guidelines from the journal whether statements are mandatory)

Hunan Liang, contributed to the conception of the study;

Guodong Zhu performed the experiment;

Yan Li contributed significantly to analysis and manuscript preparation;

Dayu Yu performed the data analyses and wrote the manuscript;

Wei Shang helped perform the analysis with constructive discussions.

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Figures

Figure 1

FTIR curves of samples

Figure 2

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Cross-sectional images of (a) SPEEK membrane (without LS), (b) SPEEK/LS membrane (a 10% LS content).

Figure 3

Water uptake of prepared membrane at different temperature

Figure 4

Swelling ratio of prepared membrane at different temperature

Figure 5

Proton conductivities of prepared membrane at different temperature

Figure 6

Schematic of proton transport in SPEEK/LS membrane

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