

# Robust Piperidinium-Enriched Polystyrene Ionomers for Anion Exchange Membrane Fuel Cells and Water Electrolyzers

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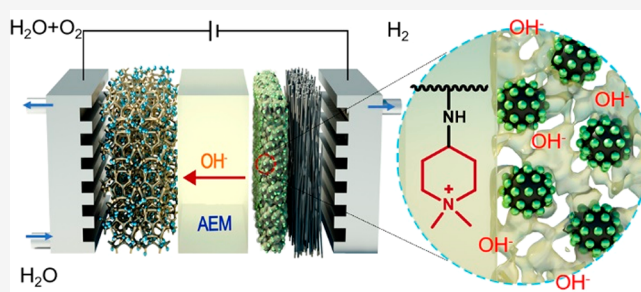


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Supporting Information

**ABSTRACT:** Durable and efficient anion exchange polyelectrolytes (AEPs) are crucial for the long-term operation of cost-effective anion exchange membrane fuel cells (AEMFCs) and water electrolyzers (AEMWEs). Here, we present a new class of  $\gamma$ -amine-piperidinium-functionalized polystyrene AEPs (P-AP-Ca), featuring a carbazole segment to tune ion exchange capacities (IECs). The P-AP-Ca AEPs possess high  $\text{OH}^-$  conductivity and outstanding alkaline stability in 1 M NaOD/ $\text{CD}_3\text{OD}/\text{D}_2\text{O}$  at 80 °C for 6,000 h, making them among the most stable AEPs reported to date. P-AP-Ca-based AEMFCs with a Co–Mn cathode achieve a highest peak power density of 1.38  $\text{W cm}^{-2}$  at 80 °C. Moreover, P-AP-Ca-based AEMWEs with a NiFeOOH anode deliver a high current density of 6.3  $\text{A cm}^{-2}$  at 2 V, and the cell can be run stably at 2 or 3  $\text{A cm}^{-2}$  over 1,100 h in 1 M KOH. These results demonstrate the remarkable robustness and effectiveness of these new AEPs for next-generation alkaline energy devices.



Solid polyelectrolyte water electrolyzers (WE) and fuel cells (FCs) are emerging technologies that produce and utilize hydrogen as a clean energy carrier.<sup>1,2</sup> While proton exchange membrane (PEM) water electrolyzers (PEMWEs) and fuel cells (PEMFCs) are the currently dominating technologies due to their high efficiency and durability, they use costly and rare platinum-group-metal (PGM) catalysts (such as platinum and iridium) as well as fluoropolymer-based PEMs that are raising environmental concerns.<sup>3,4</sup> Within this context, anion exchange membrane (AEM) fuel cells (AEMFCs) and water electrolyzers (AEMWEs) are drawing increasing attention, as they can potentially use PGM-free metal catalysts, hydrocarbon-based polyelectrolytes, and affordable bipolar plates. Nevertheless, the development of AEMFCs and AEMWEs is still at an early stage.<sup>5–7</sup> The cell durability remains limited due to the lack of key materials such as anion exchange polyelectrolytes (AEPs) and electrocatalysts.<sup>8–10</sup>

AEPs, which can be used as AEMs or ionomers, are critical components of AEM devices. AEPs serve as the medium for transferring  $\text{OH}^-$  and water, isolating the anode and the cathode, and constructing effective three-phase interfaces in AEMFCs and AEMWEs (Figure 1A).<sup>11–15</sup> A suitable AEP should have high alkaline stability, sufficient ion conductivity, and qualified dimensional stability under alkaline conditions to ensure the long-term operation of AEMFCs and AEMWEs.

AEPs are polymers containing pendant cationic groups<sup>16–21</sup> such as quaternary ammonium or phosphonium groups. The stability of AEPs in alkaline media has been a challenge for many years. Most cationic groups and polymer backbones are vulnerable under alkaline conditions due to several degradation pathways. Consequently, numerous efforts have been devoted to the development of stable cationic groups and polymer backbones for AEPs.<sup>22–24</sup>

Mario et al.<sup>20</sup> and Fan et al.<sup>17</sup> have systematically screened the alkaline stability of different cationic groups and polymer backbones. They found that six-membered N-heterocyclic ammonium (NHA) groups (Figure 1A), such as dimethyl piperidinium (DMP) and 6-azaspiro[5.5] undecanium (ASU), have outstanding alkaline stability compared to other cation species, such as typical benzyl ammonium, hexyltrimethylammonium (HTMA), and bulky imidazolium groups. Specifically, DMP groups simultaneously display high alkaline stability and ion conductivity in AEPs.<sup>11,12,15,24,25</sup> However, it is challenging to effectively and properly link DMP groups into the polymer

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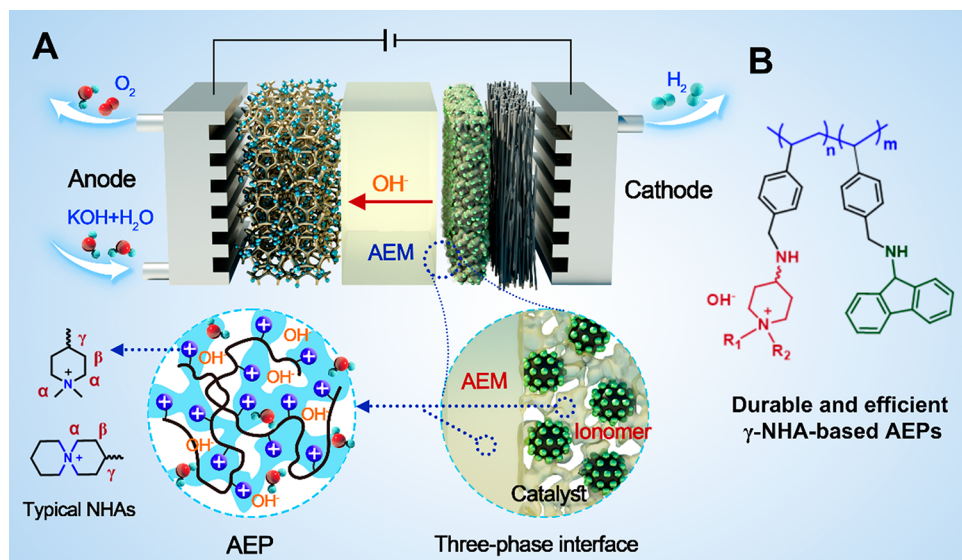


Figure 1. Elucidation of cathode-dried AEMWEs and NHA-based AEPs. (A) Schematic diagram of AEMWEs and the general structure of the three-phase interface and AEPs (which can be used as AEMs or ionomers). (B) The chemical structure of  $\gamma$ -NHA-functionalized polystyrene AEPs.

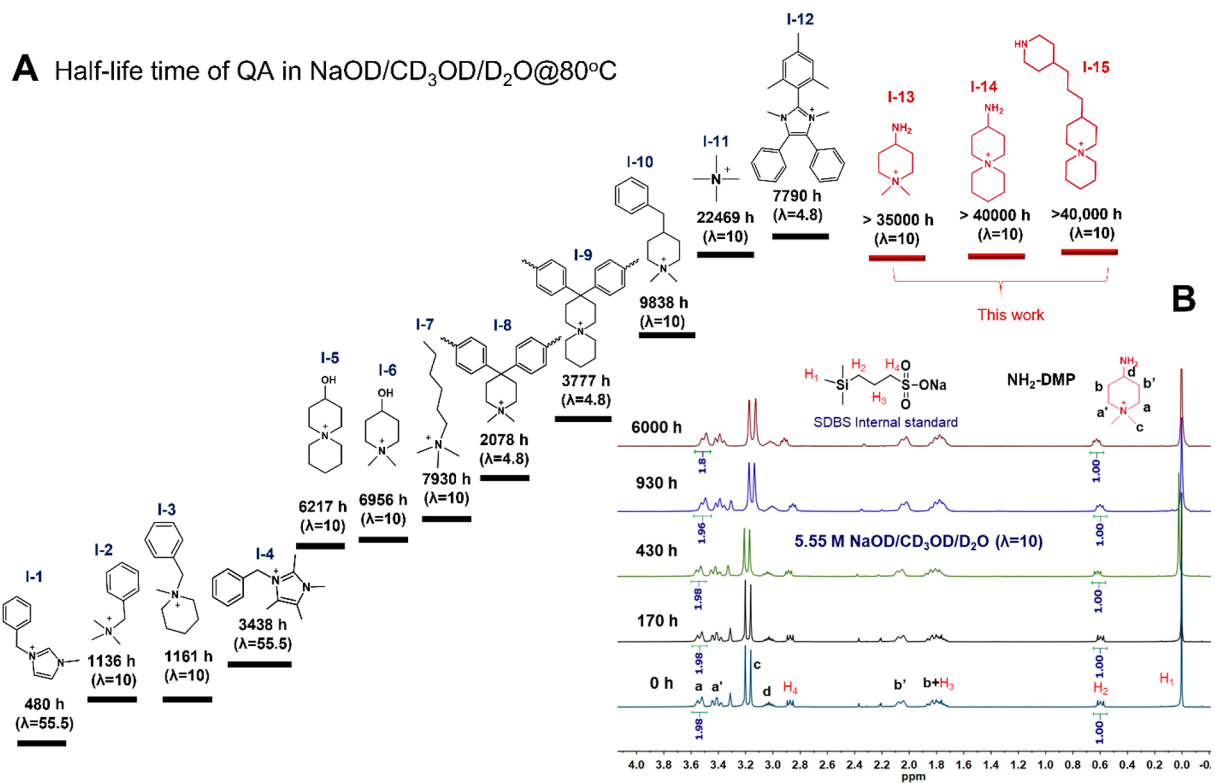
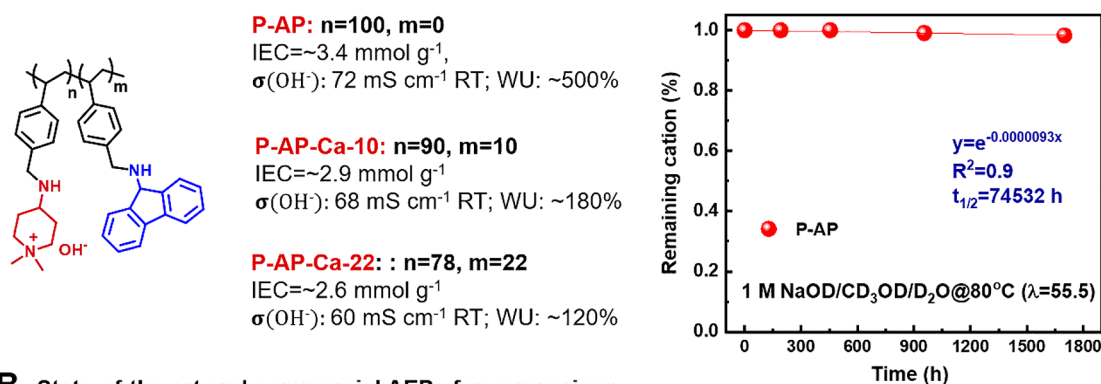


Figure 2. Half-life time of different cationic groups. (A) Half-life time of currently common ammonium groups (I-1 to I-12)<sup>17,18,21,26</sup> and  $\gamma$ -amine-DMP and ASU groups (I-13 to I-15). (B) <sup>1</sup>H NMR spectra of NH<sub>2</sub>-DMP after alkaline treatment in NaOD/D<sub>2</sub>O/CD<sub>3</sub>OD ( $\lambda = 10$ ) at 80 °C at different periods of time.

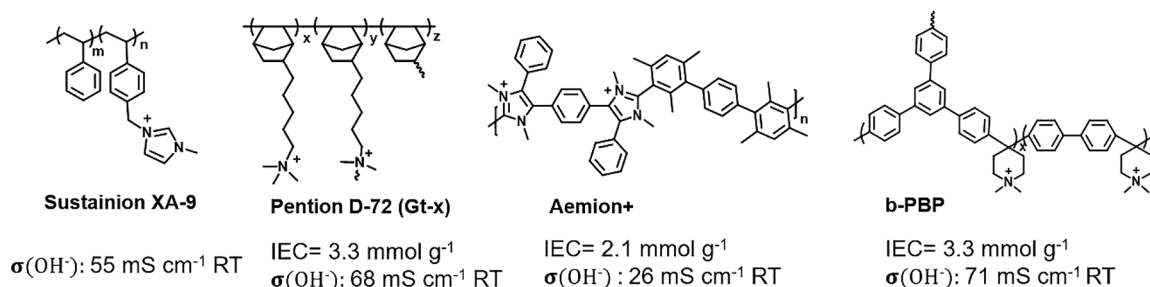
backbone of AEPs. Chen et al.<sup>26</sup> demonstrated that different linking groups attached to DMP groups had significant effects on their alkaline stability, which was attributed to the molecule symmetry and electronic properties of the substituents. Symmetric  $\gamma$ -substituted DMP groups with electron-donating substituents possess a higher alkaline stability than  $\alpha$ - or  $\beta$ -substituted DMP groups. Nevertheless, DMP-based AEPs are mostly linked via the  $\alpha$ -position of DMP, so their stability is

not sufficient for operation under harsh alkaline conditions.<sup>26–30</sup> In contrary, poly(aryl piperidinium) (PAP) AEPs, which combine  $\gamma$ -position-linking DMP and aryl ether-free polymer backbones, exhibited outstanding alkaline stability (>2,000 h in 1 M NaOH@80 °C), ion conductivity (>130 mS cm<sup>-1</sup>@80 °C), and mechanical properties.<sup>6,7,11,12,31–33</sup> Despite this, the alkaline stability of PAPs is still limited by the electron-withdrawing phenyl groups in the  $\gamma$  position of DMP

## A Highly durable and conductive amine-piperidinium polystyrene AEPs



## B State-of-the-art and commercial AEPs for comparison



**Figure 3.** Present AEPs and state-of-the-art AEPs. (A) Physical properties and half-life time of P-AP-type AEPs after alkaline treatment in 1 M NaOD/D $_2$ O/CD $_3$ OD at 80  $^\circ$ C under  $\lambda = 55.5$  conditions. (B) Commercial and state-of-the-art AEPs for comparison.

groups.<sup>26</sup> Thus, there is still much room for improvement in the stability of AEPs.

Here, we designed and developed a series of symmetric  $\gamma$ -amine-containing NHA groups for AEP applications. We incorporated a carbazole segment to tune the ion exchange capacity (IEC) and to decrease the water uptake and ionomer adsorption, resulting in amine-linked NHA-enriched polystyrene AEPs (Figure 1B). These highly durable and conductive AEPs demonstrate remarkable robustness and effectiveness in AEMFCs and AEMWEs.

### SYNTHESIS AND STABILITY OF AMINE-CONTAINING NHAS

A series of  $\gamma$ -amine six-membered NHAs (DMP and ASU) were prepared and characterized (Figure 2 and Figures S1–S6). The amino groups allow the NHAs to be conveniently attached through the  $\gamma$ -position to various halogenated polymer backbones. The alkaline stability of  $\gamma$ -amine-containing NHAs was probed by  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{HNMR}$ ), and the accelerated stability testing was conducted in 5 M NaOD/D $_2$ O/CD $_3$ OD at 80  $^\circ$ C with a hydration number ( $\lambda$ ) of 10, where  $\lambda$  denotes the number of water molecules next to each  $\text{OH}^-$ , which represents the alkalinity of solution.<sup>17,26</sup> Sodium 3-(trimethylsilyl)propane-1-sulfonate (SDBS) was used as a standard to monitor the degradation ratio of  $\gamma$ -amine-containing NHAs. As shown in Figure 2A, all  $\gamma$ -amine-containing NHAs exhibited excellent alkaline stability in 5 M NaOD/D $_2$ O/CD $_3$ OD at 80  $^\circ$ C, and no degradation signal can be detected after 6,000 h testing. For example, the estimated half-life time ( $t_{1/2}$ ) of  $\text{NH}_2$ -DMP (I-13) is  $>35,000$  h under  $\lambda = 10$  conditions at 80  $^\circ$ C (Figure 2B and Figure S7), which is much higher than common cationic groups, such as benzyl imidazolium (I-1), methyl-substituted

benzyl imidazolium (I-2), HTMA (I-7),  $\gamma$ -phenyl piperidinium (I-8, I-9, and I-10), and bulky imidazolium (I-12) groups.<sup>17,18,26</sup>  $\gamma$ -Amine-containing ASU groups, such as I-14 (Figure S8 and Figure S9) and I-15 (Figure S10 and Figure S11), also display outstanding alkaline stability with  $t_{1/2} > 40,000$  h under  $\lambda = 10$  conditions at 80  $^\circ$ C. The alkaline stability of these  $\gamma$ -amine-containing NHAs even exceeds  $\gamma$ -benzyl piperidinium (I-10) groups,<sup>22</sup> which may be attributed to the highly symmetric molecule structures of  $\gamma$ -substituted NHA groups.

### SYNTHESIS AND PHYSICAL PROPERTIES OF $\gamma$ -AMINE-PIPERIDIUM POLYSTYRENE

These  $\gamma$ -amine-containing NHAs are useful for AEP applications. Using the  $\text{NH}_2$ -DMP group as an example, amine-piperidinium-enriched polystyrenes (P-AP) were synthesized through a Menshutkin reaction between  $\text{NH}_2$ -DMP and poly(vinylbenzyl chloride) (Cl-PS) (Figure S12). An amine-containing carbazole segment was introduced to the P-AP backbone to prepare P-AP-Ca- $x$  AEPs ( $x = 0, 10, 22$ ), where  $x$  denotes the ratio of the carbazole segment (Figure 3A). The additional carbazole segment is used to tune IECs and to decrease the water uptake and ionomer adsorption of P-AP-Ca- $x$  AEPs. The chemical structure of P-AP-Ca- $x$  is confirmed by  $^1\text{HNMR}$  spectra, as shown in Figure S13.

The physical properties of P-AP-Ca- $x$  are shown in Table S1 and Figure 3A. The pristine P-AP with a high IEC (3.4 mmol g $^{-1}$ ) possesses high  $\text{OH}^-$  conductivity (72 mS cm $^{-1}$ ) and high water uptake (WU) ( $>500\%$ ) at room temperature. After incorporation of a carbazole segment, the WU (110%  $\sim$  180%) of P-AP-Ca- $x$  AEPs is significantly decreased due to lower IEC values (2.6 mmol g $^{-1}$   $\sim$  2.9 mmol g $^{-1}$ ) and the presence of a highly rigid carbazole segment. The  $\text{OH}^-$  conductivity of P-

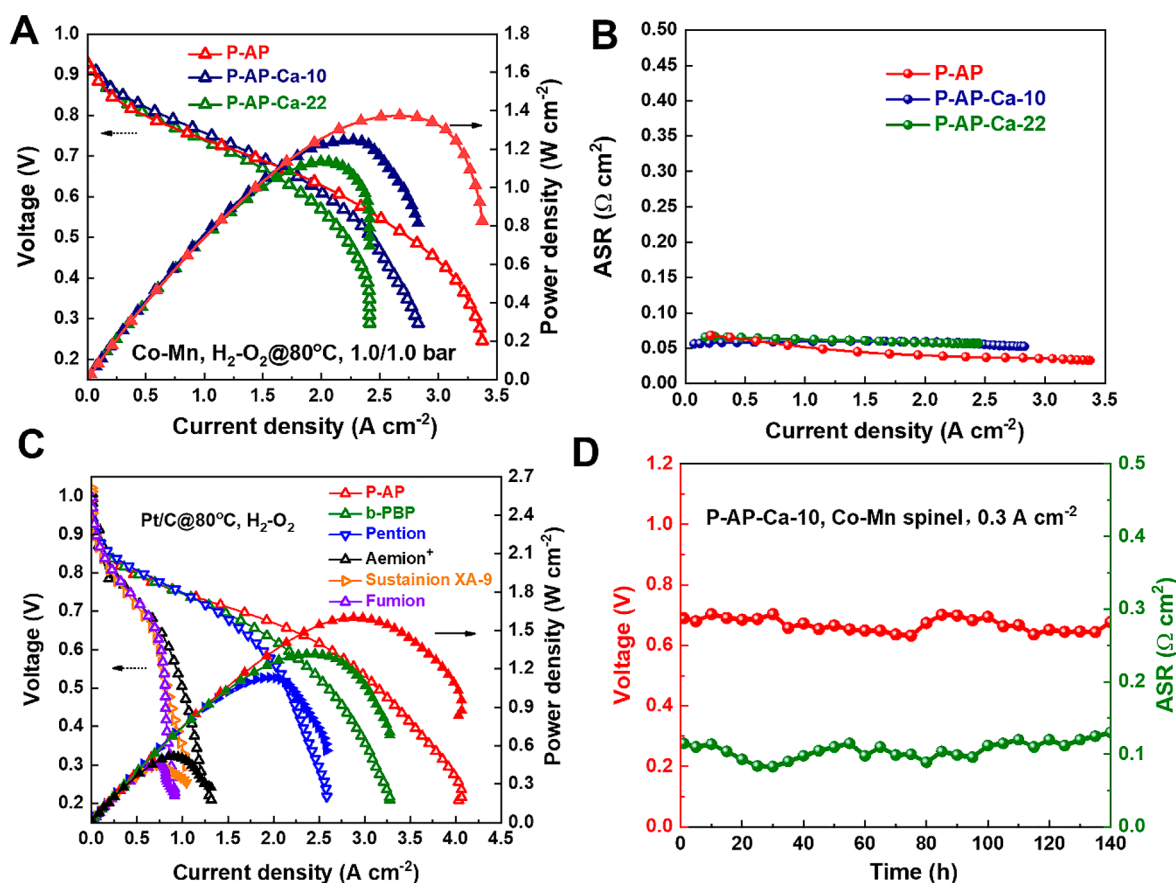


Figure 4. AEMFC performance. (A) The  $I$ - $V$  performance of P-AP-Ca-containing AEMFCs with a Co-Mn spinel cathode and a Pt-Ru/C anode in  $H_2$ - $O_2$  at 80 °C with A/C flow rates of 700/1000 mL min<sup>-1</sup> and a A/C backpressure of 1.0/1.0 bar. (B) ASR of P-AP-Ca-containing AEMFCs in Figure 4A. (C) The  $I$ - $V$  performance of AEMFCs containing different commercial ionomers with Pt/C catalysts in  $H_2$ - $O_2$  was 80 °C. (D) Stability of P-AP-Ca-10-based AEMFCs at 0.3 A cm<sup>-2</sup> and 65 °C with an A/C flow rate of 300/200 mL min<sup>-1</sup>.

AP-Ca- $x$  AEPs (60 mS cm<sup>-1</sup> to 72 mS cm<sup>-1</sup>) is higher than the most commercial AEPs at room temperature, such as Fumion (25 mS cm<sup>-1</sup>),<sup>11</sup> Aemion<sup>+</sup> (26 mS cm<sup>-1</sup>), and Sustainion XA-9 (55 mS cm<sup>-1</sup>), and is close to the Pention (65 mS cm<sup>-1</sup>)<sup>34</sup> and branched poly(benzyl piperidinium) (b-PBP) (71 mS cm<sup>-1</sup>) AEPs (Figure 3B).<sup>15</sup>

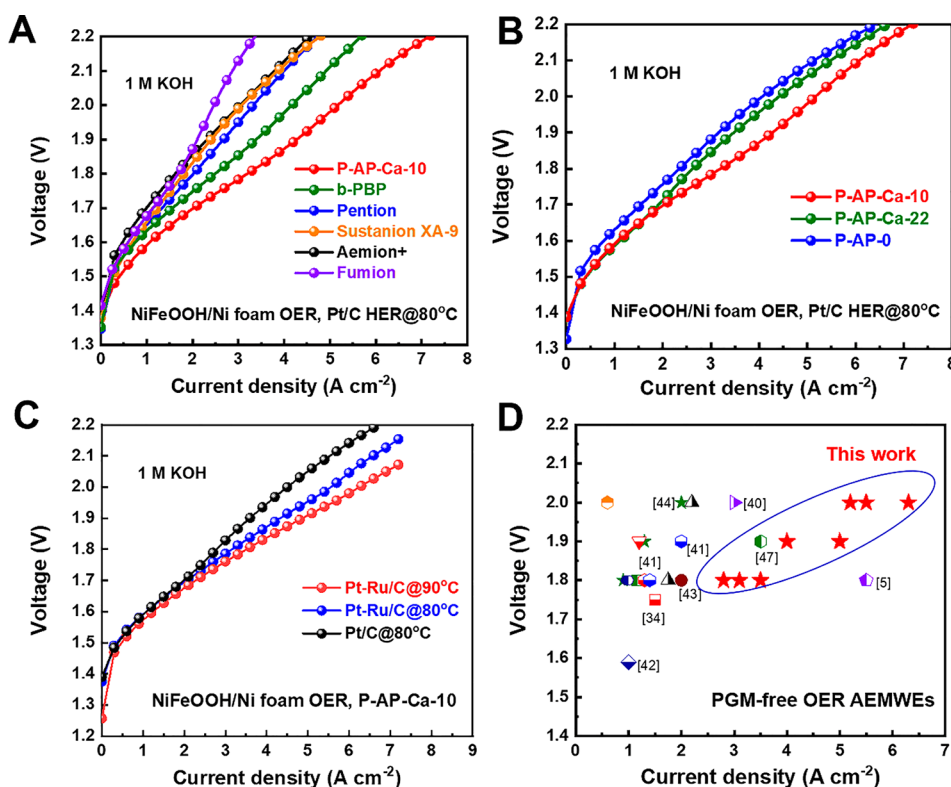
### ■ ALKALINE STABILITY OF $\gamma$ -AMINE-PIPERIDINIUM POLYSTYRENE

Soluble P-AP was used as a representative example to probe the ex situ alkaline stability due to its excellent solubility in common solvents (Table S1), including DMSO, MeOH, IPA/water, and EtOH. The ex situ alkaline stability test was conducted in 1 M NaOD/D<sub>2</sub>O/CD<sub>3</sub>OD ( $\lambda = 55.5$ ) at 80 °C by <sup>1</sup>HNMR. No chemical change was found after 6,000 h in 1 M NaOD/D<sub>2</sub>O/CD<sub>3</sub>OD at 80 °C (Figure S14 and Figure S15), indicating the excellent alkaline stability of P-AP-type AEPs due to the combination of stable  $\gamma$ -NH<sub>2</sub>-DMP groups and polystyrene backbone. Other  $\gamma$ -amine-NHA-based polystyrene AEPs (such as amine-ASU-based PS) displayed excellent alkaline stability in 1 M NaOH at 80 °C as well (no degradation was monitored after alkaline treatment for 1,700 h), as shown in Figure S16. Currently, only a few AEPs were reported to be stable in 1 M NaOH@80 °C for more than 1000 h, such as HTMA-based AEPs,<sup>14</sup> bulky imidazolium-based AEPs,<sup>17</sup> and poly(aryl piperidinium) AEPs.<sup>12</sup> In this work, the estimated  $t_{1/2}$  of P-AP-type AEPs

is over 70,000 h (Figure 3A) in 1 M NaOD/D<sub>2</sub>O/CD<sub>3</sub>OD, making them among the most stable AEPs reported to date. These results demonstrate that symmetric  $\gamma$ -amine-containing NHA groups can deliver excellent alkaline stability as well as high ion conductivity to P-AP-type AEPs, which are crucial for their applications in AEM devices.

### ■ AEMFC PERFORMANCE

Currently, most polystyrene-based AEPs possess limited mechanical properties without a proper reinforcement, especially at high temperatures.<sup>5</sup> Therefore, P-AP-Ca- $x$  AEPs were mainly used as ionomers for AEMFCs and AEMWEs in this work. The application of P-AP-Ca- $x$  ionomers in AEMFCs was probed using a membrane electrode assembly (MEA) based on a branched PAP AEM<sup>15</sup> and a catalyst-coated-substrate (CCS) configuration. FuMa-Tech Fumion, Sustainion XA-9, Pention D-70 (Gt- $x$ ), Aemion AP-2-HNN8-00X, and b-PBP ionomers were used for comparison. As shown in Figure 4A, the P-AP-containing AEMFC with a homemade Co-Mn spinel oxygen reduction reaction (ORR) cathode<sup>7</sup> exhibited an excellent peak power density (PPD) of 1.35 W cm<sup>-2</sup> at 80 °C.<sup>34,35</sup> AEMFCs containing P-AP-Ca-10 and P-AP-Ca-22 ionomers displayed slightly lower PPDs (1.15 W cm<sup>-2</sup> to 1.26 W cm<sup>-2</sup>) than P-AP-based AEMFCs due to lower IEC values, which is consistent with area specific resistance (ASR) results (Figure 4B). The ASR of P-AP-Ca-containing AEMFCs is as low as 36 to 45 mΩ cm<sup>-2</sup> at high current



**Figure 5.** AEMWE performance. The cell is made of two integrated Ni/Ni plates with a Ni-FeOOH/Ni foam anode, and the cell was fed with 1 M KOH in the anode only. (A) Pt/C cathode and different ionomers at 80 °C. (B) Pt/C cathode and different P-AP-Ca-*x* ionomers at 80 °C. (C) With different HER catalysts. (D) *I*–*V* comparison of currently state-of-the-art AEMWEs based on PGM-free anode catalysts in 1 M KOH.

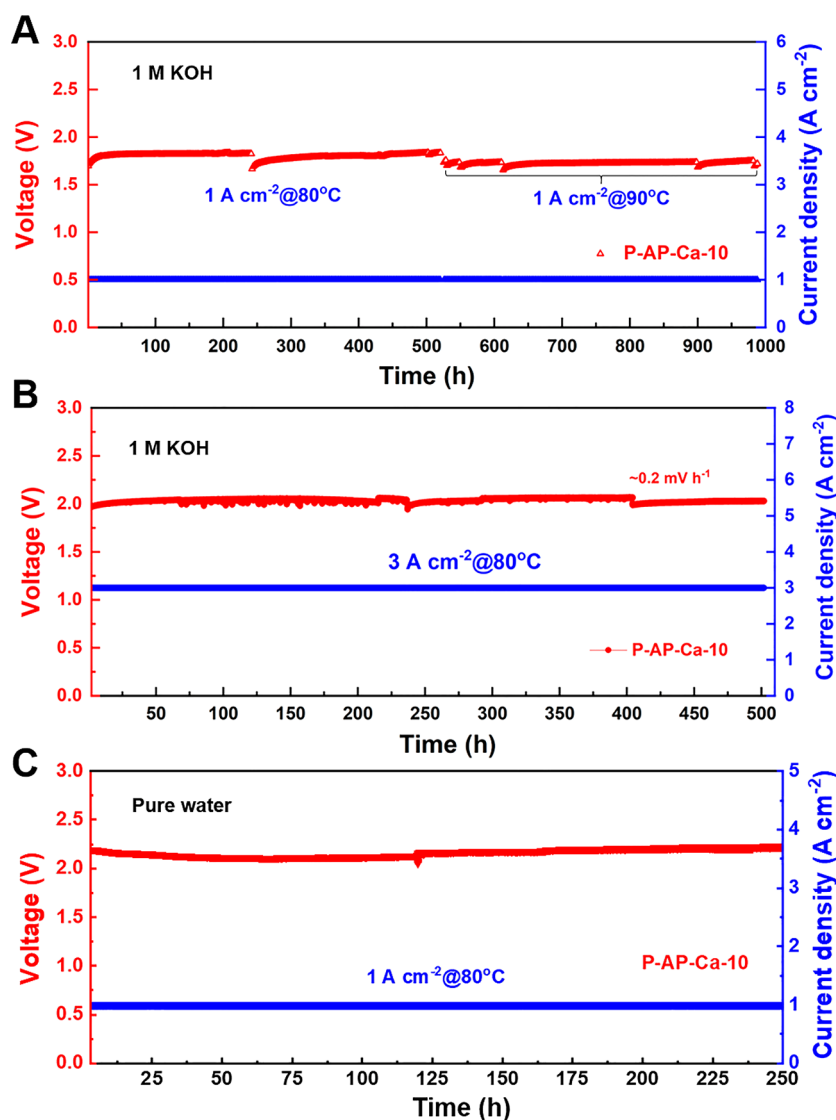
densities, which is close to the state-of-the-art Gt-*x*-based AEMFCs ( $\sim 35 \text{ m}\Omega \text{ cm}^{-2}$ ).<sup>36,37</sup> Compared to commercial ionomers (Figure 4C), P-AP-containing AEMFCs with Pt/C catalysts exhibit a higher PPD of  $1.63 \text{ W cm}^{-2}$  than those of AEMFCs containing Fumion ( $0.35 \text{ W cm}^{-2}$ ), Sustainion ( $0.36 \text{ W cm}^{-2}$ ), Aemion ( $0.58 \text{ W cm}^{-2}$ ), Pention ( $1.1 \text{ W cm}^{-2}$ ), and b-PBP ( $1.3 \text{ W cm}^{-2}$ ) ionomers under the same operating conditions. Moreover, P-AP-type AEMFCs with a Co–Mn spinel cathode can be run at  $0.3 \text{ A cm}^{-2}$  at  $65 \text{ }^\circ\text{C}$  for over 140 h with a voltage decay rate of  $\sim 0.5 \text{ mV h}^{-1}$  under a low anode (A)/cathode (C) flow rate of  $300/200 \text{ mL min}^{-1}$  (Figure 4D), indicating that these P-AP-type ionomers can deliver both high power densities and durability to cost-effective AEMFCs.

### ■ AEMWE PERFORMANCE AND DURABILITY

P-AP-Ca-*x* ionomers could be directly used in AEMWEs without any further modifications. P-AP-Ca-*x* AEPs were employed as cathode ionomers (with Pt/C) in a cathode-dried AEMWE setup. The anode utilizes self-supported NiFeOOH/Ni foam<sup>38</sup> as an oxygen evolution reaction (OER) catalyst, and it is ionomer-free. This setup was made from two integrated Ni plates that serve as end plates, bipolar plates, and current collectors. As shown in Figure 5A, P-AP-Ca-10-containing AEMWEs show a high instantaneous current density of  $5.5 \text{ A cm}^{-2}$  @  $2 \text{ V}$  in 1 M KOH at  $80 \text{ }^\circ\text{C}$ , which is higher than AEMWEs containing Fumion ( $2.5 \text{ A cm}^{-2}$  @  $2 \text{ V}$ ), Aemion ( $3 \text{ A cm}^{-2}$  @  $2 \text{ V}$ ), Sustainion ( $3.1 \text{ A cm}^{-2}$  @  $2 \text{ V}$ ), Pention ( $3.5 \text{ A cm}^{-2}$  @  $2 \text{ V}$ ), and b-PBP ( $4.5 \text{ A cm}^{-2}$  @  $2 \text{ V}$ ) ionomers under the same conditions. These data suggest that P-AP-Ca-*x* ionomers are more efficient than commercial ionomers, which is consistent with ion conductivity results. P-AP ionomer-

containing AEMWEs exhibit slightly lower current density compared to P-AP-Ca-*x*-based AEMWEs due to excessive water uptake, which increases the risk of catalyst leaching in the cathode-dried AEMWEs (Figure 5B). The *I*–*V* behaviors of P-AP and P-AP-Ca ionomers in liquid electrolyte-cycling AEMWEs are different from those in gas-powered AEMFCs. We attribute this phenomenon to the different effects of ionomer adsorption on electrocatalysts in AEMFCs and AEMWEs due to their different operation conditions.<sup>5</sup> P-AP-Ca-10-containing AEMWEs even reached  $6.3 \text{ A cm}^{-2}$  @  $2 \text{ V}$  in 1 M KOH at  $90 \text{ }^\circ\text{C}$  with a Pt–Ru cathode (Figure 5C), demonstrating that these P-AP-Ca AEPs are able to operate at high temperatures and high current densities.

Currently, most AEMWEs exhibit current densities below  $1 \text{ A cm}^{-2}$  @  $2 \text{ V}$ .<sup>1,10</sup> Commercial Sustainion-based AEMWEs from Dioxide Materials were used as a benchmark ( $1 \text{ A cm}^{-2}$  @  $1.9 \text{ V}$  at  $60 \text{ }^\circ\text{C}$ , Figure S17). Some of the current AEMWEs exhibit high current densities but required Ir-based OER catalysts as well as expensive or an unpractical flow field (such as platinum-coated titanium plate for the anode and graphite plate for the cathode). For instance, Cha et al.<sup>39</sup> reported poly(carbazole)-based AEMWEs reached a current density of  $3.5 \text{ A cm}^{-2}$  @  $1.9 \text{ V}$  in 1 M KOH with an IrO<sub>2</sub> anode. Chen et al.<sup>6</sup> reported c-PAP-based AEMWEs obtained a high current density of  $7.68 \text{ A cm}^{-2}$  @  $2.0 \text{ V}$  in 1 M KOH with an IrO<sub>2</sub> anode and a graphite cathode plate. Li et al.<sup>5</sup> reported benzylammonium polystyrene-based AEMWEs reached a current density of  $\sim 5 \text{ A cm}^{-2}$  @  $1.8 \text{ V}$  with a platinum-coated titanium anode plate and a graphite cathode plate. As shown in Figure 5D, compared to the state-of-the-art AEMWEs using PGM-free OER catalysts,<sup>5,32,40–47</sup> the P-AP-Ca-containing



**Figure 6.** Long-term durability test of P-AP-Ca-10-containing AEMWEs. The cell is made of two integrated Ni/Ni plates with a Ni-FeOOH/Ni foam anode and a Pt/C cathode. (A) 1 M KOH in the anode only, 1 A cm<sup>-2</sup>, 80 °C and 90 °C. (B) 1 M KOH in the anode only, 3 A cm<sup>-2</sup>, 80 °C. (C) Pure water, 1 A cm<sup>-2</sup>, 80 °C.

AEMWEs reported here reach outstanding current densities but with inexpensive A/C Ni bipolar plates.

We probed the cell durability of P-AP-Ca-containing AEMWEs at high current densities. As shown in Figure S18, these AEMWEs can be successively run at high current densities (1 A cm<sup>-2</sup> for 160 h, 2 A cm<sup>-2</sup> for 550 h, and 3 A cm<sup>-2</sup> for 600 h) for more than 1,300 h at 60 °C. Moreover, at elevated temperatures, the P-AP-Ca-containing AEMWEs still can be run stably at 1 A cm<sup>-2</sup> or 3 A cm<sup>-2</sup> for more than 1,000 h (80 and 90 °C) and 500 h (at 80 °C), respectively, (Figure 6A and Figure 6B), implying that the chemical stability of P-AP-Ca AEPs is sufficient for AEMWEs operating under high current densities >3 A cm<sup>-2</sup> at 80 °C. The steady-stage voltages of P-AP-Ca-containing AEMWEs are 1.67 V ~ 1.8 V@1A cm<sup>-2</sup>, 1.82 V ~ 1.95 V@2A cm<sup>-2</sup>, and 1.98 V ~ 2.05 V@3 A cm<sup>-2</sup> at 80 °C, which are comparable to the state-of-the-art PEMWEs (1.85 V@2A cm<sup>-2</sup> for 5000 h).<sup>48</sup> Additionally, the P-AP-Ca-containing AEMWEs can be operated under pure water conditions at 1 A cm<sup>-2</sup> and 80 °C with a steady-stage voltage of 2.1–2.2 V for more than 256 h (Figure 6C).

All our cells remain fully operational after the durability test. For comparison, the cell voltage of Sustainion-containing AEMWEs decayed significantly after only a few hours at 3 A cm<sup>-2</sup> at 80 °C (Figure S19). This result suggests that benzyl imidazolium (*I*-1 and *I*4 in Figure 2A)-based AEPs are not stable enough for AEMWEs operating under high current densities and high temperatures.

Currently, most reported AEMWEs displayed poor cell durability and can be only run under low current densities (0.1–0.5 A cm<sup>-2</sup>) for few hundred hours (~200 h) (Figure 7).<sup>5,6,10,32,39–47,49–51</sup> Only a few of them can be operated stably for more than 1,000 h at 0.5 A cm<sup>-2</sup> with a reasonable steady-stage cell voltage. To the best of our knowledge, our AEMWEs are the first ones that can be operated stably under high current densities (>2 A cm<sup>-2</sup> or 3 A cm<sup>-2</sup>) for more than 1,100 h. These results demonstrate that  $\gamma$ -amine-NHA-containing P-AP-Ca AEPs presented in this work can deliver both excellent cell durability and high ion transport efficiency to next-generation AEM energy devices.

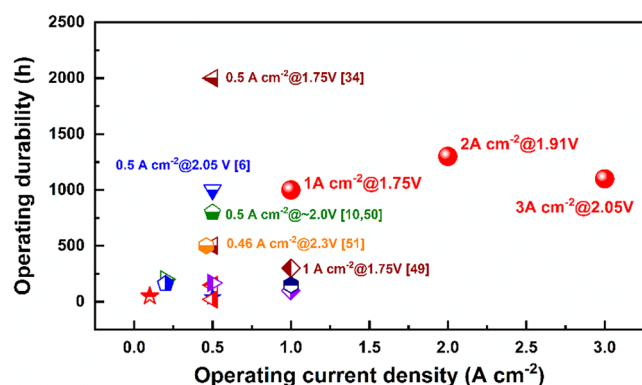


Figure 7. Durability comparison of current state-of-the-art AEMWEs with a steady-state cell voltage.

In summary, we developed a series of highly durable and conductive amine-containing NHA groups and the corresponding P-AP-Ca-*x* AEPs. The half-life time of P-AP-Ca-*x* AEPs exceeds 70,000 h in 1 M NaOD/D<sub>2</sub>O/CD<sub>3</sub>OD at 80 °C. We demonstrate that P-AP-Ca-*x* ionomers can be applied in both AEMFCs and AEMWEs to deliver high performances. For example, P-AP-Ca-containing AEMFCs with a Co–Mn spinel cathode exhibited excellent PPDs (up to 1.38 W cm<sup>-2</sup>) along with a 140 h cell durability at 0.3 A cm<sup>-2</sup>. P-AP-Ca-*x*-containing AEMWEs reached an outstanding current density of 6.3 A cm<sup>-2</sup>@ 2.0 V in 1 M KOH at 90 °C. More importantly, with P-AP-Ca-*x* ionomers, we have demonstrated for the first time that AEMWEs can run stably at high current densities (>2 and 3 A cm<sup>-2</sup>) for more than 1,100 h with a comparable steady-stage cell voltage to the state-of-the-art PEMWEs. These results elucidate the importance of robust and effective anion exchange ionomers for the AEM devices.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acseenergylett.3c01402>.

Detailed description of polymer synthesis, MEA preparation, fuel cell and water electrolyzer testing; Physical properties of P-AP-Ca-*x* AEPs (Table S1); Figure S1 to Figure S19 present <sup>1</sup>H NMR spectra of different NHA groups and NHA-based polystyrenes; alkaline stability of different NHA groups and NHA-based polystyrenes; ASR of P-AP-Ca-based AEMFCs; *I*–*V* performance of Nafion-based PEMFCs; *I*–*V* performance of Sustainion-based AEMWEs; long-term stability of AEMWEs at 60 °C at high current densities (2 A cm<sup>-2</sup> and 3 A cm<sup>-2</sup>) at 60 °C (PDF)

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## Notes

The authors declare the following competing financial interest(s): The branched PAP AEM used in this work is commercialized under the brand name Branion by an EPFL Startup NovaMea SA, of which N.J. Chen, F. Song, and X.L. Hu have a financial interest.

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