

High-Performance and Low-Cost Membranes Based on Poly(vinylpyrrolidone) and Cardo-Poly(etherketone) Blends for Vanadium Redox Flow Battery Applications

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FT-IR and SEM

The Fourier transform infrared (FT-IR) spectra were collected on the Bruker VERTEX70 spectrometer. An SU-8010 scanning electron microscope (SEM) was used to detect the surface of membranes.

Acid uptake and Swellings

The acid absorption of one membrane was performed by submersing the dried membrane (m_{dry}) in the 3 M SA solution at RT for 48 h. The SA doped membrane was wiped with filter paper and weighed (m_{wet}), and subsequently dried in an oven at 80 °C to remove moisture and quickly weighed again (m_{doped}). The water uptake (WU%) and acid doping content (ADC%) of each $x\%$ PVP-PEKC membrane is calculated by Equation S1 and Equation S2. Meanwhile, the acid doping level (ADL) of the membrane is defined as the number of SA molecules per PVP repeat unit and calculated based on Equation S3 [1,2,3]. The dimension changes of one membrane in terms of area and volume swellings were measured according to the previous reports elsewhere [4,5].

$$WU\% = \frac{(m_{wet} - m_{doped})}{m_{dry}} \times 100\% \quad (S1)$$

$$ADC\% = \frac{(m_{doped} - m_{dry})}{m_{dry}} \times 100\% \quad (S2)$$

$$ADL = \frac{(m_{wet} - m_{doped}) \times M_{PVP}}{m_{dry} \times x_{PVP} \% \times 98} \quad (S3)$$

Mechanical properties

On a tensile strength instrument (CMT2000, SHIJIN Company, China), the tensile stress-stain curves of membranes with acid were recorded at a constant crosshead speed of 5 mm min⁻¹.

Area resistance and vanadium ion permeability

The ARs of membranes were determined by an electronic impedance spectroscopy (EIS) ranging from 100 MHz to 1 Hz as reported in literature [1,6]. The acid absorbed membranes with an effective area of 2.27 cm² were fixed between two diffusion cells containing a 3.0 M H₂SO₄ solution. The area resistance (Ω·cm²) was calculated with the Equation S4.

$$AR = (R_2 - R_1) \times A \quad (S4)$$

Where R_1 and R_2 are the resistance of the cell without and with membrane, respectively; A is the effective area.

The permeability of VO²⁺ was measured in a diffusion cell as described elsewhere [1,2]. The 80 mL of 1.5 M VOSO₄ and 3.0 M H₂SO₄ solution was filled in the left compartment, while the same volume of 1.5 M MgSO₄ and 3.0 M H₂SO₄ solution was filled into the right one. The diffusion cell was placed on a magnetic stirrer and stirred vigorously to reduce concentration polarization. After a certain interval, the VO²⁺ ion concentration of the right cell was measured on an UV-vis spectrometer (Perkin Elmer Lambda 35 UV-Vis) using MgSO₄ as the reference within the scanning range of 550-800nm. The VO²⁺ permeability is calculated by the following Equation S5.

$$V_b \frac{d(C_b(t))}{dt} = A \frac{P}{L} (C_a - C_b(t)) \quad (S5)$$

Where V_b is the solution volume in the right cell. C_a is the initial VO^{2+} concentration in the left cell and $C_b(t)$ is the VO^{2+} concentration in the right compartment. A and L are the effective area and thickness of the membrane. P represents the vanadium ions permeability of one membrane.

The chemical stability of $x\%$ PVP-PEKC membranes was investigated by submersing the dry samples in the 1.5 M VO_2^+ and 3 M SA solution as described elsewhere [7,8]. The dry sample was weighted and then immersed in 10 mL solution at RT. During the test, the sample was taken out of the solution every 24 h, followed by rinsed with water and dried in an oven at 80 °C for 6 h to remove the water, and then weighed it again. The chemical stability of the samples was evaluated by determining the mass change of the membrane.

VRFB performance and cycling durability

The VRFB performance of the membrane was tested on a home-made single cell. The battery was made by sandwiching the tested membrane between two current collectors, whose effective area of electrodes was 9 cm² (3×3cm). Both positive and negative electrodes employed 25 mL of 1.65 M $\text{V}^{3+}/\text{VO}^{2+}$ in 3.0 M H_2SO_4 as the cell electrolyte [3,9]. The battery performance was determined at 80-180 mA cm⁻² by a battery test system (Neware CT-3008 (5 V/6 A)). The cut-off voltage window was set between 1.00 to 1.65 V. The current density of the long-term cycle test was evaluated at 100 mA cm². In addition, no stabilizer was added to the electrolyte during the test. According to Equations S6-S8, the coulombic efficiency (CE), energy efficiency (EE) and voltage efficiency (VE) are calculated, where I is the current, V is the voltage and t is the time, and the subscripts d and c mean the discharge and charge process, respectively.

$$CE\% = \frac{\int I_d dt}{\int I_c dt} \times 100\% \quad (\text{S6})$$

$$EE\% = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \quad (\text{S7})$$

$$VE\% = \frac{EE}{CE} \times 100\% \quad (\text{S8})$$

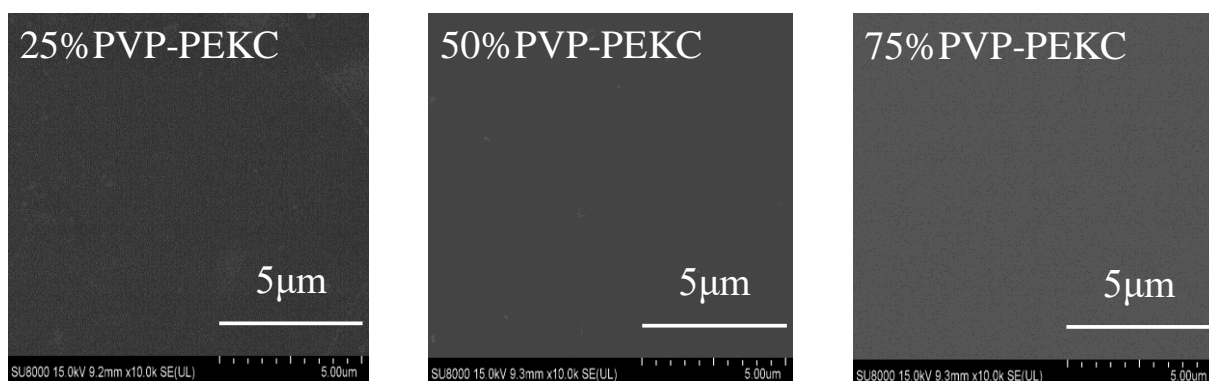


Figure S1. Surface SEM images of 25%PVP-PEKC, 50%PVP-PEKC and 75%PVP-PEKC.

Table S1. Comparison of the battery performance of various membranes in this work and literature at the current density of 80 mA cm⁻².

Membrane	Thickness / μm	CE / %	VE / %	EE / %	Reference
50%PVP-PEKC	35	99.2	84.1	83.8	This work
BI _p PBI ^a	27	~100	~82	~82	[1]
PBI-40%SiO ₂	63	100	~88	~88	[2]
SPEEK/PVP 30%	145	~99	~84	~83	[10]
CPVC ^b /PVP-M14	--	99.2	90.0	89.3	[11]
PSF ^c /PVP-50	35	~98	~91	~90	[12]
PES ^d /PVP-M3	115	92.4	82.4	76.1	[13]
SP3 ^e	110	~96	~88	~84	[14]
PBI	30	~99	~65	~66	[15]
PF-21 ^f	25	98.9	84.8	83.9	[16]
PBI-EDB ^g -30-20	19	99	92.2	91.3	[17]
SIPNs-60 ^h	50	~99	~83	~84	[18]

PTP-CHPTMA ⁱ	50	~99	~89	~88	[19]
PAEK-API 2.0 ^j	133	~97	~84	~82	[20]
Q2-ADMPEK-4 ^k	40	~99	88	~88	[21]

a: poly[2,20-(2-benzimidazole-p-phenylene)-5,50-bibenzimidazole];

b: chlorinated polyvinyl chloride;

c: polysulfone;

d: poly (ether sulfone);

e: poly(ether ether ketone) (SPEEK) membranes with DS of 0.91;

f: blending meta-PBI with FAA3i, while '2' being the weight based ratio of PBI to FAA3;

g: 1,2-dibromoethane;

h: semi-interpenetrating polymer networks consisting of cross-linked polyvinylpyrrolidone (PVP) and polysulfone (PSF);

i: hydroxypropyltrimethyl ammonium grafted poly(terphenyl piperidinium) membrane;

j: poly(arylene ether ketone) with 1-(3- aminopropyl) imidazole pendant groups membrane;

k: quaternized 2-adamantane containing poly(ether ketone) membrane.

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