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Supporting information

Phosphoric acid doped polybenzimidazole with leaf-like three-layer porous structure as high-temperature proton exchange membrane for fuel cell

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Fabrication of pristine and porous OPBI membranes

Pristine OPBI membranes were prepared *via* a solution casting process, in which OPBI (0.4 g) was dissolved in DMAc (10 mL). The resultant homogenous solution was cast onto a 10 × 10 cm glass panel, and was placed into an oven maintained at 80 °C for 12 h, then at 100 °C for 12 h to evaporate the DMAc. The thickness of the membrane was about 50-60 μm.

A two-layered membrane was prepared *via* a two-step non-solvent induced phase separation (NIPS) method.[1] In this method, a homogeneous 12 wt.% OPBI in DMAc solution was formed, then was cast as a 250 μm thick layer onto a clean glass plate using a doctor blade. The prepared layer then quickly immersed in a mixed solvent of EDB and HEP with a weight ratio of 4:6 for 40 s. Immediately afterwards, the glass plate was quickly immersed in water until the membrane was formed. Finally, the membrane was peeled off from the glass plate and any remaining solvent was removed using ethanol. The resultant membrane was then dried in an oven at 100 °C for 24 h. The thickness of the membrane was about 50-60 μm.

A three-layered membrane was prepared *via* a two-step method. Firstly, a homogeneous solution of 12 wt.% PBI in DMAc was formed. Then was cast as a 200 μm layer onto a clean glass plate using a doctor blade, before being placed into an oven maintained at 80 °C for 4–6 h to evaporate the majority of the DMAc. Afterwards, the above casting solution was cast onto the PBI layer prepared above to form a further 250 μm layer using a doctor blade, which was then quickly immersed in a mixed solvent of EDB and HEP with a weight ratio of 4:6 for 40 s. Immediately after this, the glass plate was quickly immersed in water until the membrane was formed. Finally, the membrane was peeled off from the glass plate and any remaining solvent was removed using ethanol. The resultant membrane was dried in an oven at 100 °C for 24 h. The thickness of the membrane is about 50-60 μm.

The preparation of a cross-linked three-layered membrane was achieved following the similar process used of preparing the three-layered membrane, but using 12 wt.% of OPBI in DMAc solution with 1 wt.% of KH-560. The thickness of the membrane is about 50-60 μm.

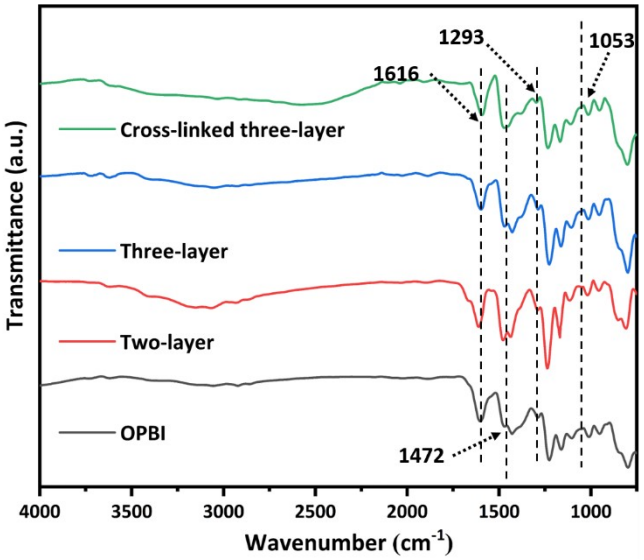

Fig. S1 FT-IR spectra of the OPBI and porous membranes.

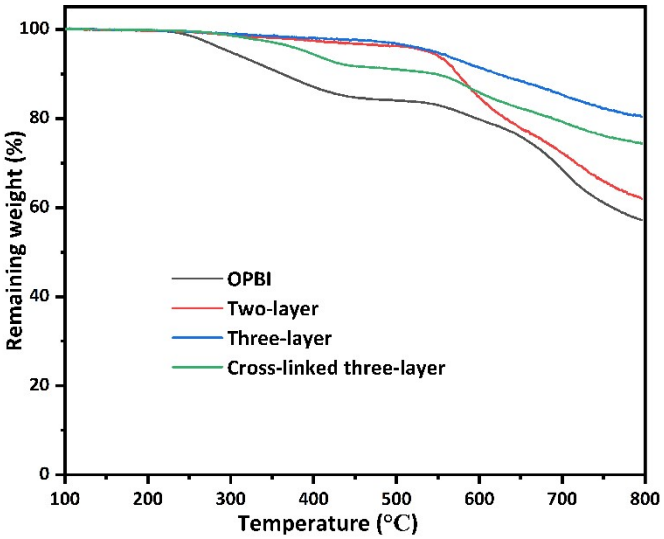

Fig. S2 TGA curves of the pristine OPBI and the OPBI porous membranes.

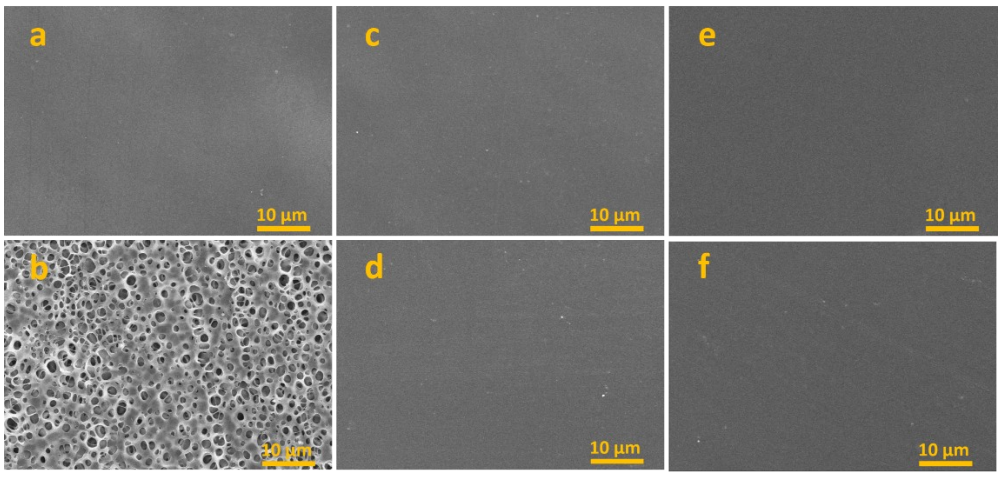

Fig. S3 The surface morphology of the OPBI porous membranes. The skin layer surface (a) and porous surface (b) of two-layer membrane; the thick (c) and thin (d) skin layer surface of three-layer membrane; the thick (e) and thin (f) skin layer surface of cross-linked three-layer membrane.

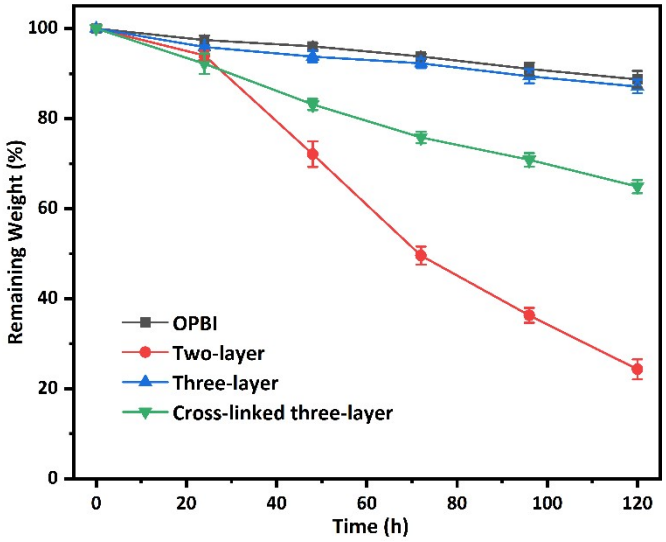

Fig. S4 The remaining weights of the pristine OPBI and the OPBI porous membranes during the Fenton test at 80 °C.

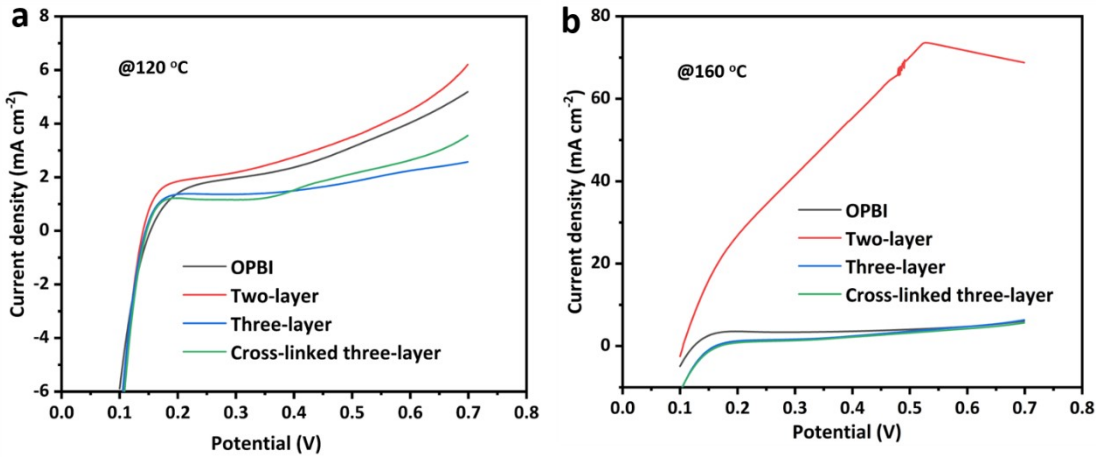

Fig. S5 The crossover current density of PA-doped pristine OPBI and porous membranes on single cells at (a) 120 and (b) 160 °C.

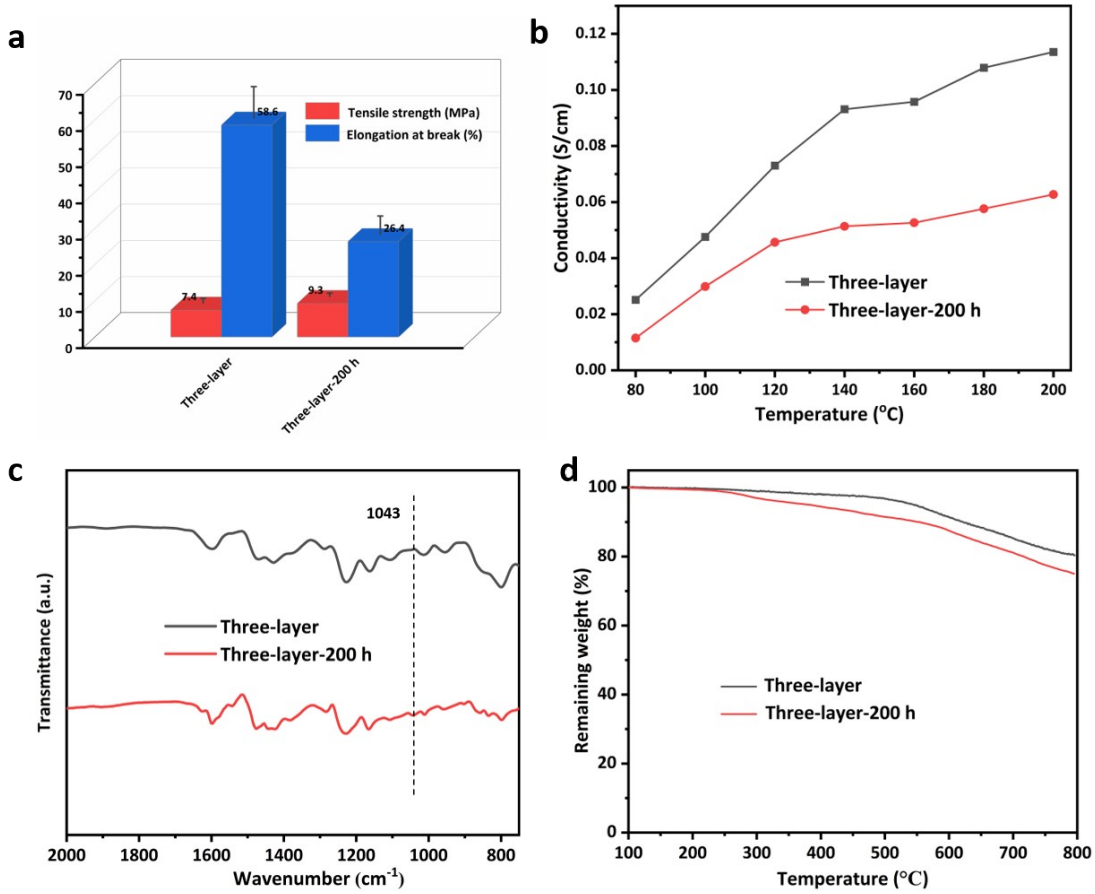

Fig. S6 Tensile strengths, elongation at breaks (a), proton conductivities (b), FT-IR (c) and TGA curves of PA-doped three-layer membrane before and after a 200-h durability test of MEA (200 mA cm^{-2}). For the FT-IR and TGA test, PA was removed in advance.

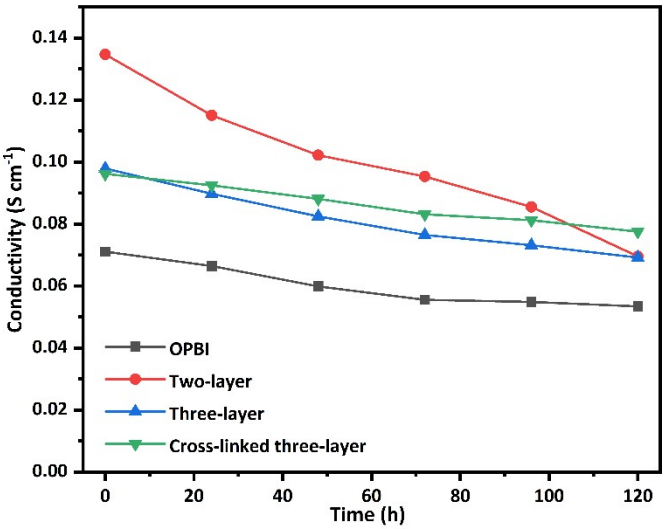

Fig. S7 Conductivity stability of the membranes at 160 °C without humidification.

References

1. M. Shi, Q. Dai, F. Li, T. Li, G. Hou, H. Zhang and X. Li, *Adv Energy Mater*, 2020, **10**, 2001382.