

## Supplementary Information

### **Enhanced ionic conductivity and chemical stability of anion exchange membrane prepared from ether-free poly(biphenyl alkylene piperidinium) with alkyl spacer for water electrolysis**

*Thi Cam Thach To, Anh Le Mong, and Dukjoon Kim\**

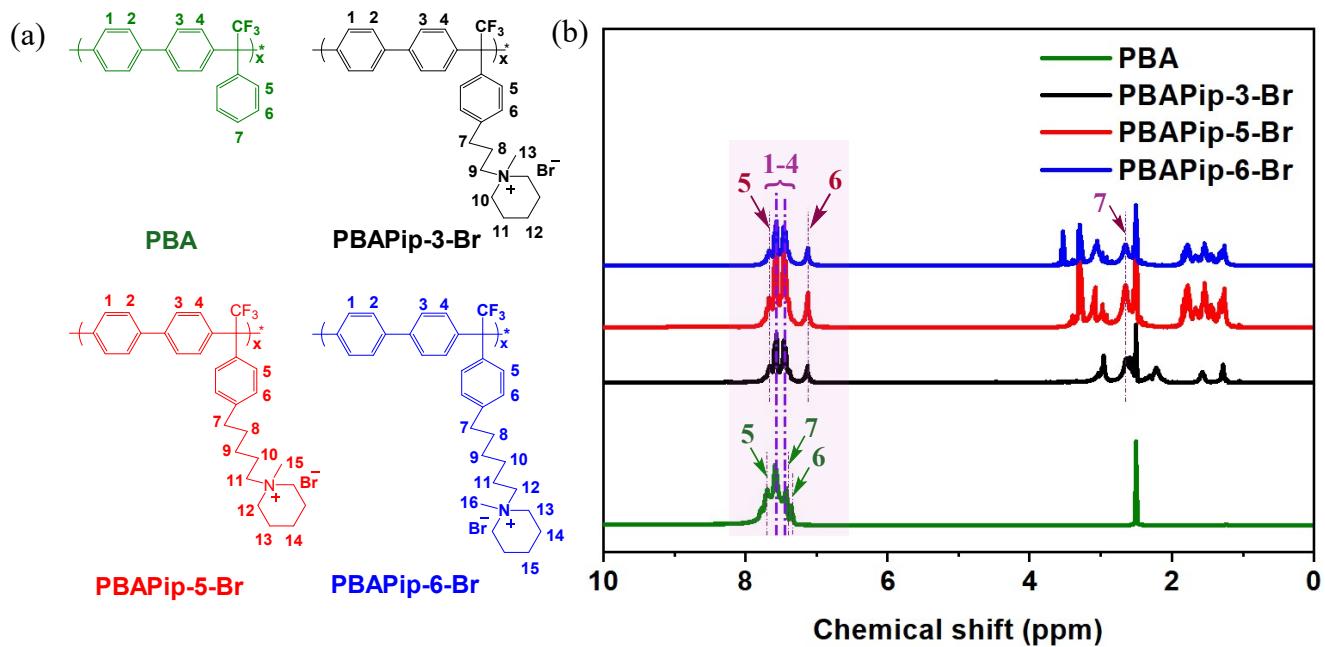
T.C.T. To, A.L. Mong, Prof. D. Kim

School of Chemical Engineering, Sungkyunkwan University, Gyeonggi, Suwon, 16419,  
Republic of Korea.

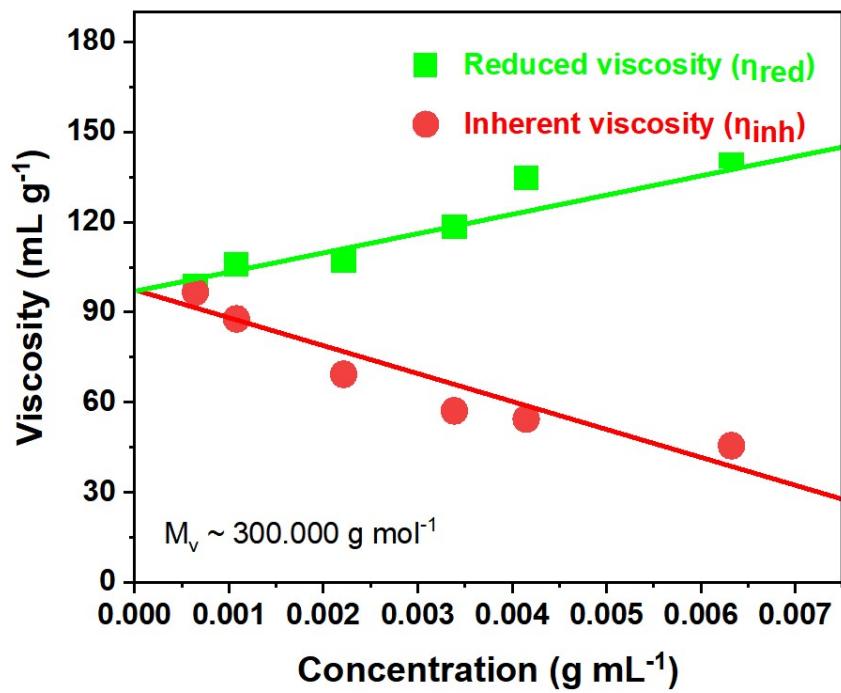
E-mail: djkim@skku.edu

Number of figures: 10

Number of pages: 18



**Figure S1.** (a) Chemical structures; and (b)  $^1\text{H}$ -NMR spectra of PBA and PBAPip-n-Br membranes ( $n = 3, 5$ , and  $6$ ).



**Figure S2.** Viscosity of PBAPip-6-Br solution at different concentrations.

The intrinsic viscosity ( $[\eta]$ ) of PBAPip-6-Br was determined using an Ubbelohde viscometer. The sample was dissolved in DMSO to obtain a homogeneous solution at different concentrations (c), and the efflux time ( $t_c$ ) of each solution was recorded at 25 °C. The reduced ( $\eta_{\text{red}}$ ) and inherent ( $\eta_{\text{inh}}$ ) viscosities can be calculated using the following equations:

$$\eta_{\text{red}} = (t_c/t_0 - 1)/c \quad (\text{S-1})$$

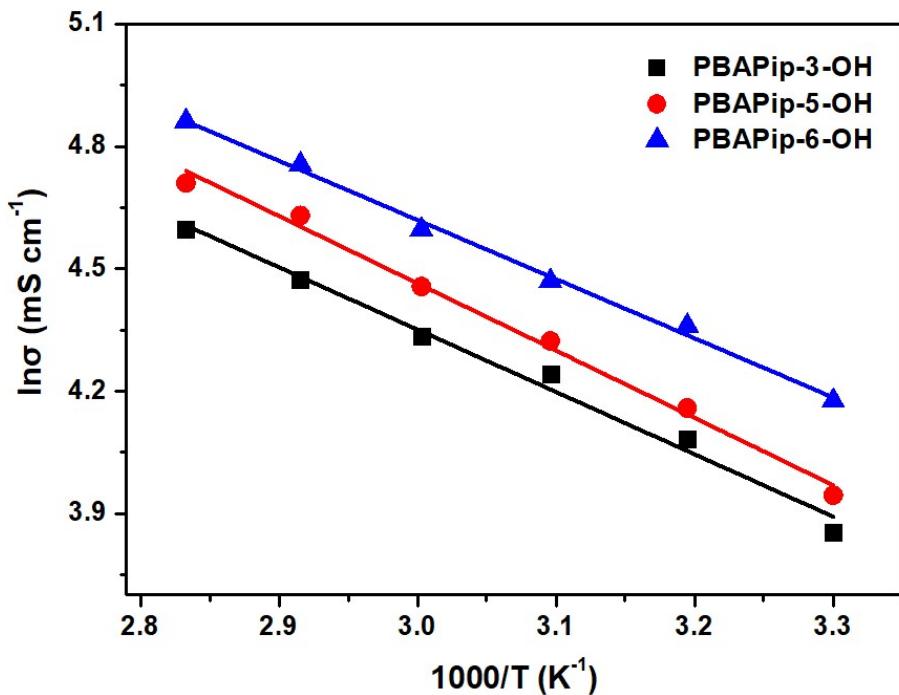
$$\eta_{\text{inh}} = (lnt_c/t_0)/c \quad (\text{S-2})$$

Here,  $t_0$  is the efflux time for a DMSO solvent. In a plot of viscosity versus concentration, the intrinsic viscosity  $[\eta]$  was the y-intercept value obtained by extrapolating the  $\eta_{\text{red}}$  and  $\eta_{\text{inh}}$  to  $c = 0$ .

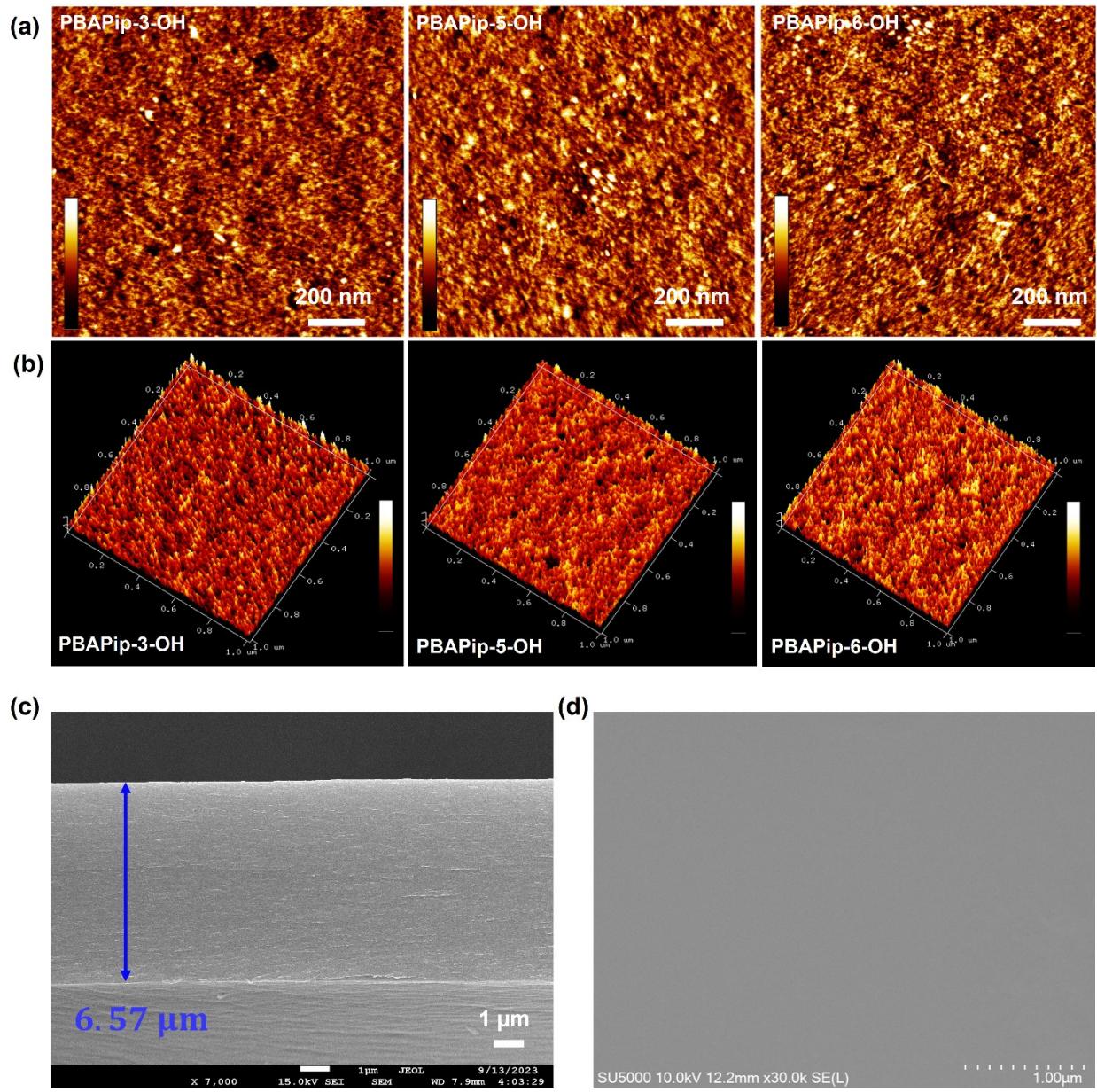
The  $M_v$  of PBAPip-6-Br was calculated by equation S-3:

$$[\eta] = k \cdot M_v^a \quad (\text{S-3})$$

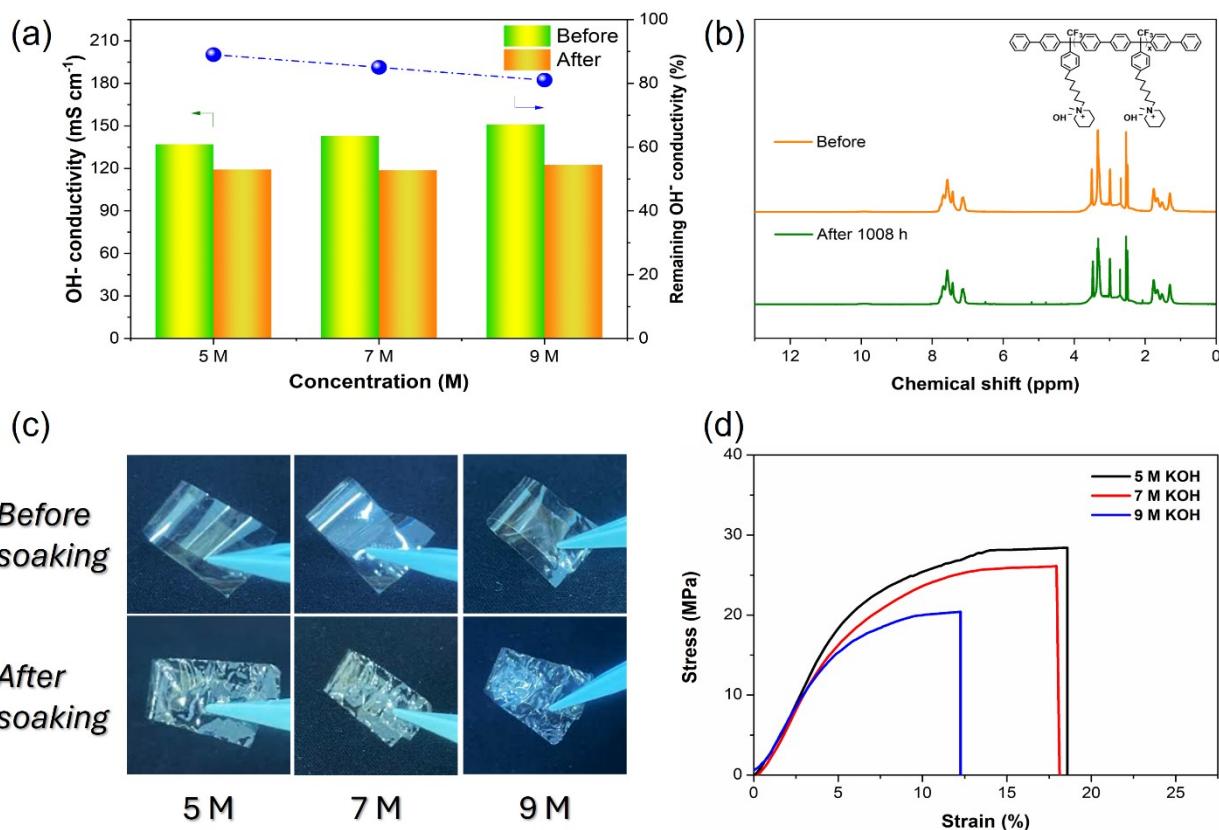
Here,  $k = 0.03$  and  $a = 0.75$  are assumed for PBAPip-6-Br and DMSO combination.



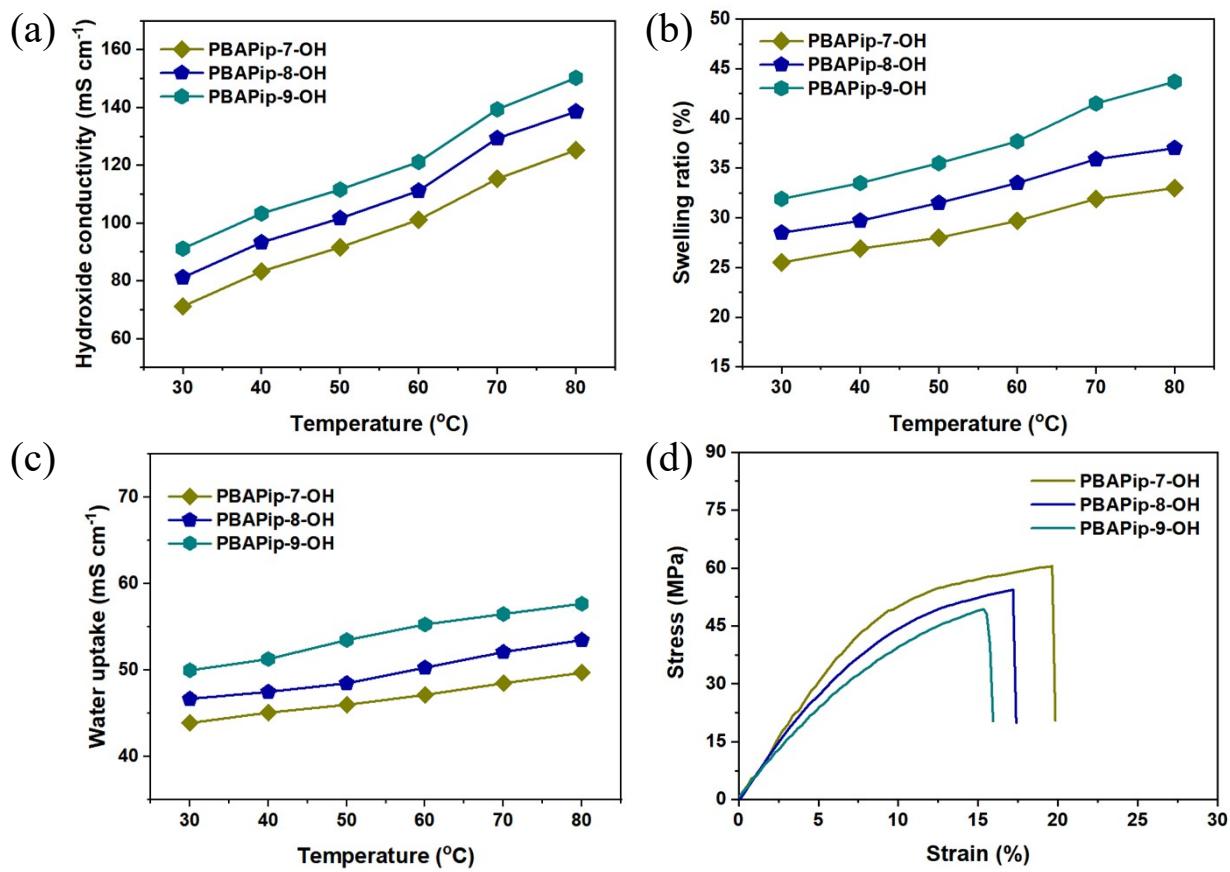
**Figure S3.** Arrhenius plots of the AEMs with different side chain lengths at various temperatures.



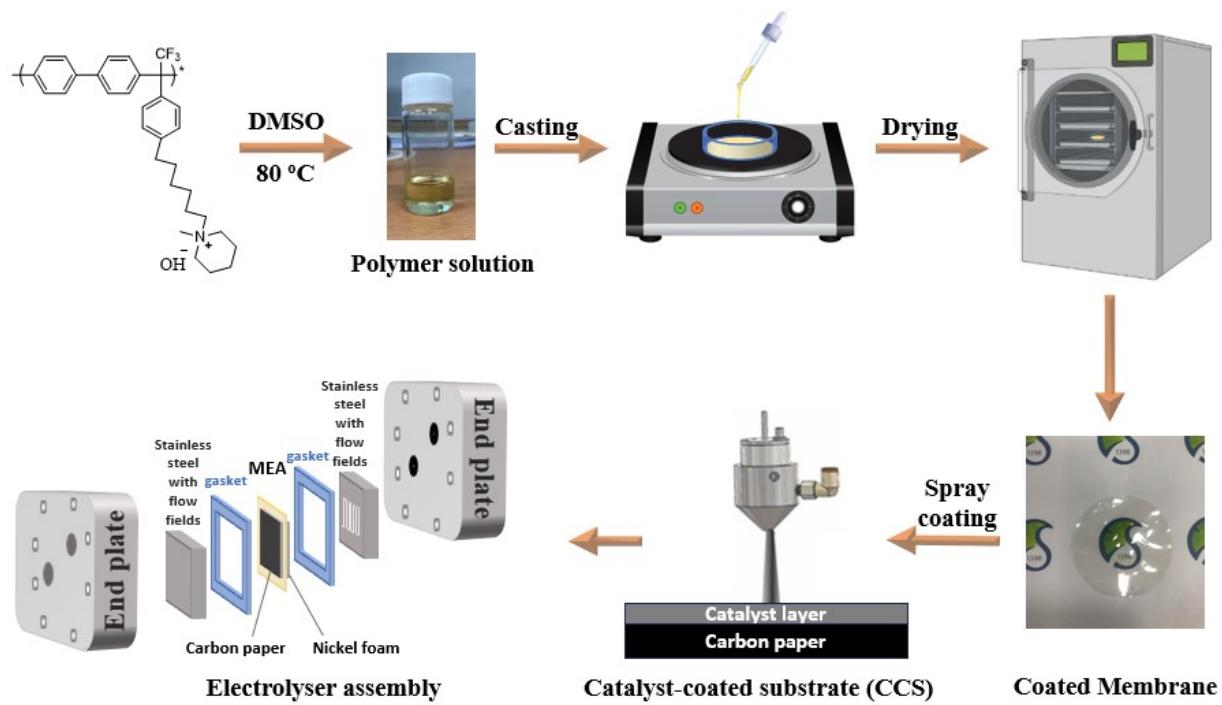
**Figure S4.** (a-b) Two- and three-dimensional AFM images of PBAPip-n-OH ( $n = 3, 5$ , and  $6$ ) membranes and (c-d) cross-sectional and surface SEM images of PBAPip-6-OH membrane.



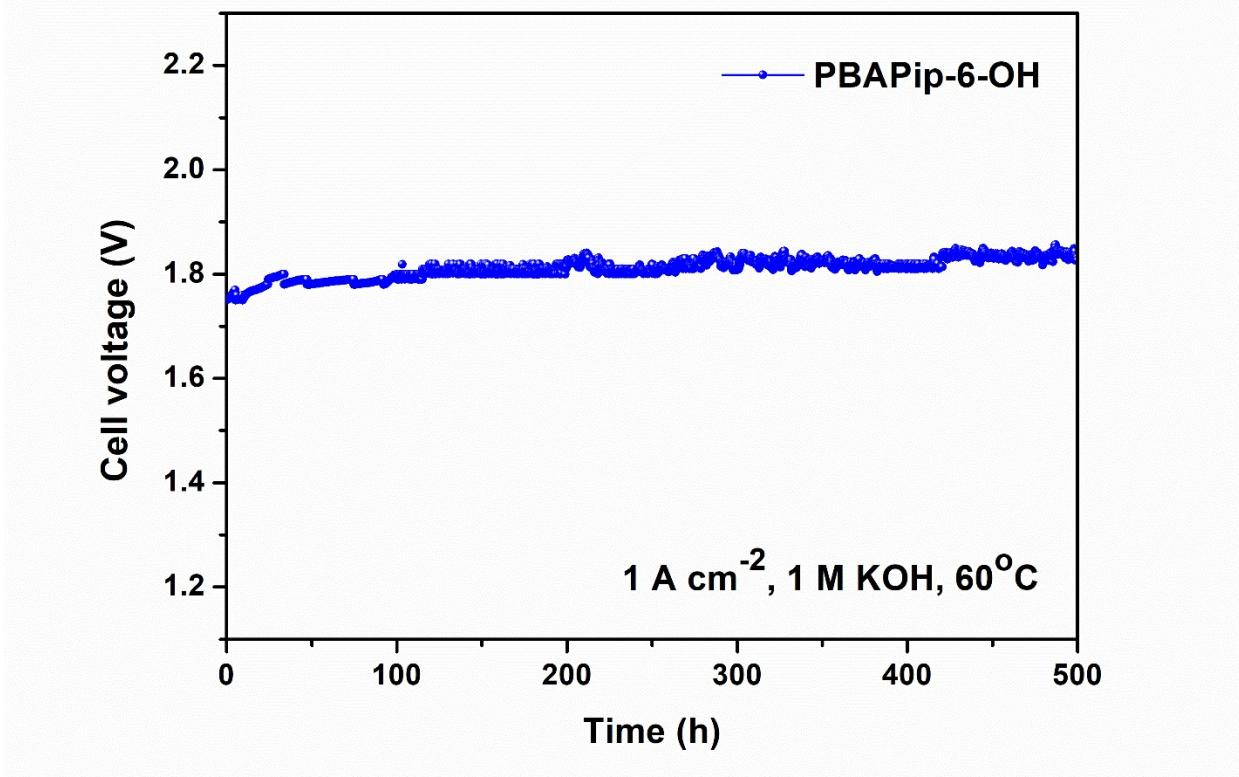
**Figure S5.** (a) Hydroxide conductivity of PBAPip-6-OH membrane before and after immersion in different KOH concentrations at 60 °C for 1008 h; (b) <sup>1</sup>H-NMR spectra of PBAPip-6-OH membrane before and after immersing in 5 M KOH solution at 60 °C for 1008 h; (c) visual images; and (d) the mechanical properties of PBAPip-6-OH membrane after soaking with different KOH concentrations for at 60 °C for 1008 h.



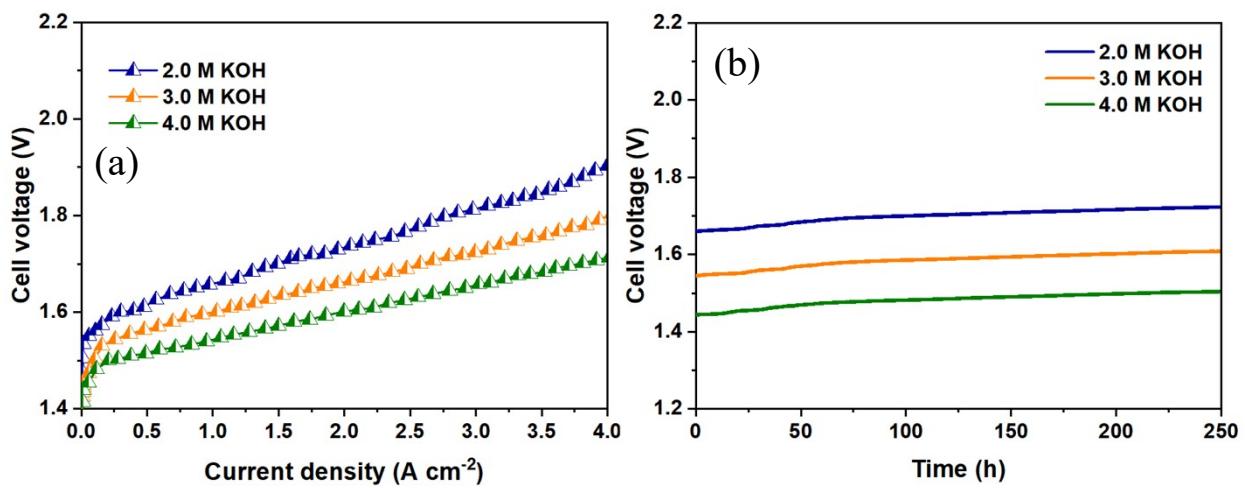
**Figure S6.** (a) Hydroxide ion conductivity; (b) swelling ratio; (c) water uptake; and (d) mechanical properties of PBAPip-n-Br membranes ( $n = 7, 8$ , and  $9$ ).



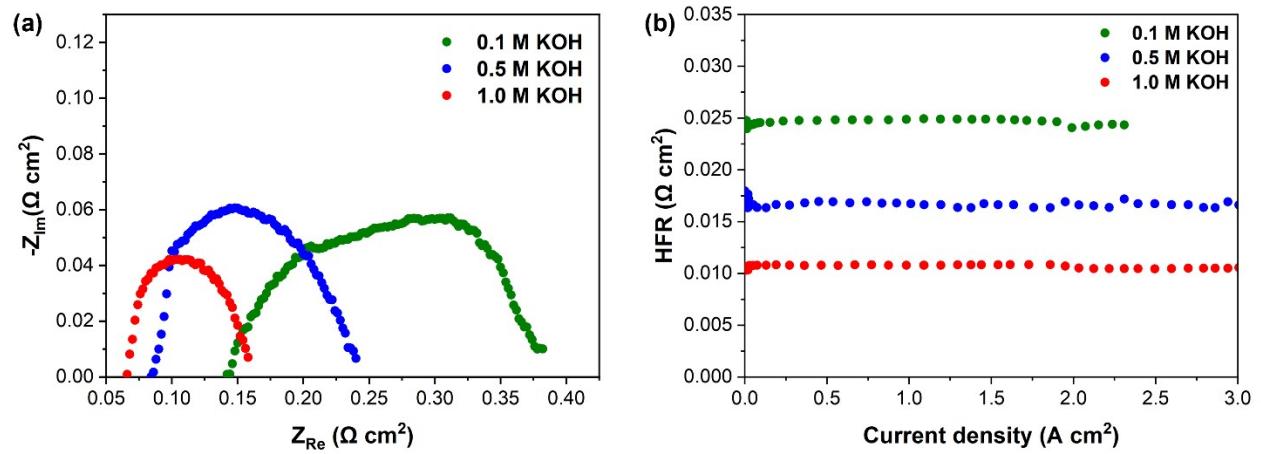
**Figure S7.** Preparation of anion exchange membranes, MEA, and the water electrolysis cell.



**Figure S8.** Long-term stability test of the PBAPip-6-OH-based AEMWE cell during 500 h.



**Figure S9.** (a) Polarization curves at different KOH solution concentrations and (b) long-term stability test during 250 h at 1  $\text{A cm}^{-2}$  of PBAPip-6-OH membrane.



**Figure S10.** (a) Nyquist plot; and (b) HFR of AEMWE cells using PBAPip-6-OH membrane at various KOH concentrations.

**Table S1:** The degree of alkyl chain grafting and the quaternization level of N-methylpiperidine.

	$I_{H_6}$	$I_a$	$I_p$	$\eta_g$	$\eta_q$
<b>PBAPip-3-Br</b>	2.10	2.19	2.26	96%	97%
<b>PBAPip-5-Br</b>	2.32	2.41	2.55	95%	95%
<b>PBAPip-6-Br</b>	2.27	2.35	2.37	96%	97%

Here,  $I_{H_6}$ ,  $I_a$ , and  $I_p$  are the intensity of the proton signals of the  $H_6$ , alkyl side chain, and piperidium functional groups, respectively. Besides,  $\eta_g$  and  $\eta_q$  are the degree of alkyl chain grafting and the quaternization level of N-methylpiperidine, respectively.

**Table S2:** Mechanical properties of the prepared AEMs at the dry states.

Samples	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
PBAPip-3-OH	52.5 ± 1.0	21.5 ± 0.4	1.18±0.0045
PBAPip-5-OH	60.1 ± 0.2	22.6 ± 0.7	1.00±0.0037
PBAPip-6-OH	67.5 ± 0.6	23.1 ± 0.3	0.96±0.0021

**Table S3:** The high-frequency resistance (HFR) and OH<sup>-</sup> conductivity of the prepared membranes.

Concentration	HFR ( $\Omega \text{ cm}^2$ )	$\sigma$ ( $\text{mS cm}^{-1}$ )
<b>0.1 M KOH</b>	0.025	27.5
<b>0.5 M KOH</b>	0.017	39.3
<b>1.0 M KOH</b>	0.011	65.1

Here, the high-frequency resistance (HFR) of the anion exchange membranes can be determined using the following formula:

$$HFR (\Omega \text{ cm}^2) = \frac{L}{\sigma \times A}$$

(S-4)

Where L is the thickness (cm),  $\sigma$  is the hydroxide conductivity, and A is the effective area ( $\text{cm}^2$ ) of the prepared membranes.

**Table S4:** Comparison of cell performance between AEM fabricated in this study and other recently reported.

Membrane type	Anode	Cathode	Temp. (°C)	Feed	Current density		Year	Ref.
						(A cm <sup>-2</sup> )		
PPO-ABCO	Ni foam	Ni foam	50	pure water	0.15		2014	[1,2]
Fumatech FAPQ	NiFe <sub>2</sub> O <sub>4</sub>	NiFeCo	60	1 M KOH	0.3		2017	[3]
PSF-ABCO	Ni/CP	Pt-Ni/CP	50	pure water	0.375		2017	[2]
PPO-TMA	Ni foam	Ni foam	50	pure water	0.6		2014	[1,2]
PSF-1M	Ni/CP	Pt-Ni/CP	50	pure water	0.6		2017	[2]
Aemion	NiFe <sub>2</sub> O <sub>4</sub>	NiFeCo	60	1 M KOH	0.63		2021	[4] 21
PSF-TMA	Ni/CP	Pt-Ni/CP	50	pure water	0.63		2017	[2] 51
FAA-3-50	<i>d</i> -Ni <sub>3</sub> Fe <sub>1</sub>	Pt/C	60	1 M KOH	0.75		2023	[4,5,6]
A-201	NiFe <sub>2</sub> O <sub>4</sub>	NiFeCo	60	1 M KOH	0.92		2021	[4]
PiperION	<i>d</i> -Ni <sub>3</sub> Fe <sub>1</sub>	Pt/C	50	1 M KOH	1.3		2023	[7]
Fumatech FAS-50	<i>d</i> -Ni <sub>3</sub> Fe <sub>1</sub>	Pt/C	60	1 M KOH	1.35		2023	[3]
AF1-HNN8-50-X	Ir black	Pt/C	50	1 M KOH	1.75		2020	[4]
FAA-3-PE-30	Ir black	Pt/C	50	1 M KOH	1.8		2019	[4]
FAA-3-PK-130	Ce <sub>0.2</sub> MnFe <sub>1.8</sub> O <sub>4</sub>	Ni	50	1 M KOH	1.85		2019	[4]
Sustainion	<i>d</i> -Ni <sub>3</sub> Fe <sub>1</sub>	Pt/C	50	1 M KOH	2.2		2023	[3,4]

PVBC-	NiFe-LDH/NF	MoNi/NF	60	1 M KOH	0.5	2019	[10]
MPy/35%PEK-							
cardo							
L-ABPBI	<i>Ni foam</i>		70	3 M KOH	0.28	2016	[11]
C-ABPBI	<i>Ni foam</i>		70	3 M KOH	0.335	2016	[11]
<b>This work</b>	<b>Ni foam</b>	<b>Pt/C</b>	<b>60</b>	<b>1 M KOH</b>	<b>2.8</b>	<b>This</b>	
						<b>work</b>	

---

## Reference

- 1 J. Parrondo and V. Ramani, *J. Electrochem. Soc.*, 2014, 161, F1015–F1020.
- 2 M. K. Cho, A. Lim, S. Y. Lee, H.-J. Kim, S. J. Yoo, Y.-E. Sung, H. S. Park and J. H. Jang, *J. Electrochem. Sci. Technol.*, 2017, 8, 183–196.
- 3 Z. Liu, S. D. Sajjad, Y. Gao, H. Yang, J. J. Kaczur and R. I. Masel, *International Journal of Hydrogen Energy*, 2017, 42, 29661–29665.
- 4 D. Henkensmeier, M. Najibah, C. Harms, J. Žitka, J. Hnát and K. Bouzek, *Journal of Electrochemical Energy Conversion and Storage*, 2021, 18, 024001.
- 5 I. Gatto, A. Caprì, C. Lo Vecchio, S. Zignani, A. Patti and V. Baglio, *International Journal of Hydrogen Energy*, 2023, 48, 11914–11921.
- 6 J. E. Park, S. Y. Kang, S.-H. Oh, J. K. Kim, M. S. Lim, C.-Y. Ahn, Y.-H. Cho and Y.-E. Sung, *Electrochimica Acta*, 2019, 295, 99–106.
- 7 T.-H. Kong, P. Thangavel, S. Shin, S. Kwon, H. Choi, H. Lee, N. Park, J.-J. Woo and Y. Kwon, *ACS Energy Lett.*, 2023, 8, 4666–4673.
- 8 T. Caielli, A. R. Ferrari, S. Bonizzoni, E. Sediva, A. Caprì, M. Santoro, I. Gatto, V. Baglio and P. Mustarelli, *Journal of Power Sources*, 2023, 557, 232532.
- 9 P. Fortin, T. Khoza, X. Cao, S. Y. Martinsen, A. Oyarce Barnett and S. Holdcroft, *Journal of Power Sources*, 2020, 451, 227814.
- 10 H. Li, M. R. Kraglund, A. K. Reumert, X. Ren, D. Aili and J. Yang, *J. Mater. Chem. A*, 2019, 7, 17914–17922.
- 11 L. A. Diaz, J. Hnát, N. Heredia, M. M. Bruno, F. A. Viva, M. Paidar, H. R. Corti, K. Bouzek and G. C. Abuin, *Journal of Power Sources*, 2016, 312, 128–136.