Supporting Information for

Advanced adjustable ionic conductivity of polybenzimidazole membranes with arrayed two-dimensional AlOOH nanosheets for water electrolysis

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Characterization

The porosity of the membrane

The membrane was immersed in 1-butanol for 2 h and then weighed after wiping off the 1-butanol on the surface with tissue paper. The porosity of the membrane was calculated as follows:

$$E = \frac{M_w - M_d}{\rho \times S \times l} \tag{1}$$

where Mw and Md are the mass of the wet and dried membrane, respectively; ρ is the density of 1-butanol; S is the surface area of the dried membrane; l is the thickness of the dried membrane.

Water uptake (WU), Swelling ratio (SR) and Hydrophilic

The water uptake (WU) and swelling ratio (SR) was determined using the following method. The membrane samples were immersed in deionized water at room temperature for 24 h; After 24h, each membrane was removed from the deionized water, and its surface was dried with tissue paper. Next, the sample was weight to obtain the wet weight (W_{wet}) and size (L_{wet}） of wet membranes, Then dried under vacuum at 100 °C for 12 h to obtain the dry weight (W_{dry}) and size (L_{dry}） of the dry membranes.

The water uptake (WU), swelling ratio (SR) were calculated by equations (2), (3) and (4):

$$WU(\%) = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100\% \tag{2}$$

$$SR(\%) = \left(\frac{L_{wet} - L_{dry}}{L_{dry}}\right) \times 100\% \tag{3}$$

The static water contact angles of the γ-AlOOH-PBI porous composite membranes were measured by a video-supported contact angle measuring instrument (OCA 20, Dataphysics, Germany) using a sessile drop method.

Results and discussion

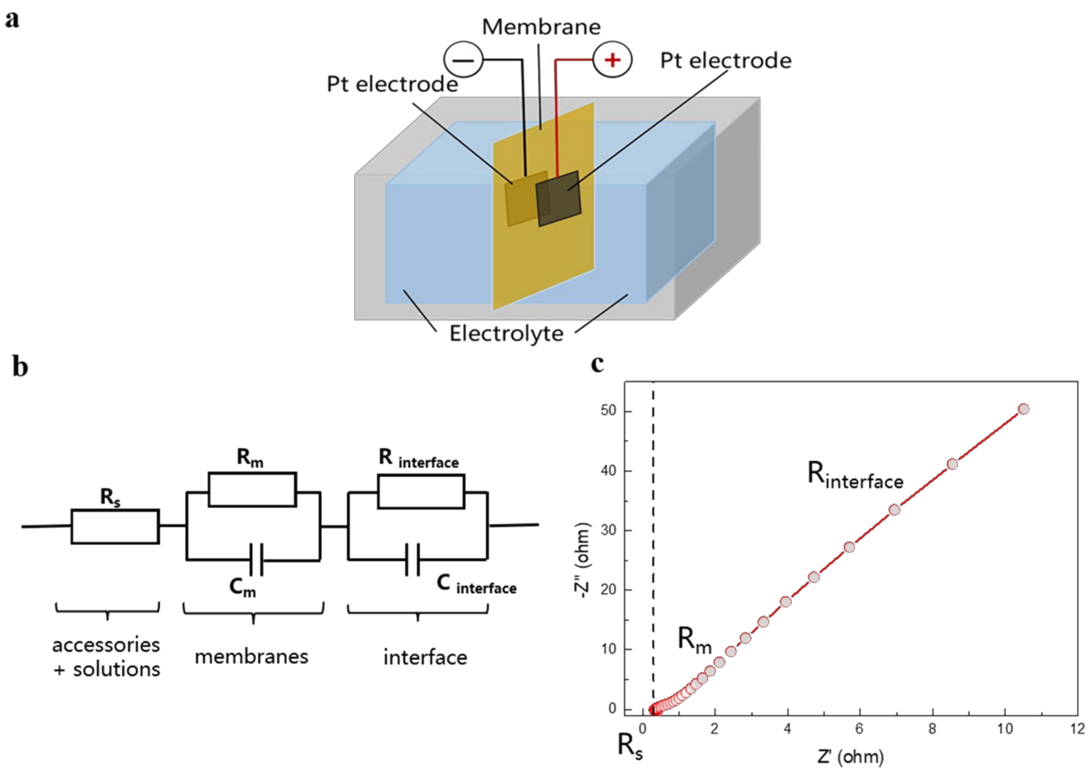

Fig. S1. a) Schematic diagram illustrating the components of ionic conductivity measurements unit. b) Equivalent circuit model used to fit the Nyquist plots in this work. c) An example of the Nyquist plot of γ-AlOOH PBI composite membranes. In equivalent circuit, R_s refers to the contact resistance of accessories in conductivity test cells and the ohmic resistance of solutions. R_m is the impedance of charge transfer through membranes, which could be obtained by extrapolating semi-circle to the x-axis, taking the value of the horizontal coordinate corresponding to the intersection of the high frequency semicircle and the low frequency line in the curve. If the test frequency is not too high or the system conductivity is high, the high frequency semicircle does not appear and the value of the high frequency endpoint is taken as the horizontal coordinate. $R_{interface}$ is the impedances for ion-migration through interface between solutions and membranes. C_m and $C_{interface}$ are capacitive processes. Based on the analysis of bode plots, there are two steps of diffusive processes corresponding to the different frequency, (a) ion diffusing through interface between membranes and solutions, and (b) a typical Warburg diffusive process at low frequency. The approximate 45° diagonal line indicates Warburg diffusion.

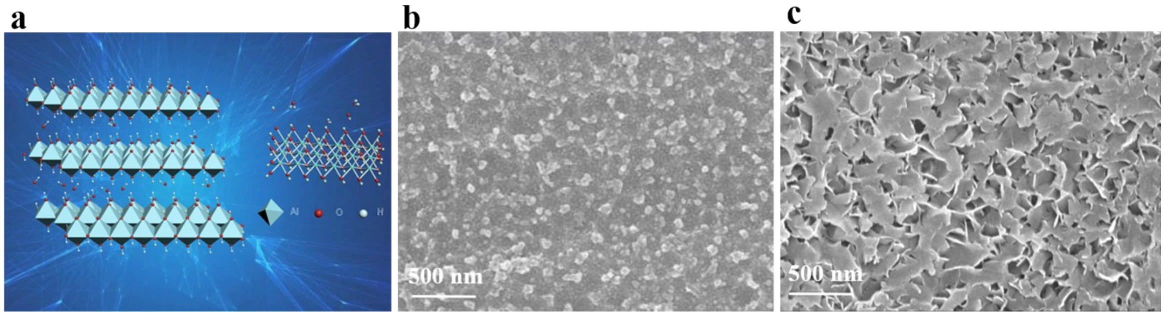

Fig. S2. SEM morphologies of aluminum-based surface nanostructures at different water bath temperatures. a) Schematic structure of γ-AlOOH, b) γ-AlOOH-50℃(SEM), c) γ-AlOOH-70℃(SEM).

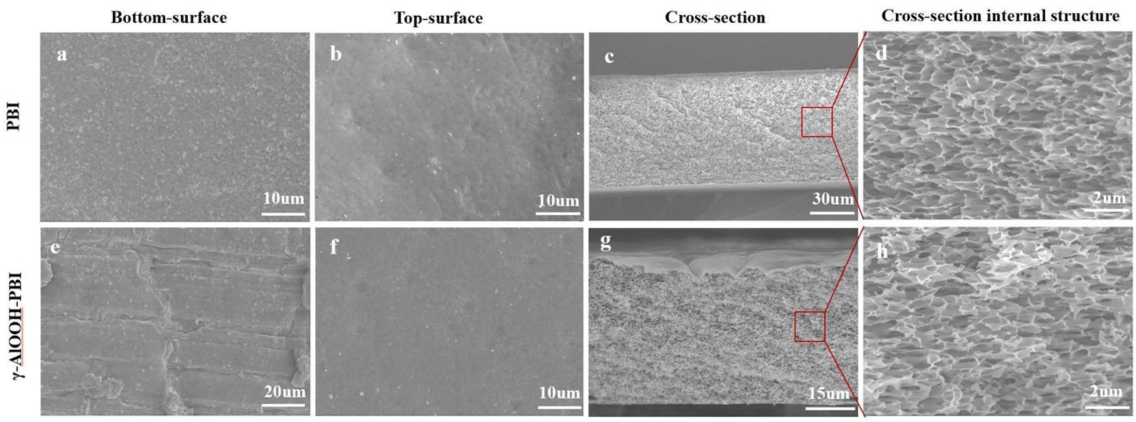

Fig. S3. SEM morphology of pristine PBI membranes and γ-AlOOH-PBI composite membranes.

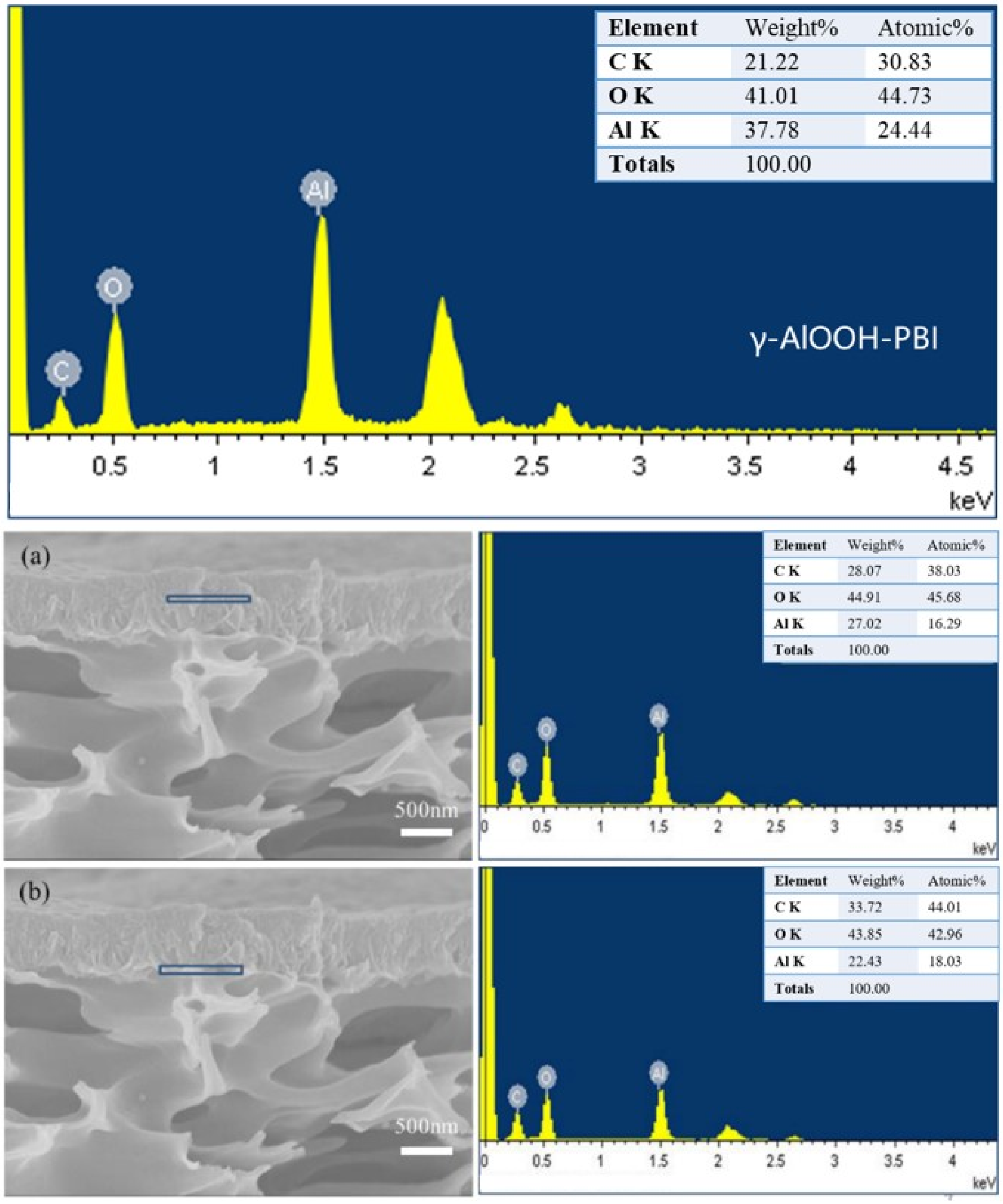

Fig. S4. EDS of γ-AlOOH PBI composite membranes and γ-AlOOH nanosheets a) γ-AlOOH nanosheet layers structure in the middle; b) γ-AlOOH nanosheet layers structure at the interface with the membrane.

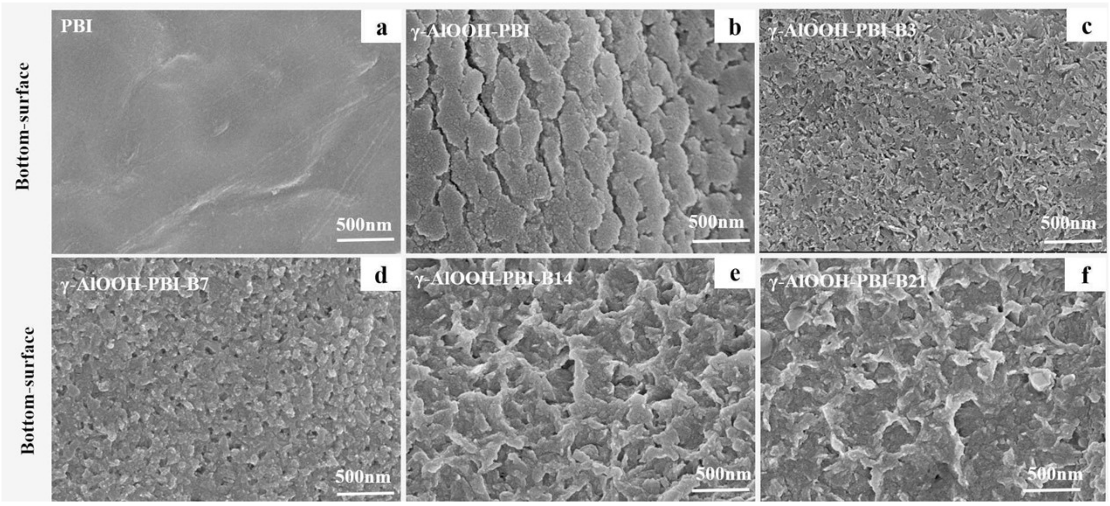

Fig. S5. SEM morphologies of pristine PBI and γ-AlOOH-PBI composite membranes. **a)** bottom-surface andbottom-surface of **a)** pristine PBI, **b-f)** γ-AlOOH-PBI composite membranes at different days of alkali immersion.

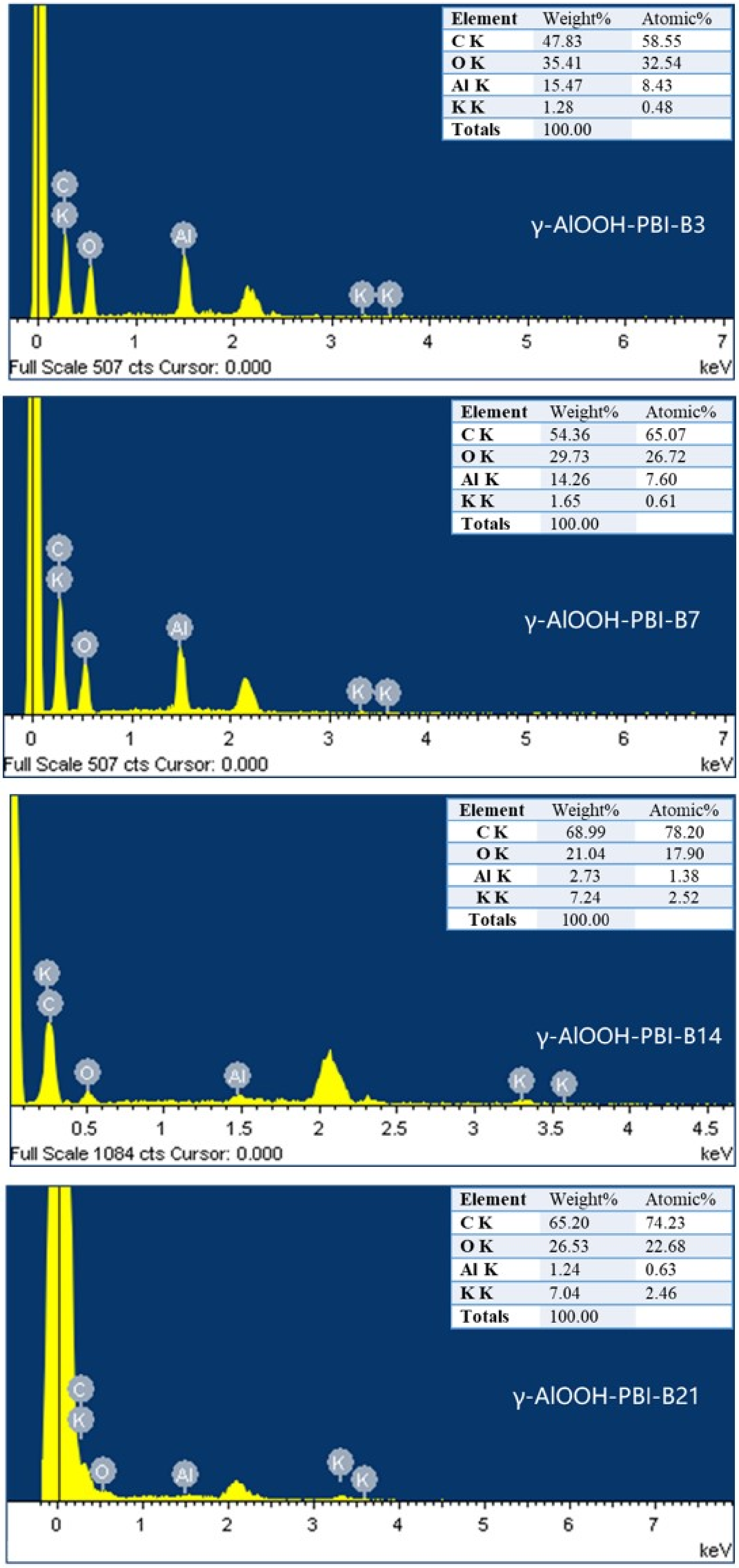

Fig. S6. EDS of γ-AlOOH PBI composite membranes with different days of alkali immersion. B3, B7, B14, B21 are soaking days, respectively.

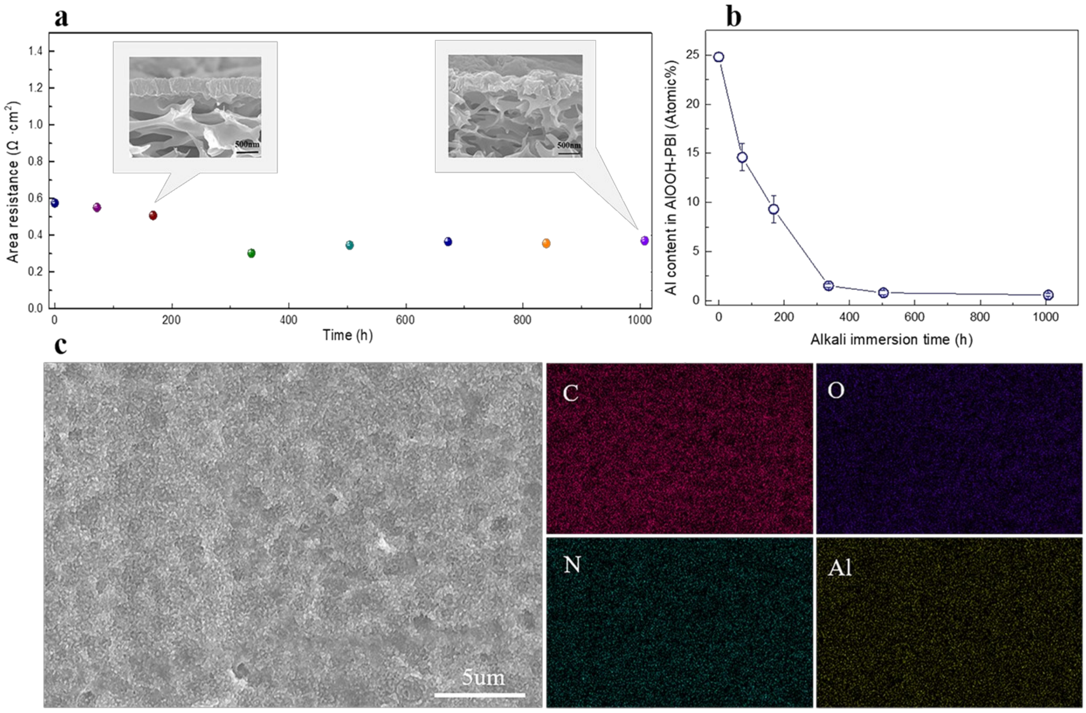

Fig.S7 **a)** The stability of γ-AlOOH-PBI composite membrane in 1MKOH environment; **b)** Variation curves of alkali immersion time and Al content in γ-AlOOH-PBI; **c)** The SEM image and elemental mapping of γ-AlOOH-PBI composite membrane after immersion in $3MH_2SO_4$ environment at 80℃ for 20h.

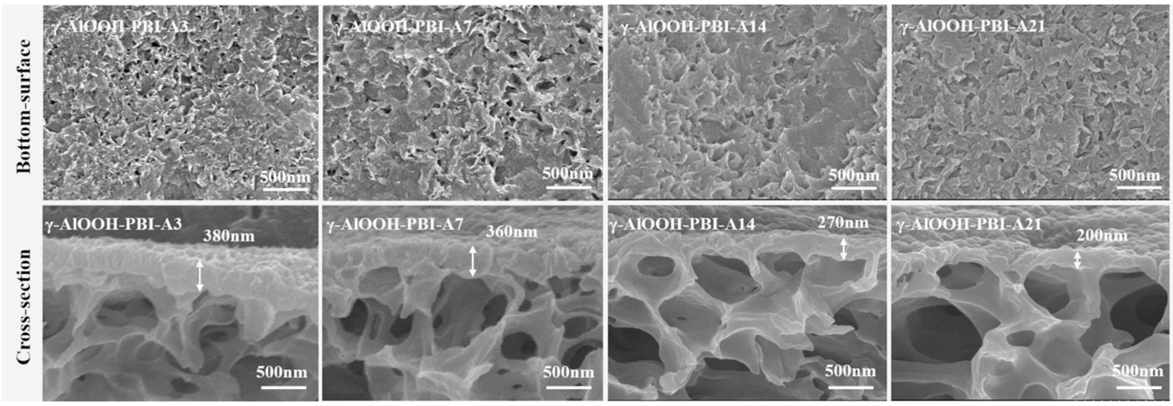

Fig. S8. SEM morphology of pristine PBI membranes and γ-AlOOH PBI composite membranes with different days of Acid immersion. A3, A7, A14, A21 are soaking days in in acid solution, respectively.

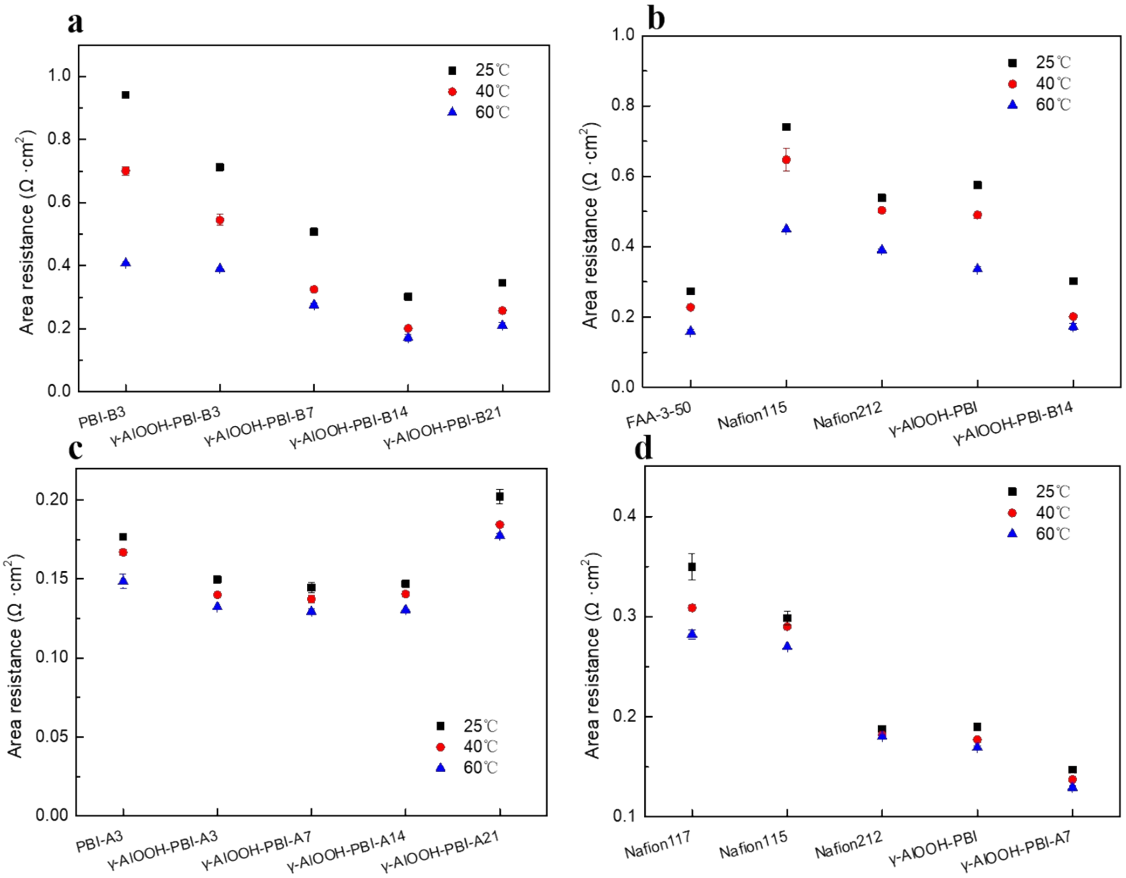

Fig. S9. Area resistance of γ-AlOOH-PBI composite membranes. a-b) Area resistance of different membranes at different temperatures in 1M KOH environment, c-d) Area resistance of different membranes at different temperatures in 3MH_2SO_4 environment. Error bars are standard deviations obtained using three measurements from different samples.

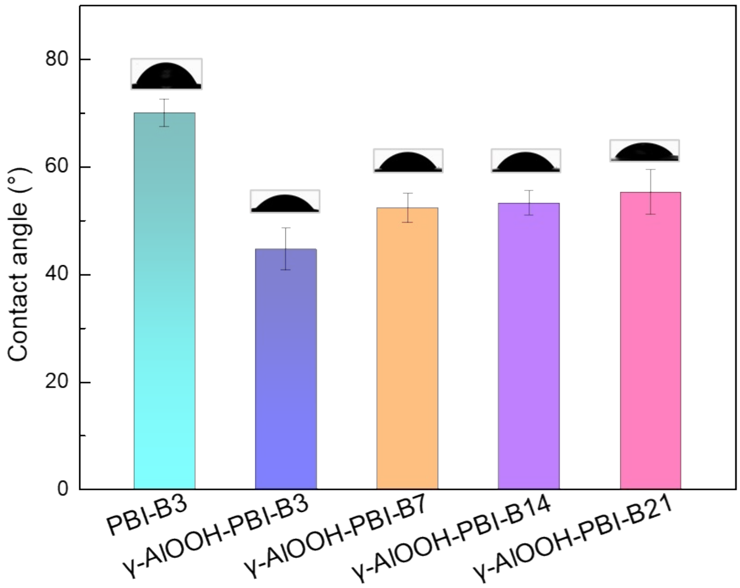

Fig. S10. The water contact angle of PBI-B3, γ-AlOOH-B3, γ-AlOOH-B7, γ-AlOOH-B14, γ-AlOOH-B21 membranes under dry state.

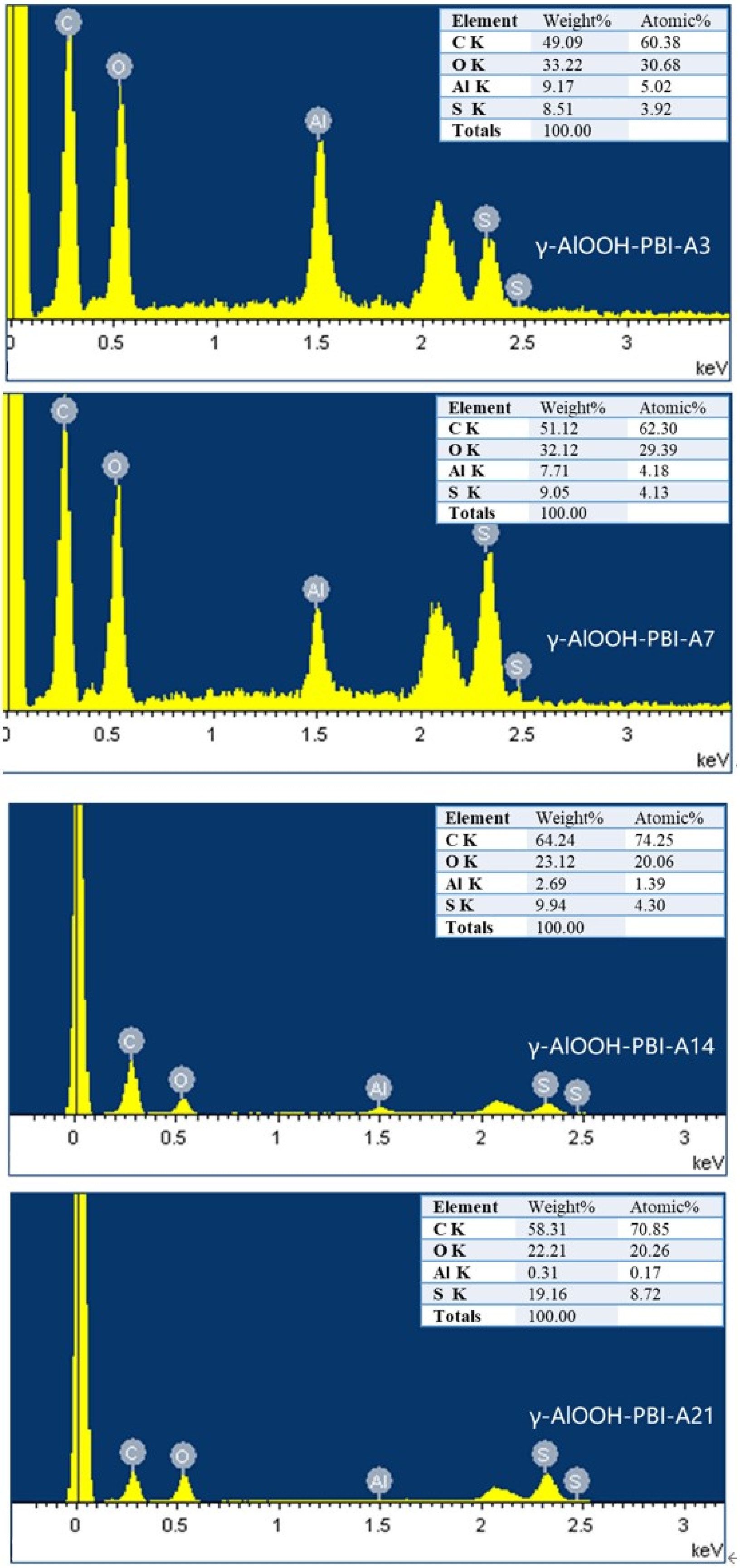

Fig. S11. EDS of pristine PBI membranes and γ-AlOOH PBI composite membranes with different days of acid immersion. A3, A7, A14, A21 are soaking days, respectively.

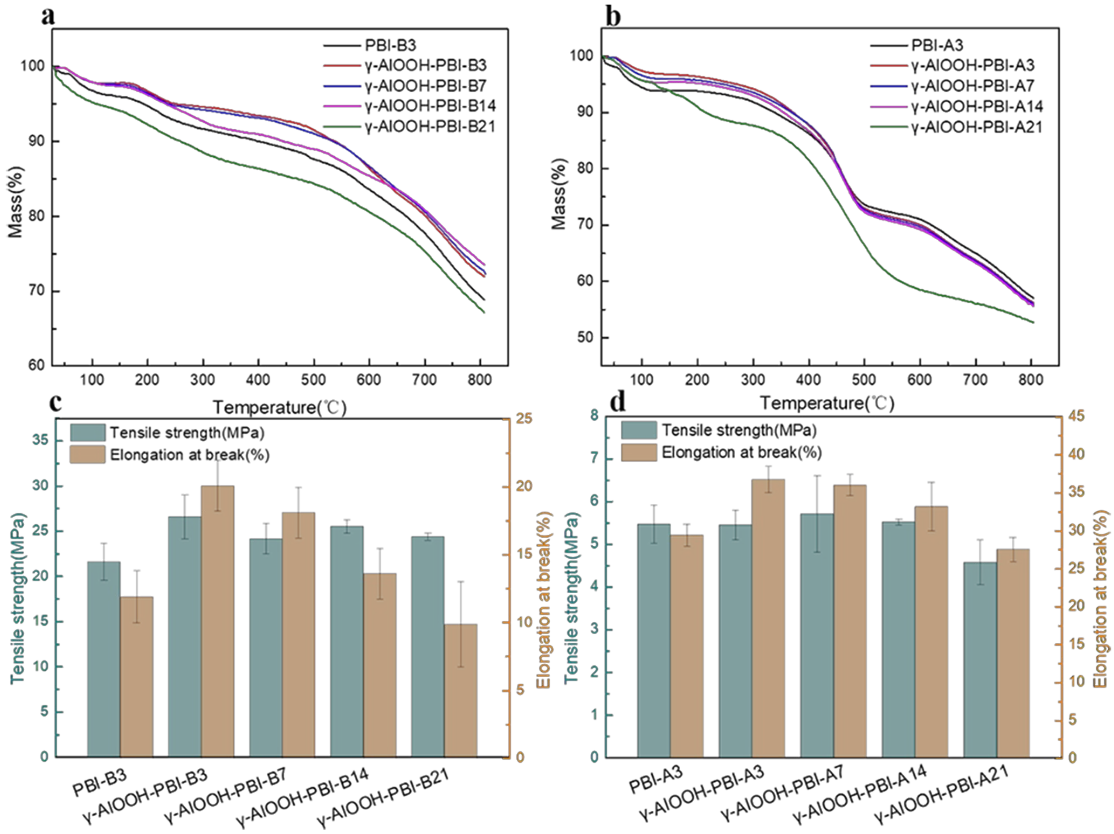

Fig. S12. a and b) TGA curves and c and d) stress–strain behaviors of pristine PBI andγ-AlOOH-PBI. Of note, B3, B7, B14, B21, A3, A7, A14, and A21 represent soaking days in alkaline and acid solution, respectively.

Table. S1 Physicochemical properties of pristine PBI and γ-AlOOH-PBI

Sample	**Thickness（μm）**	**WU （%）**	**SR （%）**
PBI-B3	75±5	149.81±1.01	4.33±0.58
γ-AlOOH-PBI-B3	75±5	150.77±3.64	2.60±0.05
γ-AlOOH-PBI-B7	75±5	175.39±0.72	2.73±0.08
γ-AlOOH-PBI-B14	75±5	181.51±0.99	2.78±0.56
γ-AlOOH-PBI-B21	75±5	185.62±4.26	2.80±1.44

Table. S2 Comparison of the electrolysis performance for water electrolysis reported in literatures.

The types of water electrolysis	**Membrane**	**Temperature (℃)**	**Feed**	**Current density(mA⓾cm^{-2}) at cell voltage 1.8V**	**Reference**
Alkaline	γ-AlOOH-PBI-B14	25	1M KOH	500.00	This work
	Linear PBI	80	30wt% KOH	20.00	[1]
	Crosslinked PBI	80	30wt% KOH	85.00	[1]
	Thermally cured PBI	80	30wt% KOH	40.00	[1]
	L-ABPBI	70	1.9mol⓾dm^{-3}	63.00	[2]
	C-ABPBI	70	1.9mol⓾dm^{-3}	60.00	[2]
	PVA-PBI	50	15wt% KOH	50.00	[3]
	FAA3-PBI	60	20wt% KOH	40.00	[4]
	PAEK-APBI	60	10wt% KOH	250.00	[5]
	mes-PBI	80	30wt% KOH	45.00	[6]
Acid-alkaline amphoteric	mPBI	40	6MKOH(Anode)//3MH_2SO_4(Cathode)	~360.00	[7]
	OPBI	20	6MKOH(Anode)//3MH_2SO_4(Cathode)	~38.00	[7]
Alkaline	FAA3-50	60	1M KOH	320.00	[8]

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