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Supporting Information

A twisted imidazole-tethered aromatic polymer for high-performance membranes in vanadium-based redox flow batteries

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1. Experiment

1.1 Materials

1-Methyl-2-imidazolecarboxaldehyde (MIC), *p*-terphenyl (PT), methanesulfonic acid (MSA), trifluoroacetic acid (TFA), and trifluoromethanesulfonic acid (TFSA) were purchased from Adamas, and hexafluorobisphenol A (6FBPA) was purchased from J&K Scientific. Dichloromethane (DCM), sodium bicarbonate (NaHCO₃), *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and anhydrous magnesium sulfate (MgSO₄) were provided by Sinopharm Chemical. VOSO₄·3H₂O was procured from Haizhongtian Chemical Company. All the chemicals were used without purification.

1.2 Synthesis of polymers and membrane casting

The synthesis of poly(*p*-terphenylene methylimidazole) (PTMIm) was carried out as described in the literature [1]. 6FBPA-MIC was synthesized by a superacid-mediated polycondensation reaction. First, hexafluorobisphenol A (8.08 g, 24 mmol) and 1-methyl-2-imidazolecarboxaldehyde (3.47 g, 31 mmol) were added to a dry two-neck flask and dissolved in DCM (40 mL). Next, TFA (5 mL) was added to

the flask while cooled by an ice bath. The solution then immediately changed from colorless to light yellow. TFSA (20 mL) was slowly added drop-wise to the mixture which was continuously stirred for 20 minutes before the viscous solution was poured into 1 M NaHCO₃ solution to precipitate the product. It was crushed and washed repeatedly with deionized water until neutral and then dried in a vacuum oven at 120 °C for 24 h. 6FBPA-MIC was obtained as a white powder.

Membranes of PTMIm and 6FBPA-MIC were prepared by solution casting method. The two polymers were separately added to two bottles and dissolved in appropriate amounts of DMSO and DMAc, respectively, to obtain 2 wt% homogeneous and clear solutions. The polymer solutions were poured onto clean glass petri dishes and the membranes were cast in an oven at 80 °C. After removal from the dishes, they were repeatedly washed in deionized water and further dried at 80 °C for 24 h to finally obtain uniform and transparent membranes.

1.3 Acid doping content and swelling

Completely dry membranes were soaked in aq. 3 M SA solution at room temperature until reaching doping content. Based on the mass and size changes of the membranes before and after soaking, the acid doping content (ADC%), area swelling (AS%) and volume swelling (VS%) were measured and calculated according to Equations 1,2 and 3, respectively:

$$ADC\% = \frac{m_1 - m_0}{m_0} \times 100\%$$
(1)

$$AS\% = \frac{(a_1 \times b_1) - (a_0 \times b_0)}{(a_0 \times b_0)} \times 100\%$$
(2)

$$VS\% = \frac{(a_1 \times b_1 \times c_1) - (a_0 \times b_0 \times c_0)}{(a_0 \times b_0 \times c_0)} \times 100\%$$
(3)

, where m_0 and m_1 represent the membrane mass before and after SA doping respectively, and a_0 , b_0 , c_0 and a_1 , a_2 , a_3 represent the length, width and thickness of the membrane before and after SA immersion, respectively.

1.4 Characterization

The ¹H NMR spectra of the samples were collected on Bruker AVANCE 600 MHz instrument with deuterium dimethyl sulfoxide (DMSO- d_6) as solvent. Fourier transform infrared (FTIR) spectra of the samples were measured using a Bruker VERTEX70 spectrometer with attenuated total reflection (ATR) attachment. X-ray diffraction (XRD) spectra of different membrane materials were acquired by Empyrean diffractometer. The surface morphology of all membranes was analyzed using an SU8010 scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was employed to assess the thermal stability of the polymer at a heating rate of 10 °C min⁻¹ in N₂ atmosphere within the temperature range 30 to 800 °C using the Mettler Toledo TGA/DSC³⁺. The mechanical properties of the membranes were measured on a tensile strength meter (CMT2000, SHIJIN Company, China) at a constant speed of 5 mm min⁻¹ under an ambient atmosphere. All the membranes were soaked and balanced in 3 M SA solution and cut into a dumbbell shape, with the middle part having a length of 25 mm and a width of 4 mm.

The herent viscosity (η) of the polymer was determined using a Ubbelohde viscometer at 30 °C. The polymer was dissolved in DMAc to obtain a solution with a concentration of 100 mg dL⁻¹. The viscosity is calculated as:

$$\eta = \ln(\frac{t_x}{t_0}) / c \tag{4}$$

Where t_x and t_0 represent the flow time of the polymer solution and the blank DMAc solution, respectively, and c represents the concentration of the polymer solution.

AR of the membranes was evaluated between 1 kHz and 1 MHz by electrochemical impedance spectroscopy (EIS).

$$AR = (R_1 - R_0) \times A \tag{5}$$

where R_1 and R_0 are the resistance of the test cell with and without membrane, respectively, and A is the effective area (2.27 cm²) between the two diffusion units.

To measure the vanadium ion permeability, membranes were sandwiched between two semi-

diffusion tanks, the right tank was filled with 80 mL 3 M SA/1.5 M MgSO₄ solution, and the left tank was filled with 80 mL 3 M SA/1.5 M VOSO₄ solution, constantly stirred to prevent concentration polarization. Samples from the solution in the right tank were collected periodically and the absorbance of VO²⁺ was determined by ultraviolet-visible spectrometry (PerkinElmer Lambda 35 UV-Vis), using a MgSO₄ solution as the reference. After the measurement, the solution was poured back into the right tank. The vanadium ion permeability of the membrane was calculated according to Equation 6.

$$V_b \frac{d(C_b(t))}{dt} = A \frac{P}{L} (C_a - C_b(t)) \tag{6}$$

where V_b is the solution volume in the right tank. C_a is the initial VO²⁺ concentration in the left tank and $C_b(t)$ is the VO²⁺ concentration in the right tank. A is the effective area of the membrane (1.69 cm²), L is the thickness of the membrane, t is the penetration time, and P is the vanadium ion permeability of the membrane.

The H⁺ permeability of the membranes was determined by the same device used to determine the permeability of vanadium ions. The left ventricle was filled with 80 mL 3M SA solution and the right ventricle with 80 mL 3M (NH_4)₂SO₄ solution. The H⁺ concentration in the right ventricle was measured at intervals with a pH meter [2].

In order to comprehensively consider the diffusion ability of conducting ions and vanadium ions in the membrane, the ion selectivity of the membrane was calculated as:

$$Ion \ selectivity = \frac{D / AR}{P}$$
(7)

where, D is the thickness, AR is the area resistance, and P is the vanadium ion permeability of the membrane.

Membrane samples were soaked in a 1.5 M VO_2^+ and 3 M SA solution to evaluate chemical stability. The membrane samples were regularly removed, thoroughly cleaned in deionized water, dried, and weighed. The chemical stability of the membranes was evaluated according to the weight change of the membrane.

Vanadium redox flow batteries (VRFBs) were assembled and measured based on our previous work [3]. Coulombic efficiency (CE), energy efficiency (EE), and voltage efficiency (VE) for the battery were obtained from Equations 8, 9, and 10, respectively, where I, V, and t represent current, voltage, and time, respectively, and the subscripts d and c represent the discharge and charge procedures, respectively.

$$CE(\%) = \frac{\int I_d dt}{\int I_c dt} \times 100\%$$
(8)

$$EE(\%) = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\%$$
(9)

$$VE(\%) = \frac{EE}{CE} \times 100\% \tag{10}$$

The iron-vanadium redox flow battery (IVRFB) evaluation was performed using a battery tester, specifically the Neware CT-3008 (5 V/12 A), and laboratory-grade flow cells designed for IVRFB systems. Driven by a peristaltic pump, 5 mL of electrolyte solution was circulated between each half-cell and the tank at a fixed flow rate of 20 mL min⁻¹. The negative and positive electrolytes of IVRFB were 1.7 M V³⁺/3 M SA and 1.7 M Fe²⁺/3 M SA, respectively. For battery performance tests, current densities were preset at 100 mA cm⁻², 150 mA cm⁻², 200 mA cm⁻², 250 mA cm⁻², and 300 mA cm⁻², respectively. The current density was set to 150 mA cm⁻² in the cyclic test. The self-discharge characteristics were evaluated on the fully charged flow cell, with the peristaltic pump rate and the current set to zero.

2. Results



Figure S1 Photographic and SEM images of surface and cross sections of 6FBPA-MIC (A) and PTMIm (B) membranes.



Figure S2¹H NMR spectra of MIC, 6FBPA, 6FBPA-MIC, and PTMIm.



Figure S3 FTIR spectra of 6FBPA-MIC and PTMIm membranes.



Figure S4 XRD data of 6FBPA-MIC and PTMIm membranes.



Figure S5 TGA trace recorded in N₂ atmosphere of the 6FBPA-MIC membrane.



Figure S6 N_2 adsorption/desorption isotherms of the 6FBPA-MIC and PTMIm membranes at 77 K.



Figure S7 MD simulations of the PTMIm (A) and 6FBPA-MIC (B) membranes, where the blue areas represent accessible free volume.



Figure S8 Ion selectivity of the SA-doped membranes.



Figure S9 Weight retention ratio of the different membranes during the chemical stability test.



Figure S10 CE, VE and EE of VRFBs assembled with 6FBPA-MIC, PTMIm and Nafion 115 membranes, respectively, at 100 mA cm⁻².



Figure S11 Self-discharge curves for IVRFBs assembled with the 6FBPA-MIC and Nafion 115 membranes.



Figure S12 SEM images of 6FBPA-MIC (A) and PTMIm (B) membranes after cycling: (1) surface in contact with negative electrolyte; (2) surface in contact with positive electrolyte.

Membrane	ADC /	AS /	VS /	Elongation	Tensile stress	Young's modulus
	%	%	%	/ %	/ MPa	/ MPa
6FBPA-MIC	30.5	0	14.3	1.3	12.3	9.5
PTMIm	22.1	2.8	1.8	9.5	34.6	8.7
Nafion 115	2.2	4.8	4.5	72.6	13.5	0.5

Table S1 SA doping content, swelling, and mechanical properties of the membranes.

Table S2 Performance of VRFBs assembled with different imidazole-based membranes compared at a current density of 100 mA cm⁻².

	Thickness /	AR / Ω ·cm ²	CE / %	VE / %	EE / %	Ref.
Membrane	μ m					
6FBPA-MIC	43	0.29	99.2	86.3	85.7	This work
PTMIm	43	0.74	98.2	66.8	65.6	This work
PTMIm-C ₃ -QA	55	0.68	99.6	77.8	77.5	1
PSSP(1-25-25-1)	52	0.14	98.5	89.7	88.4	4
6f-abSPI-60	60	1.22	98.9	78.2	77.3	5
OPBI	36	0.38	99.7	82.1	81.8	6
ABPBI	36	0.81	99.7	78.7	78.9	6
p-PBI	49	0.67	96.9	83.2	80.6	6
PVC-80%APIm	65	0.27	98.6	82.3	81.2	7
P(MeIm-co-Flu)	68	0.32	99.5	86.1	85.7	8

3. References

[1] T. Mu, W. Tang, N. Shi, G. Wang, T. Wang, T. Wang, J. Yang, Novel ether-free membranes based

on poly (p-terphenylene methylimidazole) for vanadium redox flow battery applications, J. Membr. Sci. 659 (2022), 120793.

- [2] X. Che, W. Tang, J. Dong, D. Aili, J. Yang, Anion exchange membranes based on long sidechain quaternary ammonium-functionalized poly (arylene piperidinium) s for vanadium redox flow batteries, Sci. China Mater. 65 (2022), 683-694.
- [3] T. Mu, W. Tang, Y. Jin, X. Che, J. Liu, J. Yang, Ether-free poly(p-terphenyl-co-acetylpyridine) membranes with different thicknesses for vanadium redox flow batterie, ACS Appl. Energ. Mater. 5 (2022), 11713-11722.
- [4] M. M. Ikhsan, S. Abbas, X. H. Do, H. Y. Ha, K. Azizi, D. Henkensmeier, Sulfonated polystyrene/polybenzimidazole bilayer membranes for vanadium redox flow batteries, Adv. Energy Mater. (2024), 2400139.
- [5] Y. Yu, G. Wang, Y. Jing, S. Wei, X. Li, S. Zhang, J. Chen, Y. Zhou, J. Zhang, J. Chen, R. Wang, A sulfonated polyimide containing imidazole ring with a low vanadium ion permeable for vanadium redox flow battery, Polymer 302 (2024), 127100.
- [6] L. Ding, X. Song, L. Wang, Z. Zhao, G. He, Preparation of dense polybenzimidazole proton exchange membranes with different basicity and flexibility for vanadium redox flow battery applications, Electrochim. Acta 292 (2018), 10-19.
- [7] N. Shi, G. Wang, T. Mu, H. Li, R. Liu, J. Yang, Long side-chain imidazolium functionalized poly (vinyl chloride) membranes with low cost and high performance for vanadium redox flow batteries, J. Mol. Liq. 376 (2023), 121401.
- [8] M. Zhang, P. Lv, L. Wang, J. Wang, J. Yang, Ether-free Poly(arylene methylimidazole) Membranes with High Performance for Vanadium Redox Flow Battery Applications, ACS Appl.

Polym. Mater. 7 (2025), 3164-3173.