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Supporting Information

Amphoteric nanoporous polybenzimidazole membrane with extremely low crossover for a vanadium redox flow battery

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Experimental details:

1. Synthesis of the polybenzimidazole (PBI) polymer

PBI polymer was dissolved into deuterated dimethyl sulfoxide (DMSO-d_6) at room temperature with the help of sonication. NMR spectra were measured by JEOL JNM-LA 300 at ambient conditions. To measure the FT-IR spectra, the casting solution consist of PBI polymer and dimethyl acetamide (DMAc) was prepared at ambient temperature. Further, the casting solution was poured into the petri dish and the solvent was evaporated in the oven at 80 ^{o}C for 12 h. The resultant film thickness was ~10 μm. The FT-IR spectra was measured by Jasco 460 plus by taking a total of 20 scans for sample and background with spectral resolution of 4 cm^{-1} in ambient conditions.

The proton NMR shows the signal for characteristics hydrogens in polybenzimidazole (Fig. 1S). In addition, IR spectra also confirms the synthesis of PBI polymer (Fig. 2S).

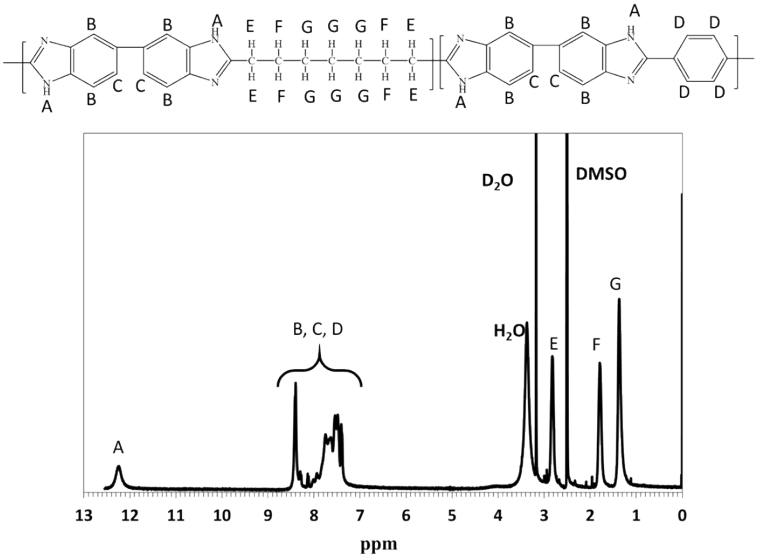

Figure 1S. ^{1}H NMR spectra of the PBI polymer; the peaks identified are shown on corresponding chemical structures

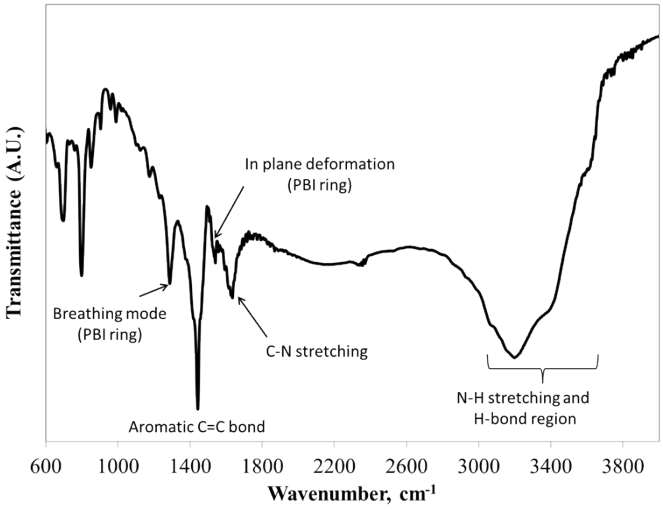

Figure 2S. FT-IR spectra of synthesized PBI polymer (PBI film, thickness ~10 μm).

2. Fabrication of nanoporous PBI membranes

Table 1S. Composition of casting solution for nanoporous PBI membranes

Membrane	PBI, wt%	PEG, vol%	DMAc, vol%
PBI-0%	8	0	100
PBI-2%	8	2	98
PBI-4%	8	4	96
PBI-6%	8	6	94
PBI-8%	8	8	92
PBI-10%	8	10	90

Characterization of nanoporous membranes:

1. Mercury intrusion porometry

Table 2S. Porosity and mean pore size of synthesized PBI membranes.

Membrane	Total pore area, $m^2\ g^{-1}$	Mean pore size, µm	Remarks
PBI-0%	2.17	1.29	Dense, Transparent
PBI-2%	0.84	28.6	Dense, Transparent
PBI-4%	0.09	12.8	Dense, Transparent
PBI-6%	16.08	0.098	Porous, Opaque
PBI-8%	110.26	0.041	Porous, Opaque
PBI-10%	140.18	0.021	Porous, Opaque

2. Membrane electrical resistance and Ionic conductivities of nanoporous PBI membranes

The ionic conductivity of the membranes was measured by a clip cell in a 0.5 M H_2SO_4 solution. The membrane electrical resistance is calculated by:

$$MER\ (\Omega\ cm^2) = (r_1 - r_2) \times A$$

where r_1 and r_2 are the total resistance of membrane (Ω) and solution, and the resistance of solution (Ω), respectively, and A is the membrane area (cm^2).

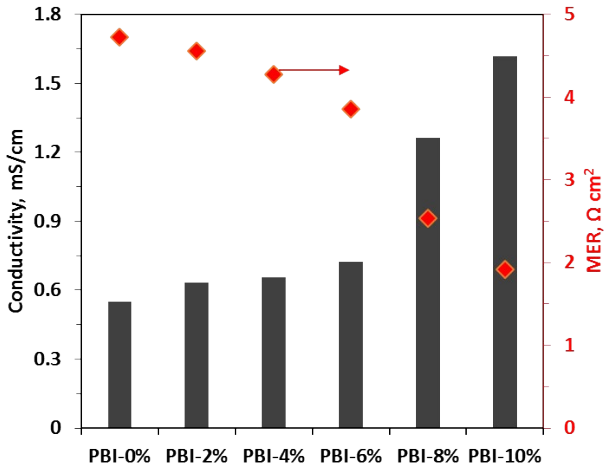

Figure 3S. Membrane electrical resistance and Ionic conductivities values for the PBI membranes.

3. Proton/vanadium (H/V) selectivity

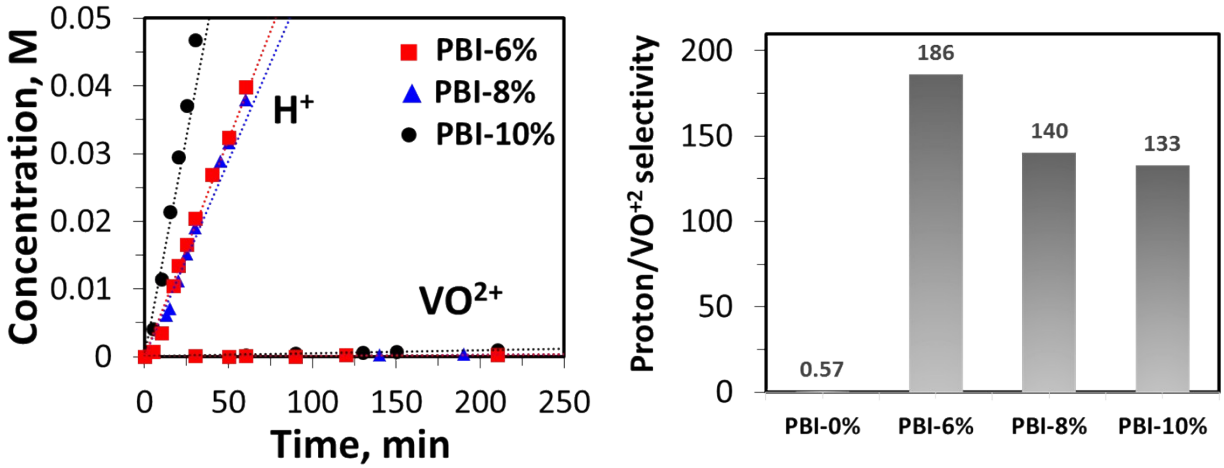

Figure 4S. Proton/vanadium ion selectivity of PBI membranes.

4. Transport number measurements

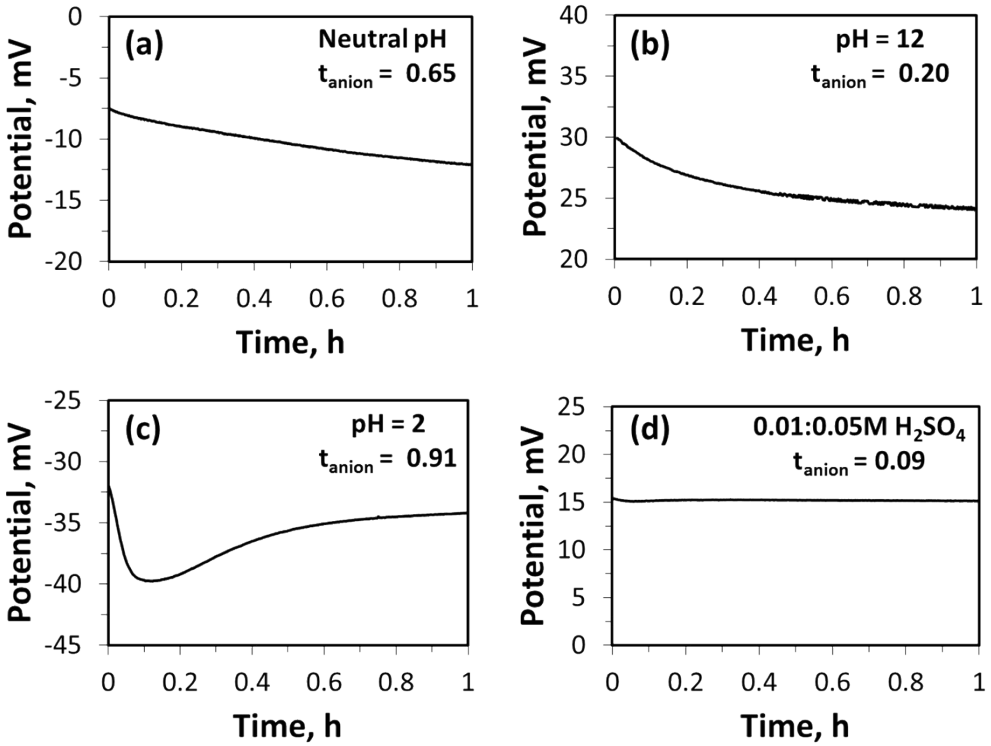

Figure 5S. Comparison of the anion transport behaviors of the m-PBI film in different types of electrolyte solutions: (a) 0.1–0.5M KCl solution at a neutral pH, (b) 0.1–0.5M KCl solution at pH 12, (c) 0.1–0.5M KCl solution at pH 2, (d) 0.01–0.05M H_2SO_4 solution.

5. Chemical stability of PBI polymers

The chemical stability of PBI polymer was evaluated by immersing the membranes in the 1.0 M VO_2^+– 2.5 M H_2SO_4 electrolyte solution. The initial VO^{2+} concentration determined and change in the concentration was noted and the concentration of VO^{2+} was calculated from the standard curve (Fig 6S (a)). PBI membrane showed comparable chemical stability with perflourosulfonic Nafion-117 membranes in terms of reduction of VO_2^+ ions (Fig. 6S (b)). Moreover, the weight loss after accelerated degradation test in electrolyte solution, PBI-10% and Nafion-117 membrane exhibited the weight loss of 5.02% and 4.61%, respectively.

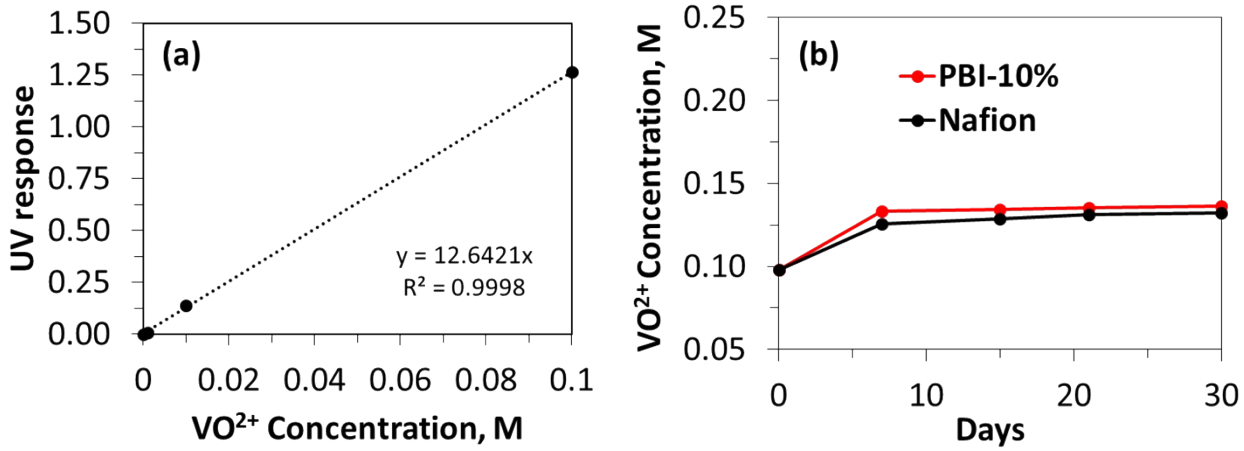

Figure 6S (a). Standard curve for VO^{2+} concentration, (b). Comparison of chemical stabilities of PBI-10% and Nafion-117 membranes.

Furthermore, the SEM micrographs of PBI-10 were compared to the pristine and after cycling test done. As it can be seen in Fig. 7S, the porous structure is physically constrained by the electrolyte flow.

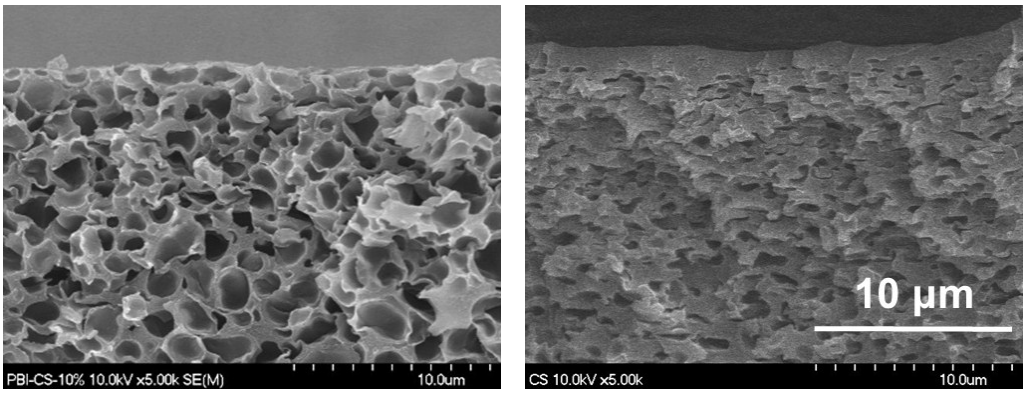

Figure 7S. SEM micrographs of a pristine PBI-10 % (left) and after cycling test (right).

6. Single cell performance at various current densities.

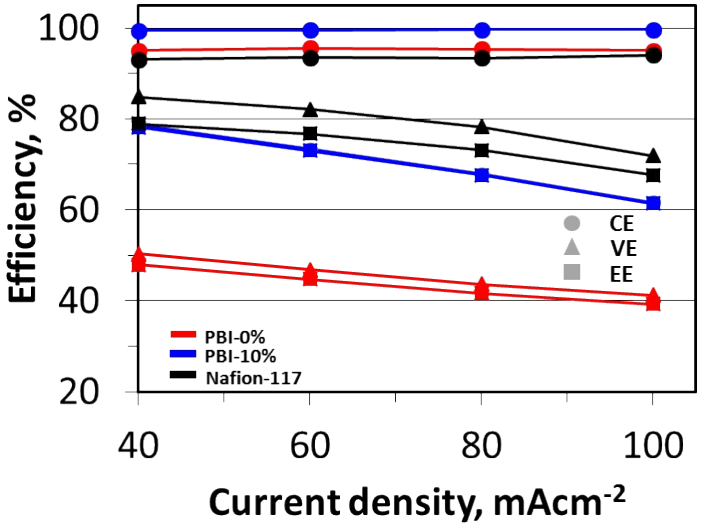

Figure 8S. Single cell performance of PBI-0%, PBI-10% and Nafion-117 membranes.