

Supplementary Information

A novel green Lignosulfonic acid/Nafion composite membrane with reduced cost and enhanced thermal stability

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Experimental section

Materials and methods

Nafion solution (D2020) and Nafion 211 membrane were supplied by DuPont. HCl, N-N-Dimethylacetamide (DMAc, 99% purity) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium lignin sulfonate was purchased from Shanghai Yuanye Biotechnology Co., Ltd. All commercially available chemicals were used without further purification.

Synthesis of lignosulfonate acid (LSA)

An appropriate amount of sodium lignosulfonate powder was added into deionized water at room temperature, and the solution was fully stirred to obtain the aqueous solution of sodium lignosulfonate. Then, 10% hydrochloric acid solution was slowly added into the above solution until the pH was 2. After reaction for 2 h, the LSA was collected by low-speed centrifugation and washed repeatedly with water. The solution was centrifuged to collect the precipitate and freeze-dried to obtain LSA powder.

Synthesis of Nafion/LSA composite membrane

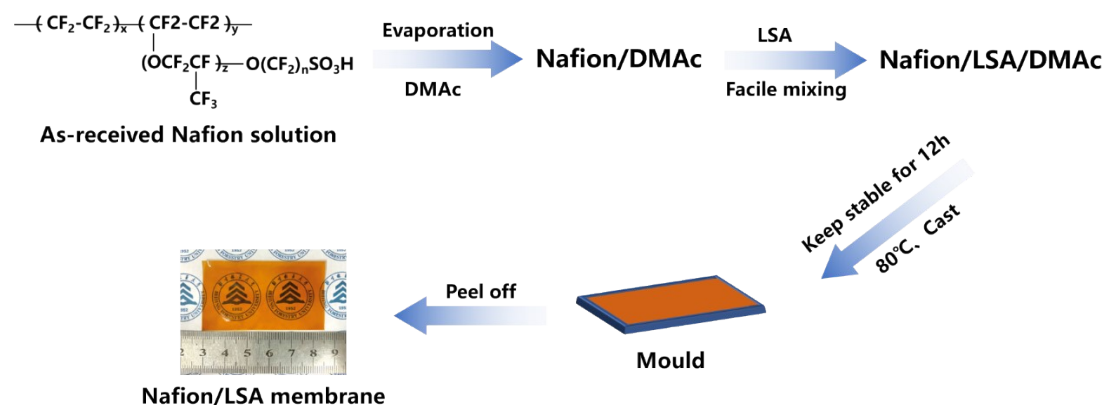


Fig. S1 Preparation procedures of Nafion/LSA composite membrane.

Fig. S1 presents the typical preparation procedure of the Nafion/LSA composite membrane. The preparation of Nafion/LSA composite membranes was as follows: 1) 10 mL of 20% Nafion solution (D-2020) was dried at 60 °C to evaporate the solvent and weighed; 2) Then dissolve 0.38 g Nafion resin in 8 mL DMAc solution to form a uniform casting solution (0.40 g Nafion resin in 8 mL DMAc solution to prepare recast Nafion); 3) 20 mg LSA was added into the above Nafion solution to form a homogeneous Nafion/LSA mixture, with sonication for 30 min

and magnetic stirring for 6 h; 4) Then Nafion/LSA solution was cast on a glass plate and then heated at 80 °C for 12 h to form a uniform membrane; 5) before use, the membrane was peeled off from the glass plate and soaked in deionized water for 24 h. For comparison, a recast Nafion membrane and Nafion 211 membrane were also immersed in deionized water for 24 h before use. Based on the loaded mass of LSA (the mass ratio of LSA instead of Nafion), the as-prepared membrane was named Nafion/LSA-5 composite membrane (for short Nafion/LSA-5). Other composite membranes were named Nafion/LSA-10, Nafion/LSA-15, Nafion/LSA-20. The thickness of the Nafion membrane and Nafion/LSA composite membranes were $25 \pm 5 \mu\text{m}$.

Characterizations

A field-emission scanning electron microscopy (FESEM) was used to observe the microstructure of the as-prepared membranes. FT-IR was carried out on Nafion and Nafion/LSA-10 membranes to verify the introduction of LSA into the polymer matrix. The spectra were recorded in the wavenumber ranging from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} .

The mechanical properties of the as-prepared membranes were obtained in an Instron Micro Tester 5848 at a tensile speed of 5 mm/min. The stretched size of the dried sample is 20mm×10mm. To reduce the testing error, five replicates of each sample were tested, and the average and standard deviation were calculated accordingly.

The membranes were completely dried in a vacuum at 60 °C, weighted, and immersed in DI water for 48 h. Subsequently, the saturated membranes were re-weighted after removing the surface-adsorbed water by filter paper. The water uptake tests were conducted three times for each membrane, and the results are expressed in terms of the mean. Water uptake was calculated as follows,

$$\text{Water Uptake} = \frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \times 100\%$$

(1)

where M_{wet} and M_{dry} are the weights of saturated and dried Nafion membranes.

The membrane specimens (40 mm×50 mm) were dried at 80 °C for 12 h, and the distance between two specified positions was measured (L_1). The measurement was repeated after the

membranes were soaked in water at 60 °C for 12 h (L_2). The swelling of the membranes was calculated as follows,

$$\Delta L(\%) = \frac{L_2 - L_1}{L_1} \times 100\%$$

(2)

where ΔL is the dimensional change of the membrane.

Thermogravimetric analysis (TGA) was carried out using a Discovery TGA 550 instrument under a N_2 atmosphere in the temperature range of 25-700 °C.

The IEC of samples was calculated by back-titration method. Before each test, all membranes were dried under vacuum at 80°C for 12 h. In this procedure, dried samples were immersed in saturated sodium chloride solutions at room temperature for 24 h to ensure that all protons were exchanged, after which the solution was titrated with 0.01 M sodium hydroxide solutions. A pH meter was used to monitor the pH values of solutions. The IEC values were calculated by the following equation,

$$IEC(m\ mol \cdot g^{-1}) = \frac{C_{NaOH} \times V_{NaOH}}{m_{dry}} \quad (3)$$

where C_{NaOH} is the molar concentration of the NaOH solution, V_{NaOH} is the volume of the NaOH solution, m_{dry} is the dry mass of the membrane.

Proton conductivities of the membranes were measured by an AC impedance technique in the frequency range of 1 Hz and 100 kHz. The prepared membranes (2 cm×2 cm) were stuck on the electrodes of two platinum sheets. Then the two platinum electrodes together with the membrane samples were sandwiched between two polysulfone sheets. The proton conductivity (σ) of the membrane was calculated according to the following equation:

$$\sigma = \frac{L}{R \times W \times T}$$

(4)

where σ is the proton conductivity, L is the length between the platinum electrodes, R is the measured resistance of the membrane, W is the width of the membrane, and T is the membrane thickness.

The activation energy (E_a) of the samples was calculated from the above conductivity data (σ) in the range of 30-80 °C at 100% RH using the Arrhenius equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where σ is the proton conductivity in membranes (in S cm⁻¹), σ_0 is a preexponential factor, E_a is the activation energy of the proton hopping (in KJ mol⁻¹), R is the universal gas constant (8.31 J mol⁻¹ K⁻¹), and T is the absolute temperature (in kelvin).

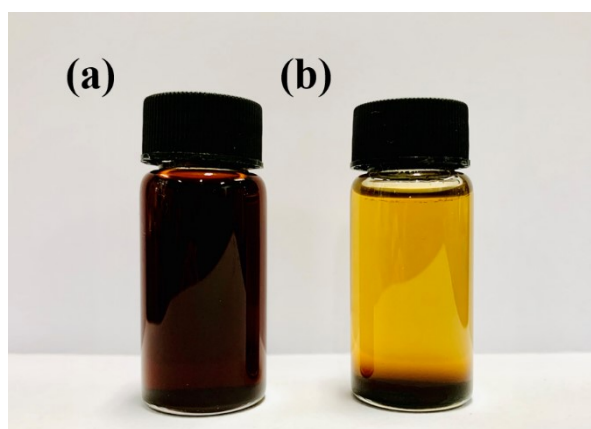


Fig. S2 Solubility of Lignosulfonic Acid (a) and Sodium Lignosulfonate (b) in DMAc.

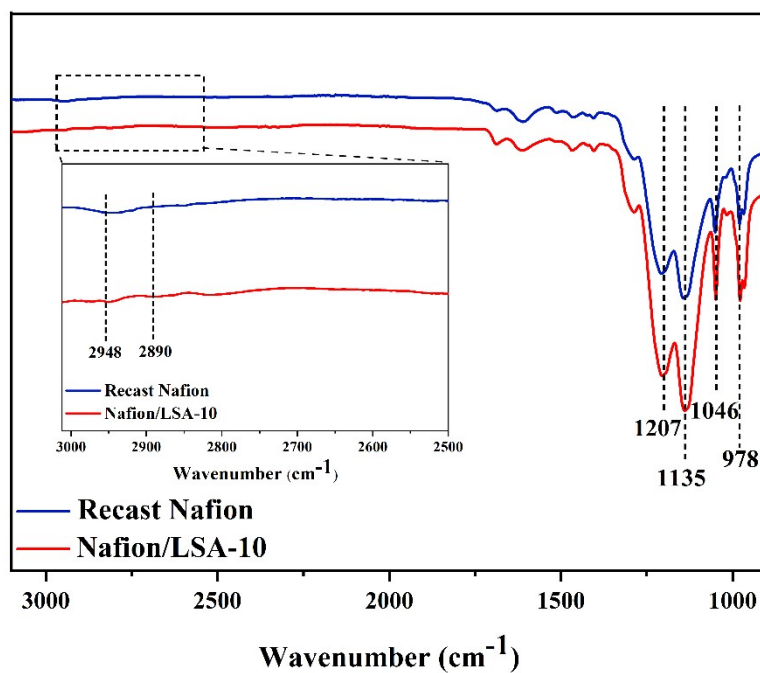


Fig. S3 FT-IR spectra of recast Nafion membrane and LSA/Nafion composite membrane.

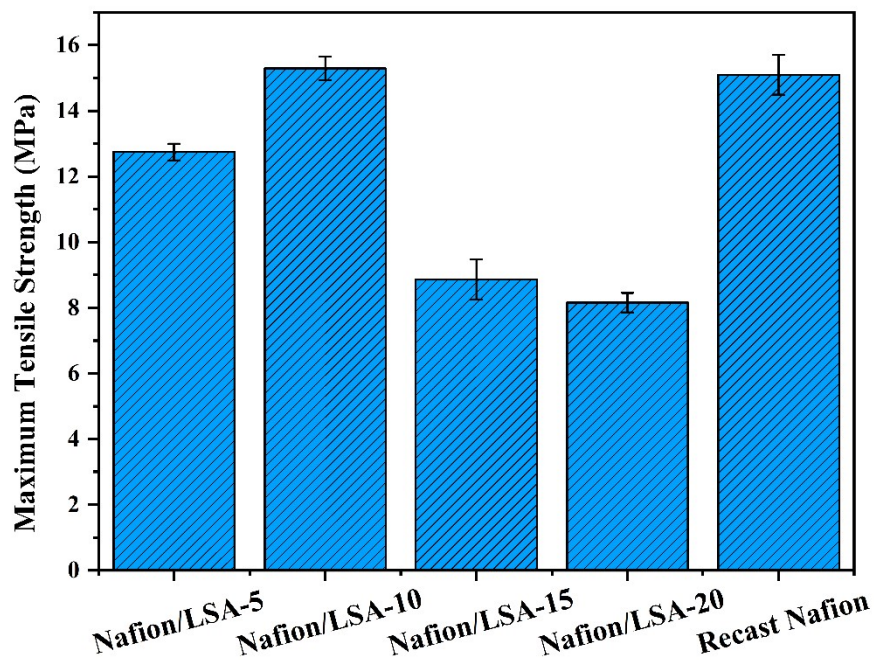


Fig. S4 Maximum tensile properties of recast Nafion membrane and composite membranes with different LSA contents.

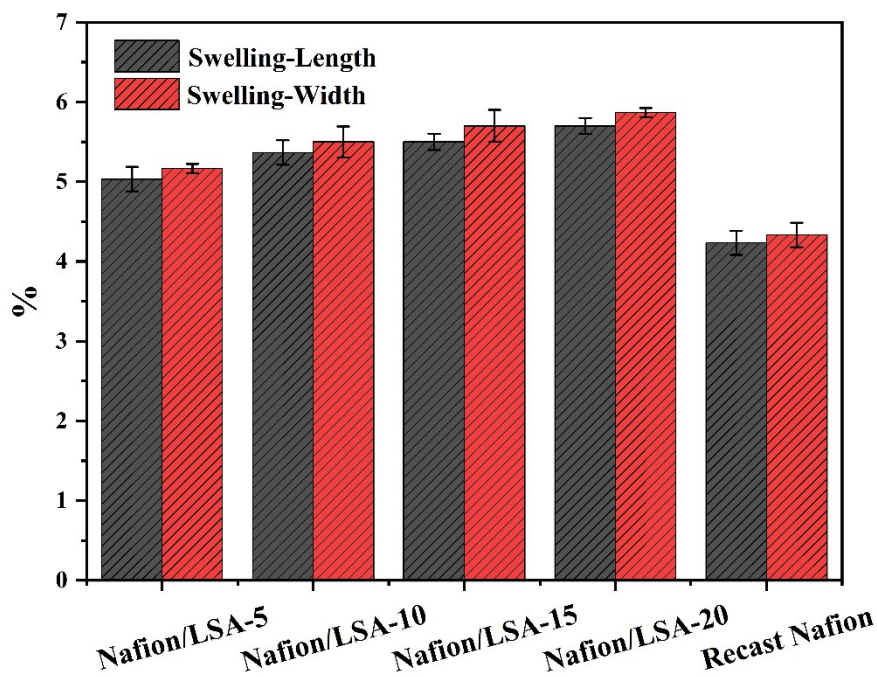


Fig. S5 Swelling of the recast Nafion membrane and composite membranes with different LSA contents.

Table S1. The thickness, IEC, WU, and cost estimation of different membranes (The total cost of a fuel cell powered truck is assumed to be 200K USD, the fuel cell systems account for 40% of the cost^{1,2}).

Membranes	Thickness (μm)	IEC (mmol/g)	WU (%)	Cost (USD)
Nafion 211	25.4	0.95~1.01	14.96	>10000
Nafion/LSA-10	26.4	1.15-1.17	14.61	<9000

[1] Khzouz, M.; Gkanas, E.; Shao, J.; Sher, F.; Beherskyi, D.; El-Kharouf, A.; Al Qubeissi, M., Life Cycle Costing Analysis: Tools and Applications for Determining Hydrogen Production Cost for Fuel Cell Vehicle Technology. *Energies* **2020**, *13* (15).

[2] Zhang, C.; Greenblatt, J. B.; Wei, M.; Eichman, J.; Saxena, S.; Muratori, M.; Guerra, O. J., Flexible grid-based electrolysis hydrogen production for fuel cell vehicles reduces costs and greenhouse gas emissions. *Appl. Energy* **2020**, 278.