Supporting Information for

A low-cost green lignosulfonic acid/sulfonated poly (ether ether ketone) composite membrane for iron-chromium redox flow batteries with high performance

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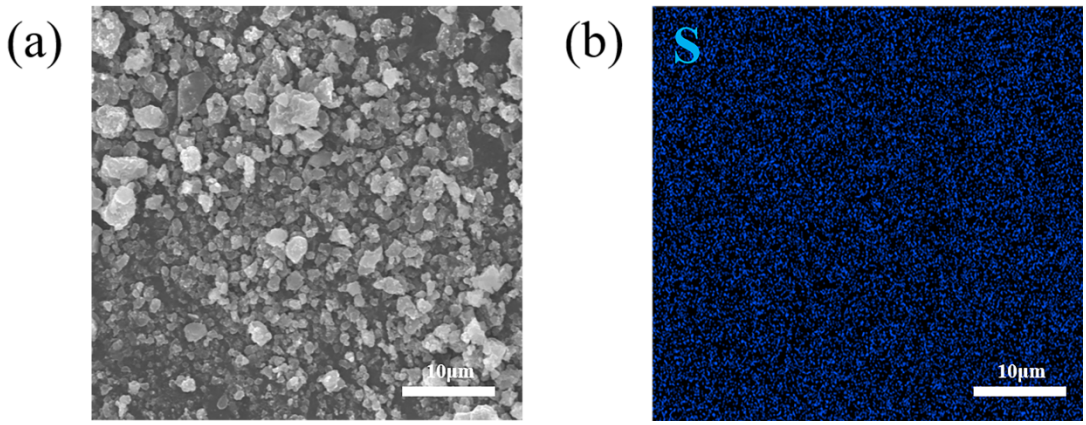

Fig. S1. Micrographs: (a) SEM image of LSA powder; and (b) EDS image of element S.

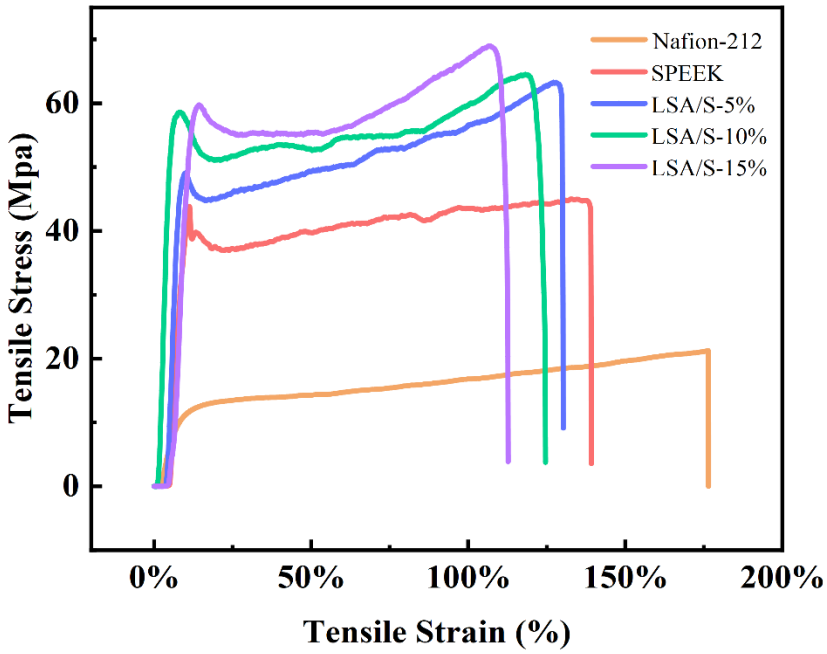

Fig. S2. Stress-strain curves for different IEMs.

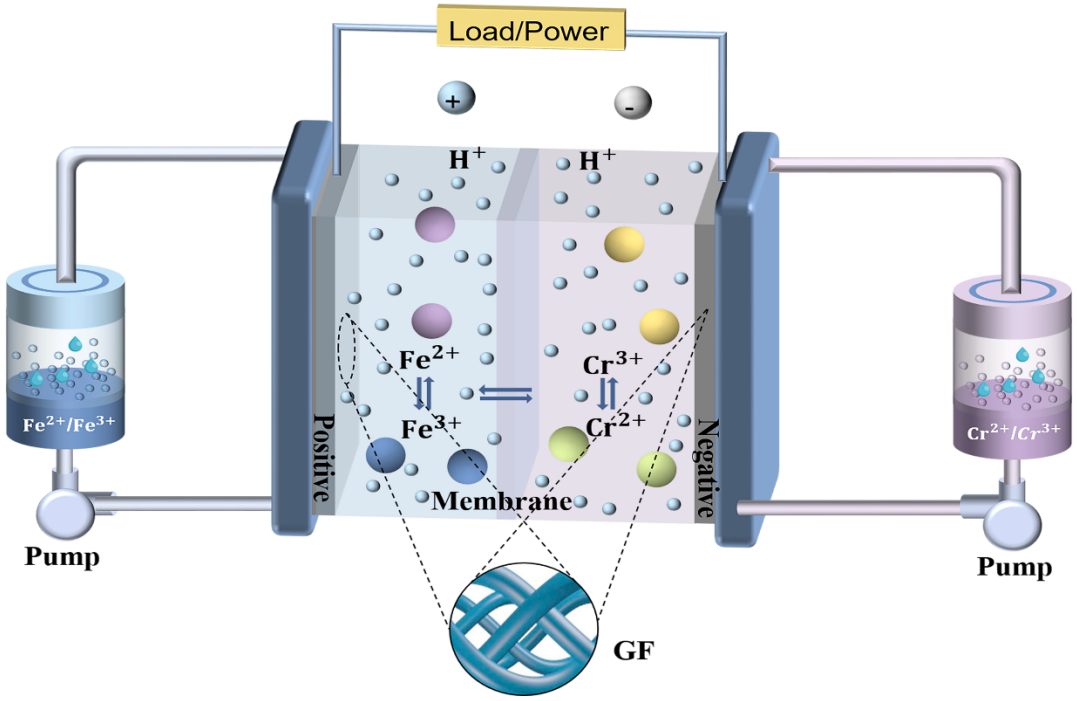

Fig. S3. Schematic diagram of ICRFB principle structure.

Table S1. Stacking resistance of single cells with different IEM.

IEMs	Nafion-212	SPEEK 57	LSA/S-5	LSA/S-10	LSA/S-15	LSA/S-20
Stack resistance (mΩ)	38.54	42.27	43.36	44.22	45.74	47.69

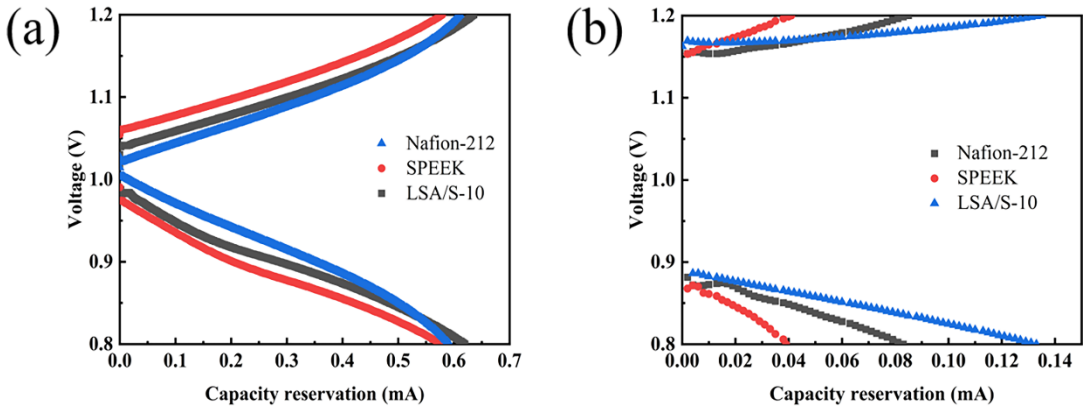

Fig. S4. Performance images of 100th charge/discharge cycles : (a) Capacity change in first cycle; (b) Capacity changes in the 100th cycles.

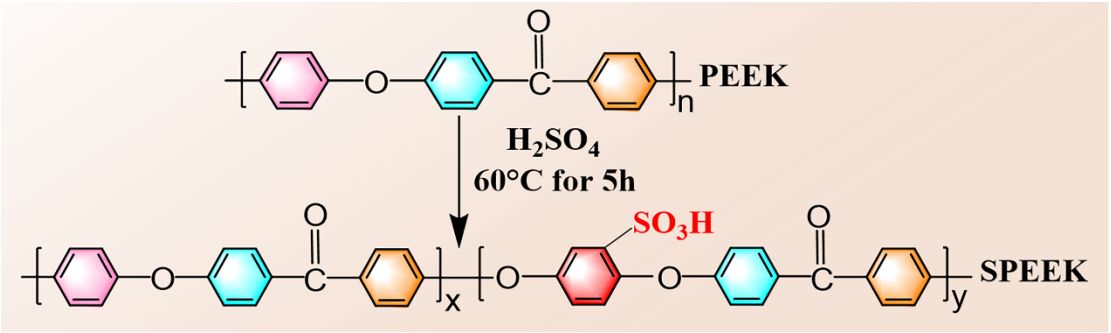

Fig. S5. Schematic diagram of the sulfonation reaction of PEEK powder to prepare SPEEK.

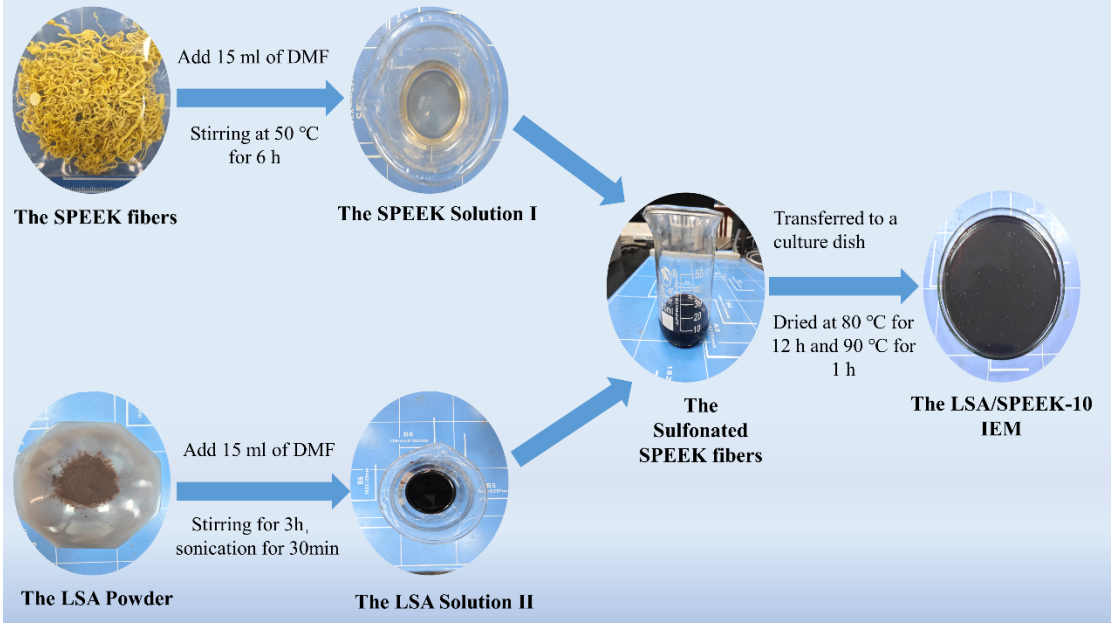

Fig. S6. Flow chart of the preparation process for the LSA/SPEEK composite membrane.

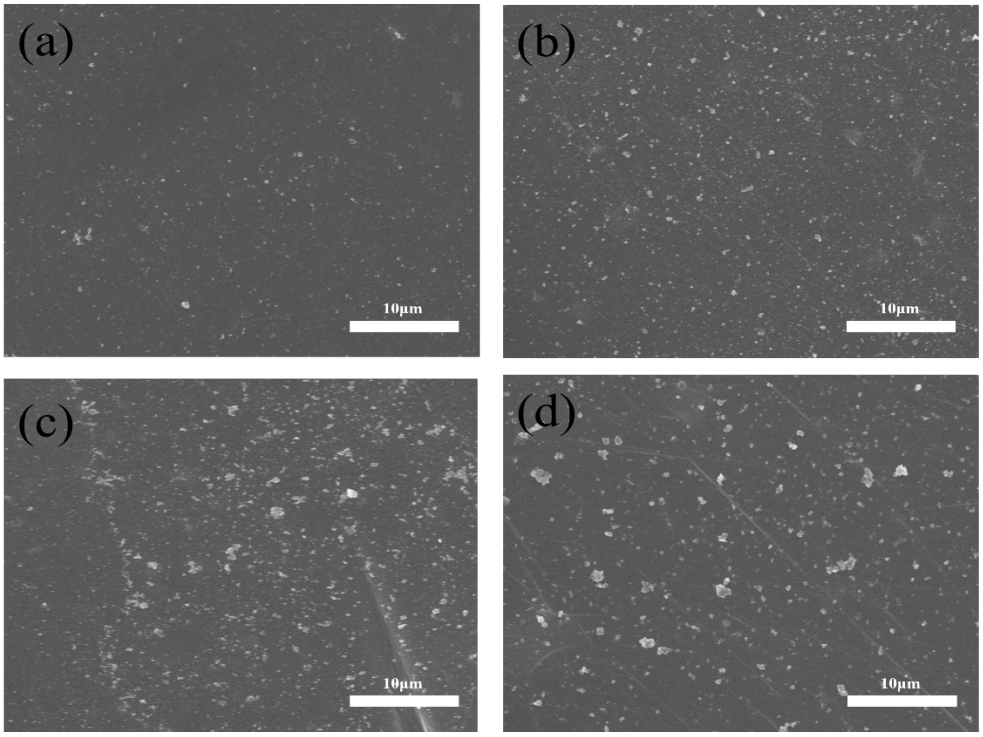

Fig. S7. SEM images of LSA/SPEEK composite membranes with different ratios: (a) LSA/S-5, (b) LSA/S-10, (c) LSA/S-15, (d) LSA/S-20.

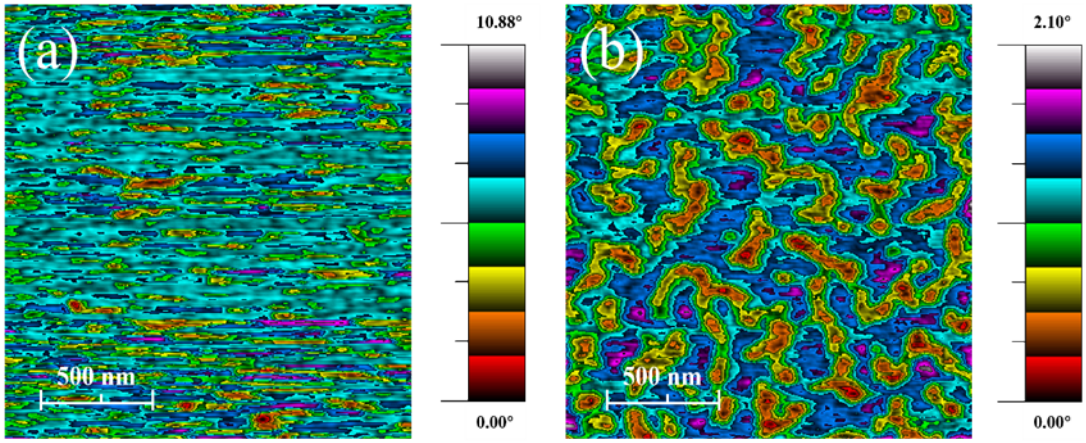

Fig. S8. AFM phase images of LSA/S-10 IEM (a) and SPEEK IEM (b)

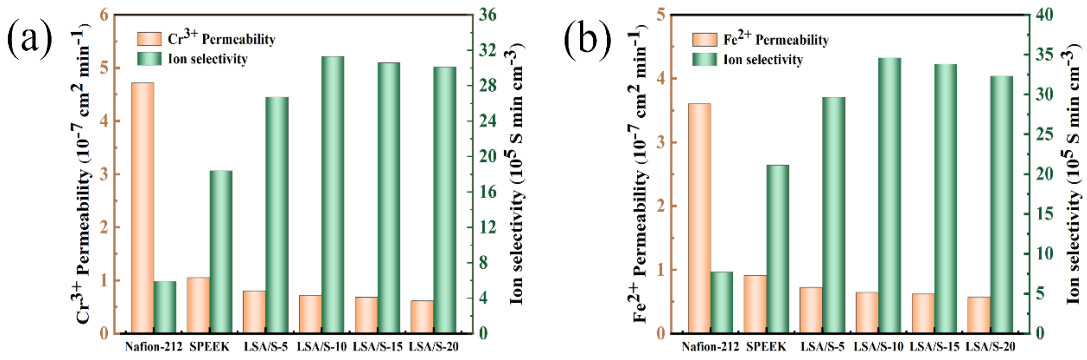

Fig. S9. (a) Cr^{3+}; (b) Fe^{2+} permeability and ion selectivity of various IEMs.

In this study, the ion permeability was measured by the H-type diffusion cell method. The absorbance of Fe^{2+} and Cr^{3+} was measured by UV-Vis spectrophotometry. The measured absorbance was fitted, and the permeability of the corresponding ions was calculated using equation (1):

$$V_R\frac{dc_R(t)}{dt} = A\frac{P}{l}[c_L(t) - c_R(t)]\#(1)$$

Where $c_R(t)$ and $c_L(t)$ are the Fe^{2+}/Cr^{3+} concentrations in the right and left side solutions. P is the permeability of Fe^{2+}/Cr^{3+}. A and l are the area and thickness of the IEM; V_R is the volume of the right-side solution.

The ion selectivity of the membrane is determined by the ratio of its proton conductivity to permeability, as shown in equation (2):

$$S = \frac{\sigma}{P}\#(2)$$

where S, σ, and P denote the ion selectivity, proton conductivity, and ion permeability of the membrane, respectively.

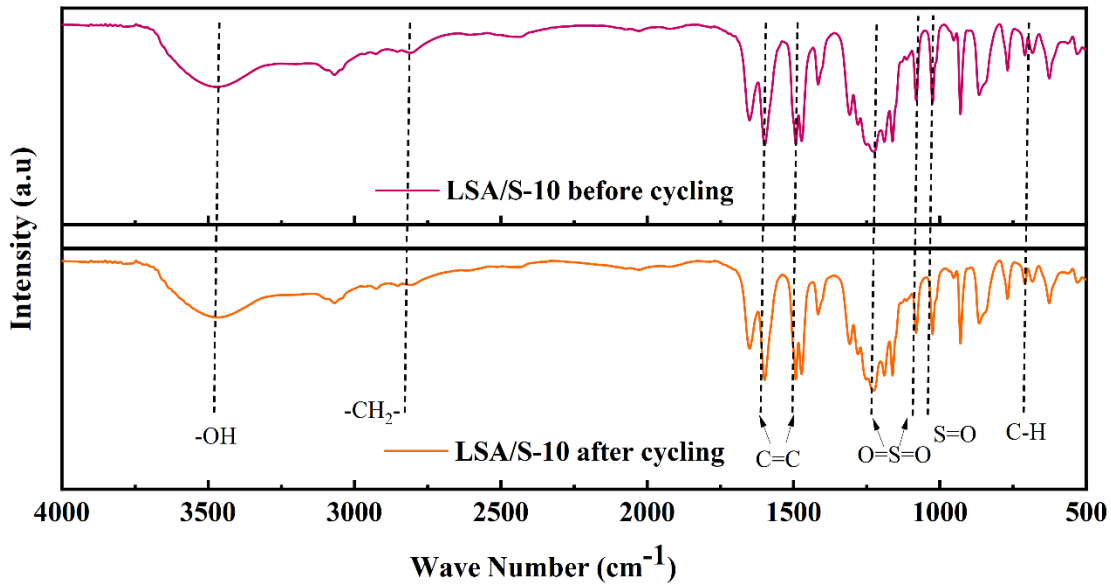

Fig. S10. FTIR spectra of the LSA/S-10 membrane before and after cycling.

1. Manufacturing process of SPEEK fibers

5g of PEEK powder were precisely weighed and dried in a drying oven to create the SPEEK polymers. A magnetic stirrer was used to mix 50ml of 98% H_2SO_4 with PEEK powder. The mixture was heated in a 60 °C water bath for 5 h until it was homogeneous. To obtain white SPEEK fibers, the solution was finally carefully placed into an ice-water bath. Deionized water was used to almost neutralize the excess acid in the SPEEK fibers. The fibers were dried in an oven set to 80 °C for 12 h after the surface moisture was removed.

2. Preparation of LSA powder

A pH-adjusted precipitation method was used to prepare LSA using SLS as the starting material. At room temperature, an appropriate amount of SLS powder was added to deionized water and stirred until a uniform SLS solution was obtained. Subsequently, a 10% hydrochloric acid solution was added dropwise to adjust the pH to 2. After a reaction period, the resulting LSA was separated by low-speed centrifugation and washed several times with deionized water until it was close to neutral. Finally, the washed precipitate was dried to obtain the LSA powder.

3. Preparation of LSA-S IEM

1) To create a homogenous solution I, 0.6 g of SPEEK fibers were dissolved in 15 ml of DMF solution and magnetically agitated in a water bath at 50 °C for 6 h. 2) To create a homogenous LSA/SPEEK mixture, LSA was added to solution I at various mass ratios (5%, 10%, 15%, and 20%). After 3 h of magnetic stirring, the mixture was subjected to a 30 min ultrasonic treatment. 3) To eliminate moisture, the LSA/SPEEK combination was transferred into a petri dish and dried for

12 h at 80 °C in a vacuum oven. To get rid of extra DMF, the temperature was then increased to 90 °C and maintained for 1 h. 4) To accomplish protonation, the composite membrane was carefully removed from the petri dish and submerged in 1 M H_2SO_4 for 24 h before use. 5) Rinse the protonated membrane with deionized water until neutral, and then put it into a sealed bag for reserve. For comparison, SPEEK and Nafion-212 IEM were also soaked in 1 M H_2SO_4 for 24 h prior to use. The prepared composite membranes were designated LSA/S-5 based on the LSA loading, while the other membranes were designated LSA/S-10, LSA/S-15, and LSA/S-20.