Supporting information

Advanced charged membranes with highly symmetric spongy structures for vanadium flow battery application

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Chloromethylated polysulfone membranes (CPSF) with highly symmetric sponge structures were first prepared via water vapour induced phase inversion method then modified with pyridine to provide these membranes with positive charged groups. As shown in Figure S1, the membrane cross-section appears uniform spongy structure, which is almost unchanged after pyridine modification.

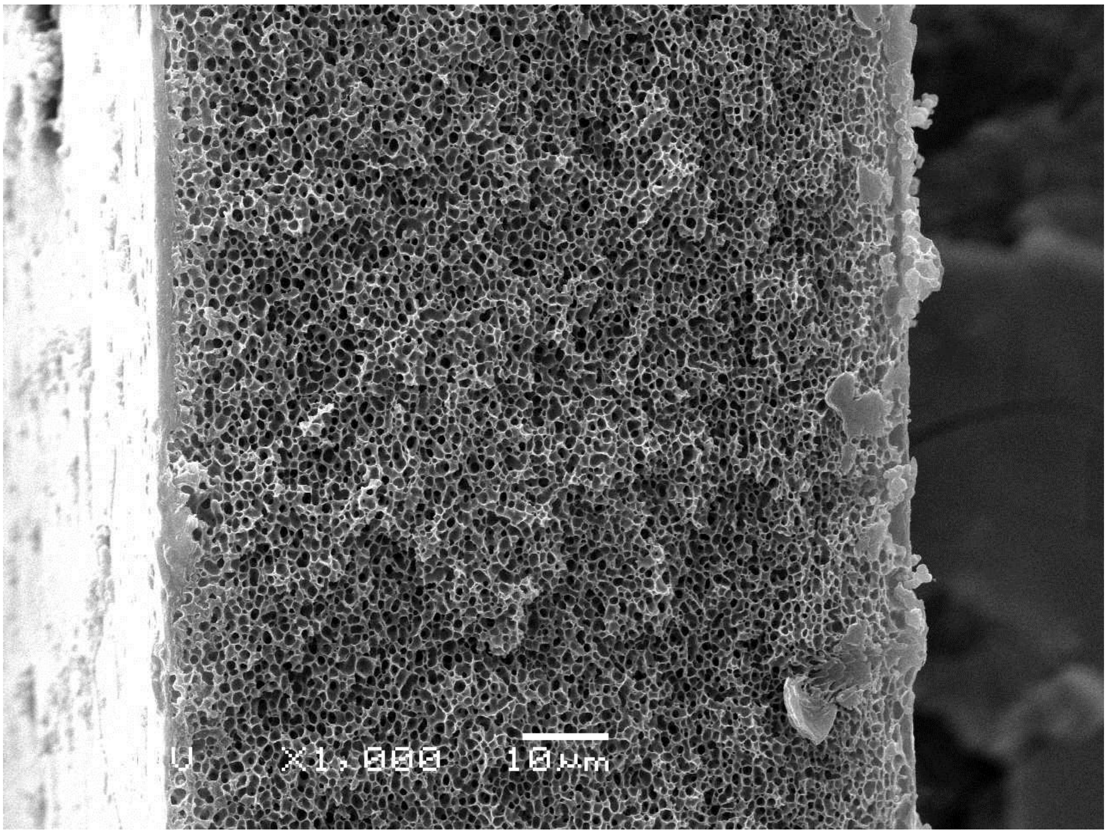

Figure S1. The cross section of CPSF membranes prepared from water vapour induced phase inversion method

Water vapor induced phase inversion is a convenient method to manufacture membranes in large scale. Figure S2 shows a digital picture of the CPSF sponge structured membranes prepared in lab (18.5×30 cm^2), which is very smooth and uniform.

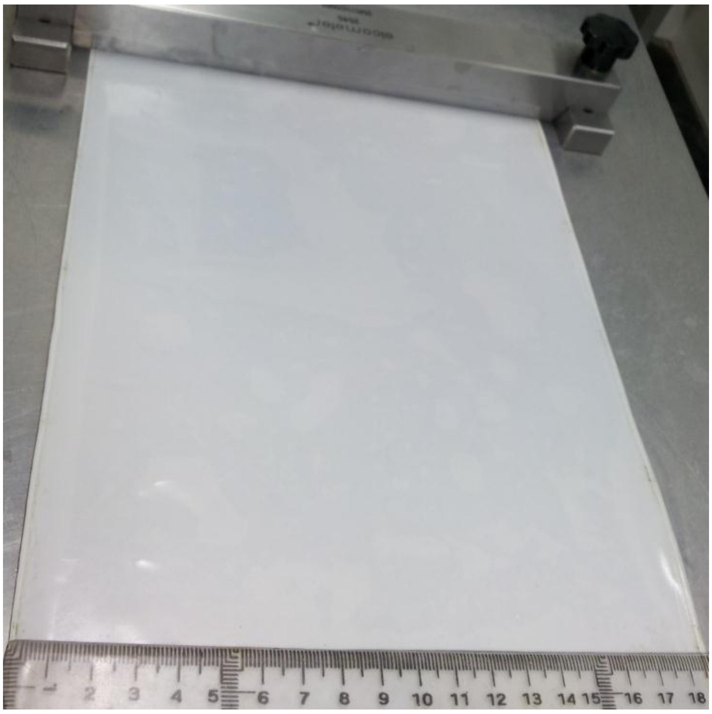

Figure S2. Digital picture of the CPSF spongy structured membrane prepared in lab

The structures of chloromethylated polysulfone and pyridine modified polysulfone membranes were further characterized by TG and FTIR. TG analysis was carried out on a Pyris-diamond TG-DTA-THERMOSTER to detect the thermal stability of prepared membranes. Before test, all the polymers were preheated to 120 °C and kept at this temperature for 30 min to remove any residual moisture and solvent. After that, the temperature was heated to 700 °C with a heating rate of 5 °C min^{-1} under nitrogen flow. As shown in Figure S3, the weight loss from 200 to 350 ^{o}C is attributed to the decomposition of pyridine and chloromethyl group. After soaking CPSF-Py in sulfuric acid solution for 24 hours, the thermal stability of pyridine is obviously enhanced, which might be caused by interaction between pyridine and sulfonic acid.

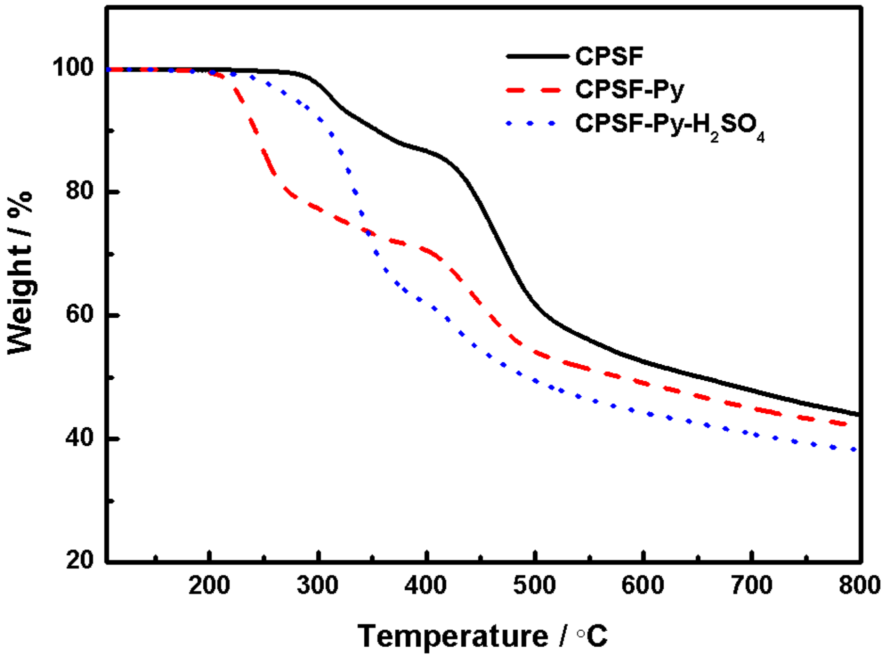

Figure S3. TG of prepared membranes before Pyridine modification, after Pyridine modification (red) and after soaking in sulfuric acid

The FTIR spectra were recorded by using the ATR (attenuated total reflection) technique with a FTIR spectrometer (Avatar.370 E.S.P., Nicolet Continuum Infrared Microscope). Figure S4 shows the FTIR spectrum of CPSF and CPSF-Py after drying in 100°C for 24 hours. The wide peak around 3300 is caused by the bound water of CPSF-Py, as a result of the hydrophilicity of pyridine group.

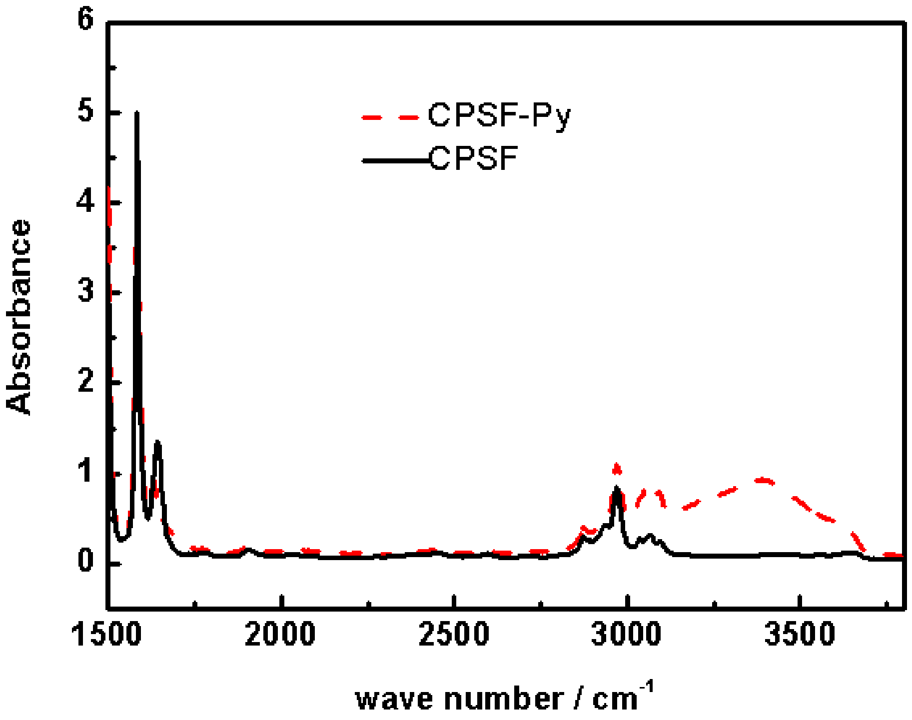

Figure S4. FTIR spectra of prepared CPSF and CPSF-Py membranes

For VFB membranes, good flexibility and extensibility is crucial for avoiding brittle rupture, which is caused by the squeeze and swash during battery manufacture and running process. The stress–strain behavior of the spongy and dense membranes was measured on a tension tester AG-2000A (Shimadzu) at room temperature. The dense membranes were prepared by directly evaporating the solvent. Membrane samples were tested by using a programmed elongation rate of 50mmmin^{-1}. All samples were kept in deionized water for 4 days before the test to ensure they were saturated with water. As is shown in Table S1, the CPSF spongy membrane shows much higher extensibility than the condensed membrane as due to the relaxed inner stress of the loosen sponge structure. Although the elastic modulus of the sponge membranes is lower than the condense ones, however its mechanical strength is still good enough for VFB assembly.

Membranes strucure	Elastic modulus/MPa	Breaking extension/%	crippling stress/MPa	tensile strength/MPa
Sponge	434.61	23.33	12.45	12.81
Dense	1858.79	5.33	56.40	56.58

Table S1. The mechanical strength of prepared CPSF spongy membranes compared with dense ones

As is discussed in the article, the main membrane resistance is determined by the condense cell walls of the spongy structured CPSF-Py. So if the cell walls could be loose enough, more sulfuric acid would be immersed into the cell walls, then the ions conductivity of the membranes will be increased to be as high as the acid solution. In order to confirm this assumption, the spongy structured CPSF-Py membranes were designed to swell in pyridine aqueous solution. As illustrated in Figure S5, the membranes are gradually expanded in three dimensions from M0 to M4, due to increasing soaking time in pyridine solution.

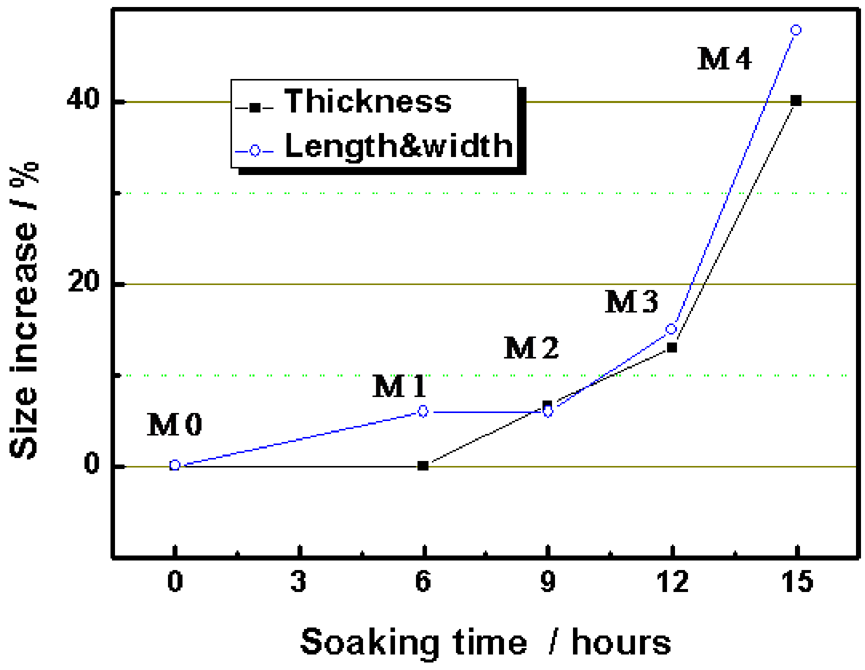

Figure S5. The size expansion of PSF-Py after soaking in pyridine solution

Then the ions conductivity cross the plane of M2, M3 and M4 was tested in 0.5

M sulfuric acid (aq) medium. As shown in Figure S6, the membrane conductivity increased to 0.2 S cm^{-1}, which surpasses that of the Nafion 115 (without soaking in pyridine) and even close to the 0.5 M sulfuric acid aqueous. This is in accordance to our supposition that the sulfuric acid inside the membrane is the major ionic conductor.

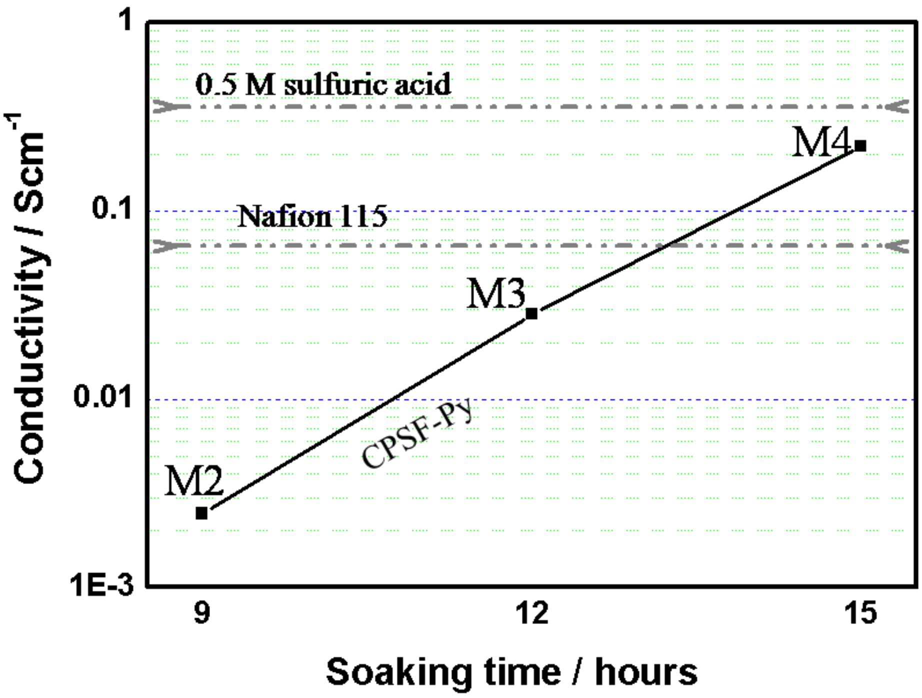

Figure S6. The membrane conductivity of M2, M3 and M4 in 0.5 M sulfuric acid

The charge-discharge curves of the VFB single cell assembled with CPSF-Py membranes (M3) was shown in Figure S7. The battery is the same to that discussed in the main article, cycling from 1.65 to 0.8 volt with 30 ml electrolyte. With the increasing current density from 120 to 40 mA cm^{-2}, the initial charge voltage decreases accordingly. The initial discharge voltage also increases from 120 to 40 mA cm^{-2}, due to the minimized battery polarization.

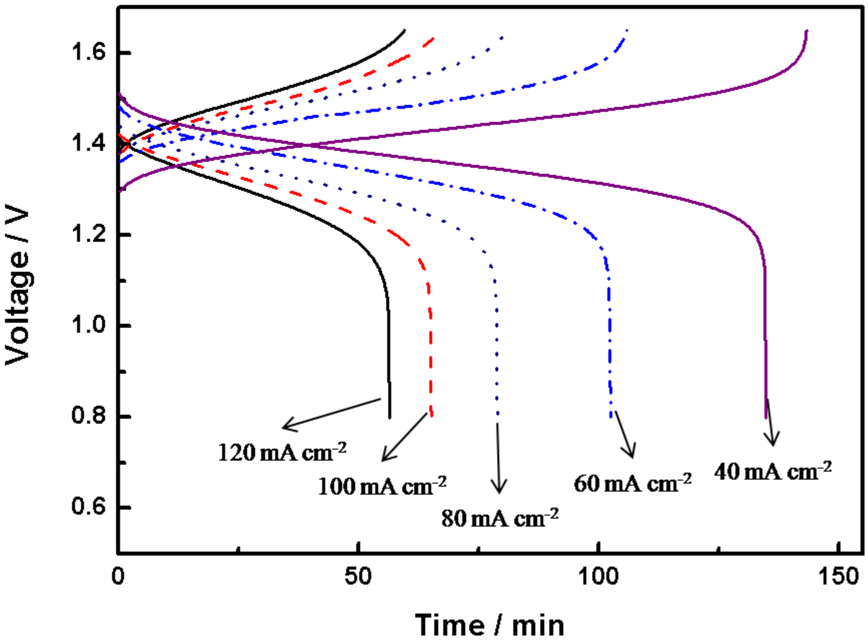

Figure S7. The charge-discharge curves of VFB single cells assembled with the prepared CPSF-Py membrane