Supporting information

A Nafion/ polybenzimidazole composite membrane with consecutive proton-conducting pathways for aqueous redox flow batteries

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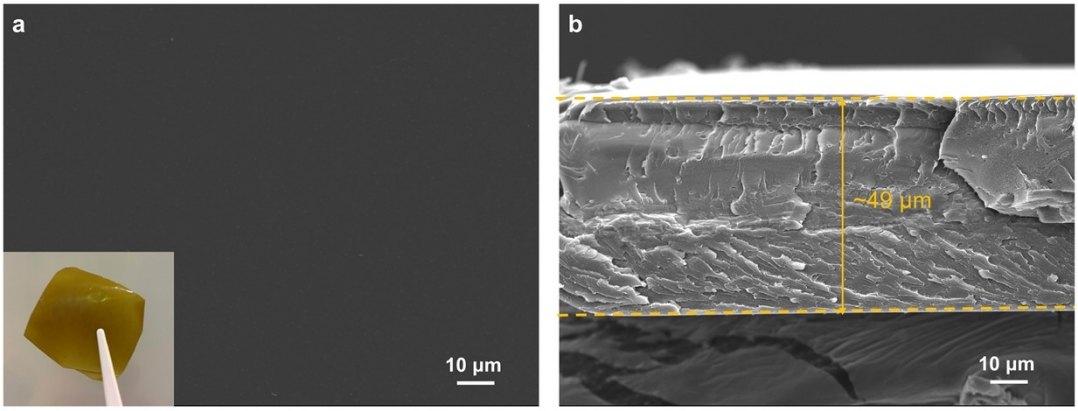

Fig. S1 SEM images of the (a) surface and (b) cross-section morphologies of NP-Blend membrane

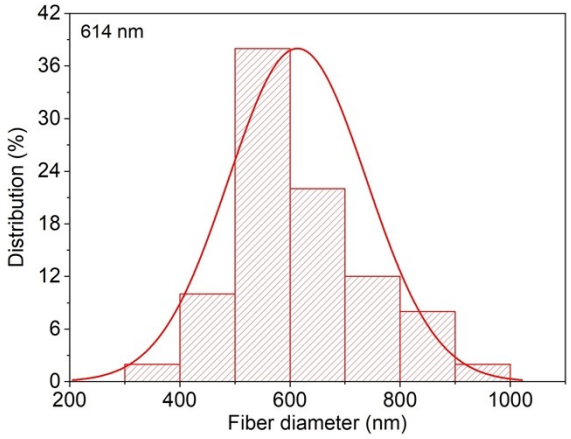

Fig. S2 Fiber diameter distribution curve of Nafion nanofibers with PEO dopant (Mw~600 kDa)

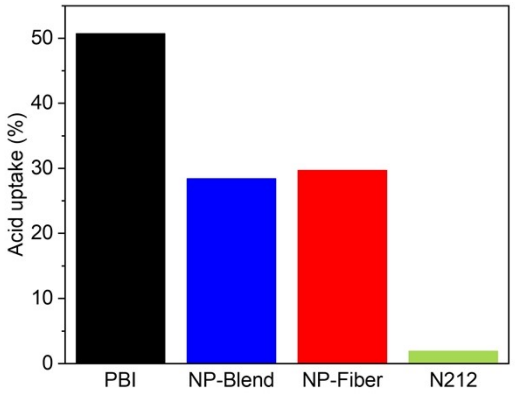

Fig. S3 Acid uptake of the PBI, NP-Blend, NP-Fiber and N212 membranes

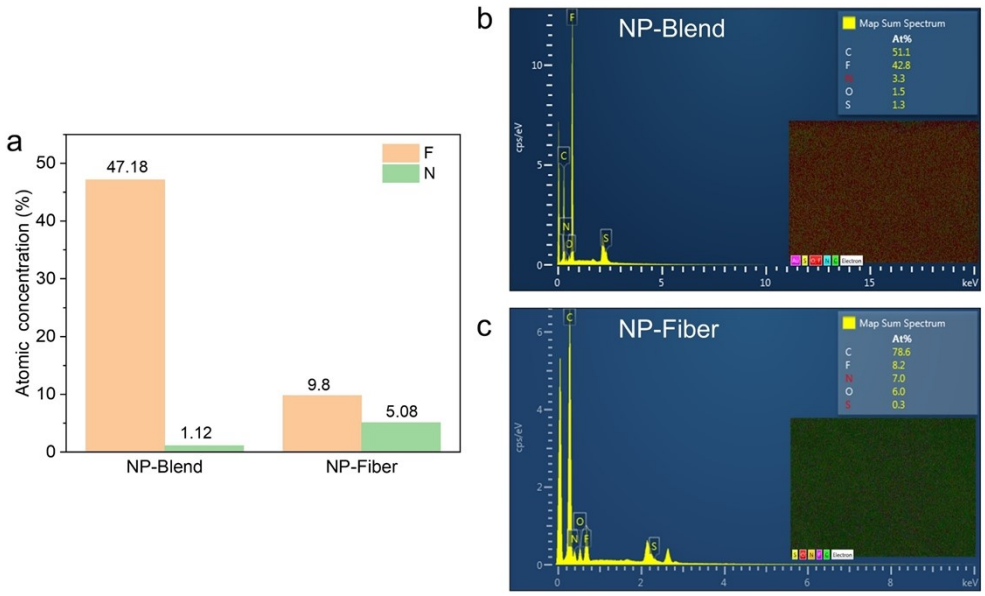

Fig. S4 Surface elemental analysis of the NP-Blend and NP-Fiber membranes through (a) XPS and (b, c) EDX mapping.

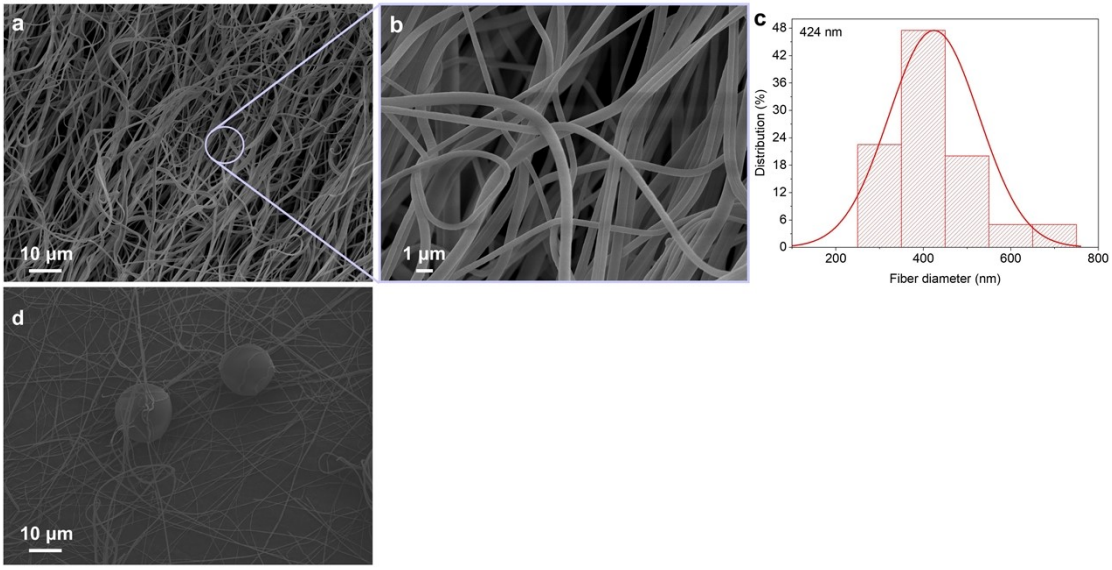

Fig. S5 (a, b) SEM images and (c) fiber diameter distribution curve of Nafion nanofibers with PEO dopant (Mw~300 kDa); (d) SEM image of Nafion nanofibers prepared with 13 wt% electrospinning solutions

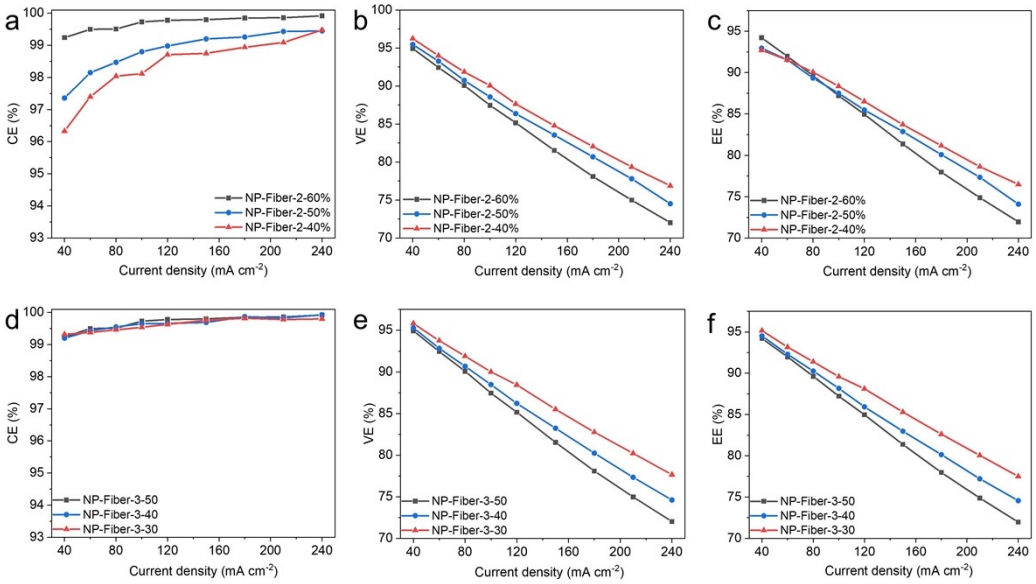

Fig. S6 The battery performance of the NP-Fiber-2 membranes with different PBI loading (a-c) and NP-Fiber-3 membranes with different thickness (d-f).

Optimizations:

1. Adjusting fiber diameter: It has been reported that thinner nanofibers would possess higher proton conductivity. The original fiber diameter applied in NP-Fiber membrane is around 614 nm. Accordingly, nanofibers with an average fiber diameter around 424 nm are prepared by 15 wt% Nafion precursors with 300 kDa PEO dopant, as shown in Fig. S5a-c. Further reducing the fiber diameter through lowering the concentration (13 wt%) of electrospinning precursors causes the formation of unfavorable bead-on-fiber structure (Fig. S5d). Therefore, the 424 nm fiber diameter could be the lower limit in our work. The optimal membrane in this direction, namely NP-Fiber-1, is made of the Nafion nanofibers with the 424 nm fiber diameter.
2. Adjusting the PBI loading: Due to the low proton conductivity of PBI, lowering the

PBI loading could be helpful to reduce the area resistance of the composite membrane. The original NP-Fiber membrane contains 60 wt% PBI loading. Hence, the composite membranes with lower PBI loading, 50 wt% and 40 wt%, are prepared, respectively. It is observed that with the decrease of PBI loading, the VE of the battery is increased, yet accompanied by the decrease of CE (Fig. S6a-b). At high current densities like 240 mA cm^{-2}, the membrane with 40 wt% PBI loading shows the best EE performance (Fig. S6c). Therefore, the optimal membrane in the second direction, namely NP-Fiber-2, contains 40 wt% PBI.

3. Adjusting the membrane thickness: Reducing the membrane thickness is an effective way to reduce the area resistance. The original NP-Fiber membrane is around 50 μm thick. Therefore, thinner membranes with the thickness of about 40 μm and 30 μm are prepared, respectively. As shown in Fig. S6d-f, with the decrease of the membrane thickness, the CE of the battery is kept nearly unchanged while the VE along with the EE is improved. The composite membrane with the smallest thickness exhibits the best EE performance at all the tested current densities (40-240 mA cm^{-2}). Therefore, the optimal membrane in the third direction, namely NP-Fiber-3, has the thickness around 30 μm.

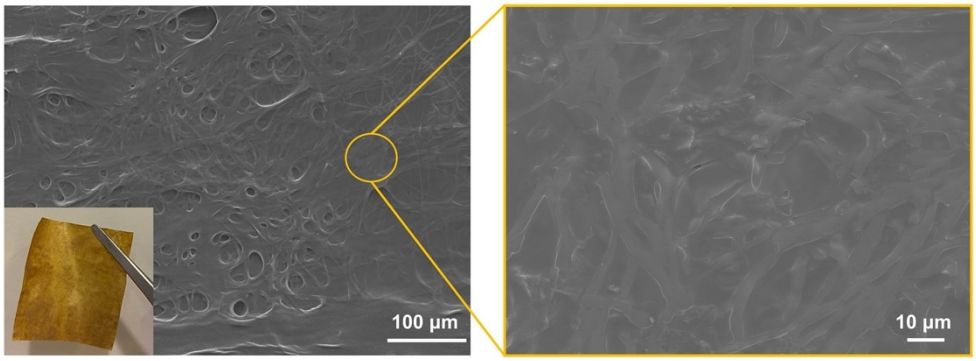

Fig. S7 SEM images of the surface morphology of NP-Fiber-2 membrane

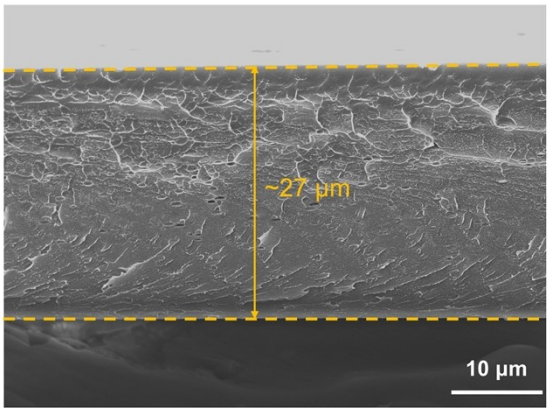

Fig. S8 SEM image of the cross-section morphology of NP-Fiber-3 membrane

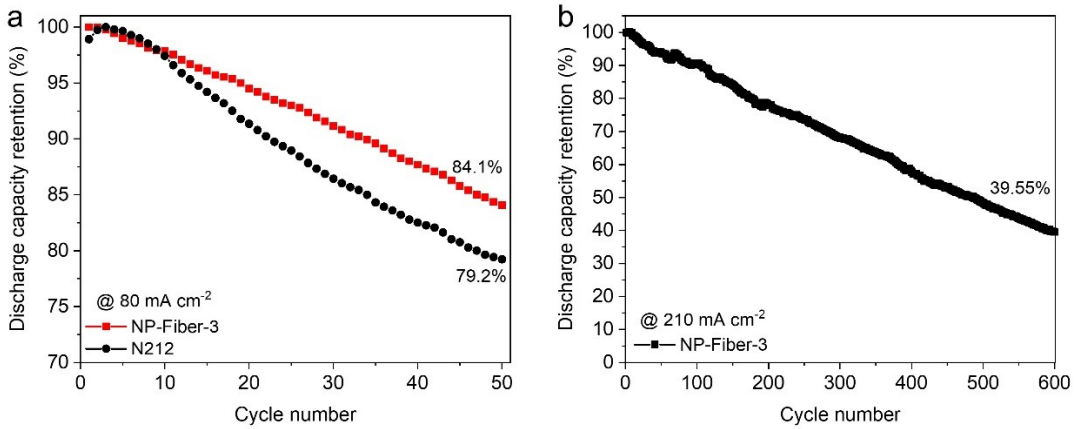

Fig. S9 The discharge capacity retention of the batteries with the NP-Fiber-3 and N212 membranes at (a) 80 and (b) 210 mA cm^{-2}.

Table. S1 Detailed parameters of the membranes

Samples	Dry thickness (μm)	Wet thickness (μm)	Nafion content (wt%)	Nafion fiber diameter (nm)
PBI	50	60	0.0	\
NP-Blend	49	57	40.0	\
NP-Fiber	52	58	38.6	614
NP-Fiber-1	50	55	39.4	424
NP-Fiber-2	46	55	61.1	614
NP-Fiber-3	27	31	40.7	614
N212	51	57	100.0	\