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Supplementary information

Doping structure and degradation mechanism of polypyrrole-Nafion® composite membrane for vanadium redox flow batteries

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Experimental Materials

Ferric chloride and and sulphuric acid (AR grade) were purchased from Beijing Chemical Reagent Company. Pyrrole and Vanadium (IV) oxide sulfate hydrate were purchased from purchased from Aladdin Chemistry Co. Ltd. The commercial Nafion® 212 (EW 2100, thickness 50 μm) membrane was purchased from Du Pont Co. All reagents were used without further purification.

Preparation of PPY- Nafion® composite membranes

Nafion® 212 membrane, used directly without further pretreatment, was equilibrated with a 1.0 M ferric chloride solution and then raised with deionized water for several times. After that, the ferric ion-form Nafion® 212 membranes (3×3 cm) had been immersed in a 50 mL 0.1 M pyrrole aqueous solution, which was vigorously stirred for a given period. The obtained dark composite membranes were washed with deionized water and labeled as PPY-N212. The composite PPY-N212 membranes were rinsed with a 0.5 M sulphuric acid solution and then equilibrated in a 0.5 M sulphuric acid solution before use, and the membranes after acidification were labeled as HPPY-N212.

Membrane morphology

The morphology of the composite membranes cross-section was recorded by scanning electron microscope (JEOL JSM-5800). The fresh cross-section was derived from breaking the membranes in liquid nitrogen with forceps. All the samples were sputtered with platinum and measured at an acceleration voltage of 5 kV.

Small-angle x-ray scattering (SAXS) experiments were performed with a highflux SAXS instrument (SAXSess, Anton Paar) equipped with Kratky block-collimation system. The scattering pattern of SAXS was simultaneously recorded on an imaging plate (IP) with a pixel size of 42.3 × 42.3 μm^2, which extended to high-angle range (the q range covered by the IP was from 0.06 to 29 nm^{-1}, $q = 4\pi (\sin\theta) /\lambda$, where the λ is the wavelength of 0.1542 nm and 2θ the scattering angle). The scattering peak positions were calibrated with silver behenate for small-angle region.

Membrane characterization

The chemical structures of the membranes were characterized by Fourier transform infrared spectrometer (FT-IR, Nicolet AVATAR 470) in the wavelength range from 4000 to 600 cm^{-1}. The morphologies of composite membranes were observed by using field emission scanning electron microscope (FESEM, JMS-7500F) at 20 kV accelerating voltage. For SEM characterization, the cross-section of samples was obtained by rupturing in liquid nitrogen. And then the cross-section of the samples was sputtered of gold for 60 s.

Raman spectra were collected using a Jobin Yvon (Laboratory RAM HR800) confocal micro-Raman spectrometer equipped with a multi-channel charge-coupled detector. The Ar^+ laser emitting at a wavelength of 633 nm was used as a source of excitation. The number of grating in the Raman spectrometer was 600. The scattered light was analyzed with a Dilor XY triple spectrometer and a liquid-nitrogen-cooled CCD multichannel detector with the accuracy better than 1 cm^{-1}. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer. The spectra were obtained using a 100 × objective lens to focus the laser beam onto a spot of 0.7 mm in diameter. In all experiments, the laser power was 0.3 mW.

X-ray photoelectron spectroscopy (XPS) measurement was performed on a PHI Quantera spectrometer (ULVAC-PHI, Inc.) with Al Kα X-ray radiation as the X-ray source for excitation.

The electrochemical polymerization of pyrrole and the measurement of cyclic voltammetry (CV) were proceeded on the CHI660C instrument with a conventional three-electrode cell assembly with catalyst modified glassy carbon electrode (0.196 cm^2) as the working electrode, platinum wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode. Polypyrrole (PPY) was electrodeposited on the glassy carbon electrode in 0.5 M H_2SO_4 and 0.5 M pyrrole aqueous solution under a constant potential 0.8 V.

The conductivity of Composite Membrane

The resistance of the membranes was measured by a separated cell that containing 3M H_2SO_4 solution, and was detected according to the four-electrode AC impedance method using a PARSTAT 2273 electrochemistry work station. Before test, the samples were immersed in 3M H_2SO_4 at room temperature for 24 h. The conductivity of membranes was calculated by the following equation:

$$\sigma = \frac{l}{RS} \qquad (1)$$

Where l (cm) is the thickness of the membrane, S (cm^2) is the effective area of the testing membrane, and R is the membrane resistance. For each reported, at least four samples were measured and results were averaged.

Vanadium ion permeability

The VO^{2+} permeability was examined on a membrane separated diffusion cell by filling 1.5 M VO^{2+}/ 3M H_2SO4 solution in left compartment and 1.5 M MgSO4/ 3M H_2SO4 blank solution in right compartment. Vigorous stirring at both compartments was performed to avoid the concentration polarization. A 4 mL solution from the right compartment was collected at a regular time interval and was measured by a UV -vis spectrometer. The VO^{2+} permeability was calculated according to the Ficker diffusion law as follows:

$$V_B \frac{dC_B(t)}{dt} = A \cdot \frac{P}{L} \cdot (C_A - C_B(t)) \qquad (2)$$

Where V_B is the solution volume in the right compartment and $C_B(t)$ *is the* VO^{2+} concentration as a function of time t in the right compartment, A is the effective area of a membrane, L is the thickness of the membrane, P is the permeability of VO^{2+} and C_A is VO^{2+} concentration in the left cell.

VRFB single cell performance

In the system, VO^{2+}/ VO_2^+/ H_2SO4 and V^{2+}/ V^{3+}/ H_2SO4 solutions serving as electrolytes were designated at the positive and negative sides, respectively. The electrolyte was cyclically pumped through the corresponding electrode via a magnetic drive pump. The cut-off voltage for the charge and discharge process was set between 0.8 V–1.7 V. The coulombic efficiency (CE), voltage efficiency (VE) and energy transfer efficiency (EE) were calculated as following equations:

$$CE = \frac{\int I_d dt}{\int I_c dt} \times 100\% \qquad (3)$$

$$EE = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \qquad (4)$$

$$VE = \frac{EE}{CE} \times 100\% \qquad (5)$$

Where I_d and I_c were discharging and charging current, V_d and V_c were discharging and charging voltage, respectively.

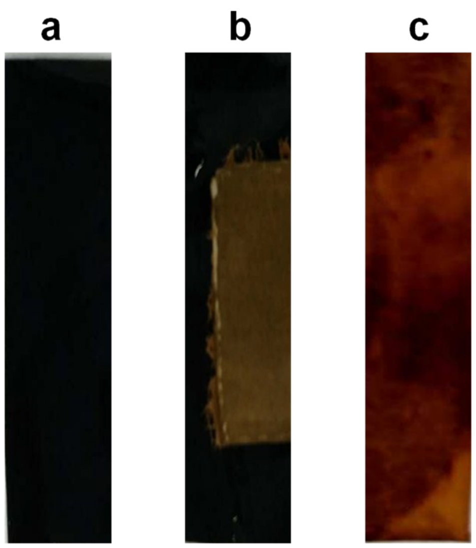

Fig. S1 The picture of (a) HPPY-N212 membrane, (b) HPPY-N212 membrane after 90 charge-discharge cycles, and (c) HPPY-N212 membrane oxidized for 1 h in the 1.5 M VO_2^+/ 3M H_2SO_4 solution.

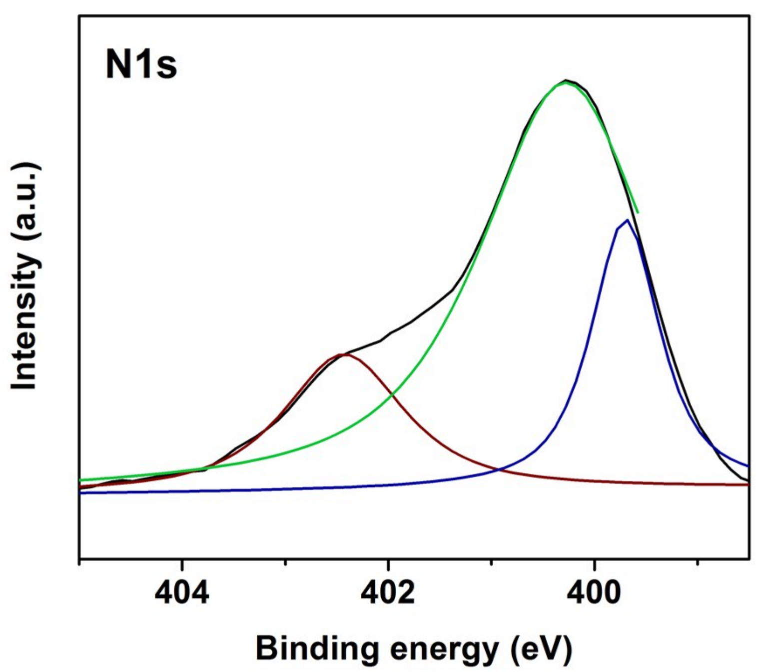

Fig. S2 XPS spectra of N1s for HPPY-N212 membrane.

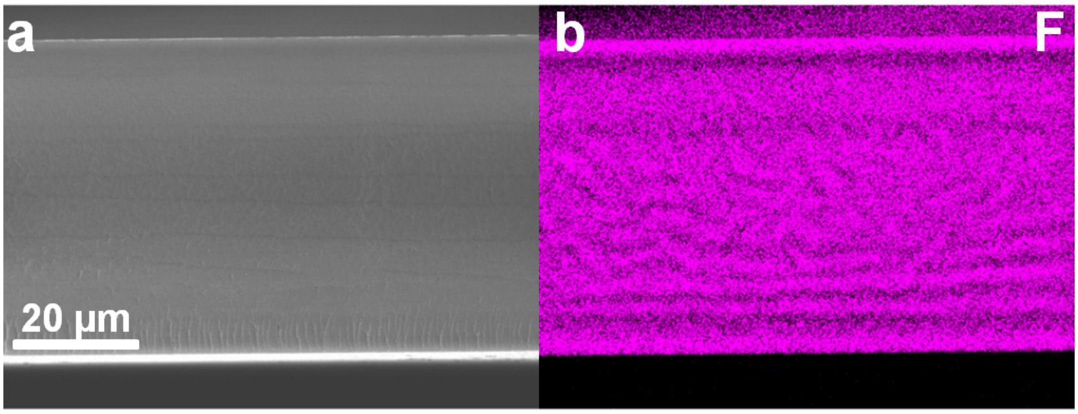

Fig. S3 (a) SEM cross-section and (b) Element F distribution images of HPPY-N212 membrane.

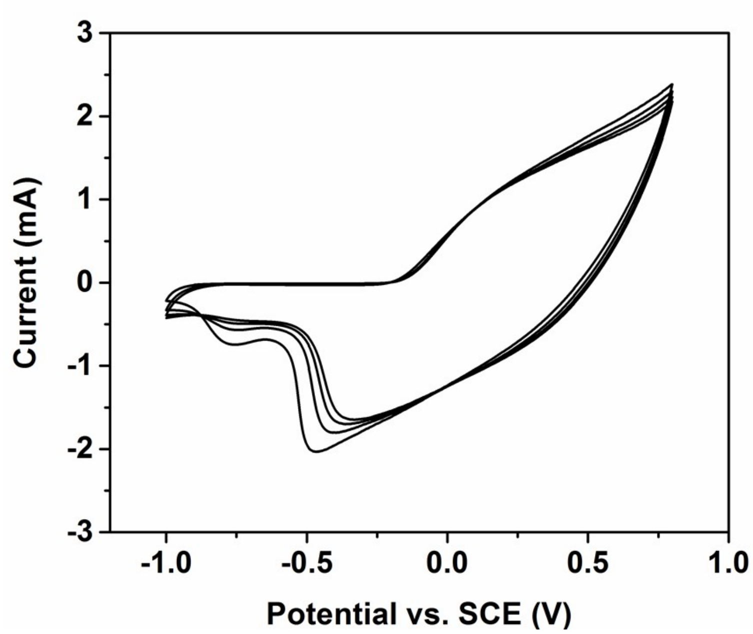

Fig. S4 The CV curve of PPY by electrodepositing on the glassy carbon electrode in 0.1 M V (Ⅳ) + 0.1 M V (Ⅴ) + 1.0 M H_2SO_4 solution at the scan rate of 5 mV/s.

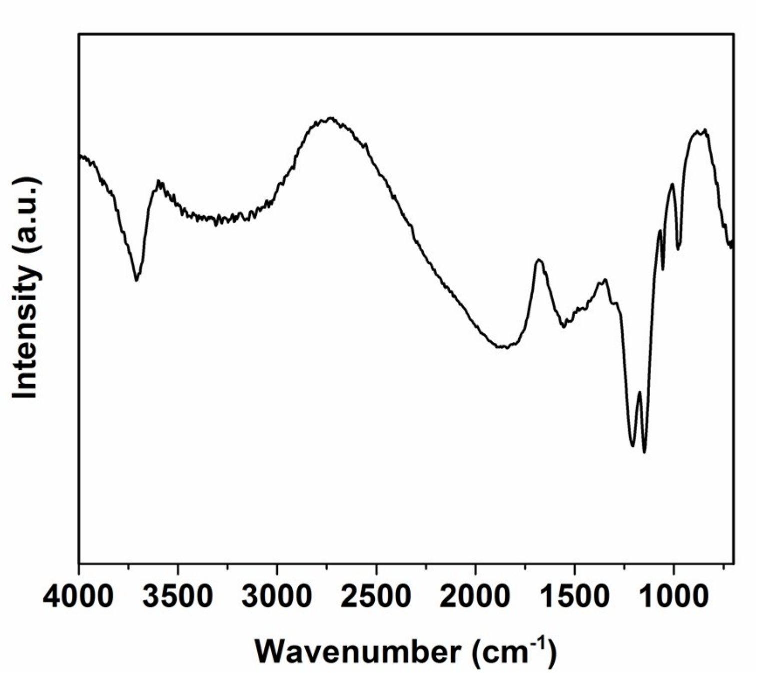

Fig. S5 The FT-IR spectra of HPPY-N212 membranes was oxidized in 1.5 M VO_2^+/ 3M H_2SO_4 solution for 80 min.