A poly(binaphthyl-co-terphenyl quinuclidinium) anion exchange membrane with excellent alkaline stability and anion conductivity†

Hongbo Zhang, Xianying He, Hanhua Feng, Cheng Li and Ming Li†*

As a crucial component of renewable energy water electrolyzers and fuel cells, the existing landscape reveals a scarcity of anion exchange membranes (AEMs) with comprehensive high performance for the commercial implementation of the above devices. In this study, we engineered an AEM with remarkable attributes, including exceptional alkaline stability (no degradation in conductivity observed for over 2556 h in a 10 M NaOH solution at 80 °C), enhanced OH⁻ conductivity (measured at 170.21 mS cm⁻¹ at 80 °C), superior dimensional stability (swelling ratio <8% in pure water), and robust mechanical characteristics (possessing a tensile strength measuring 35.5 MPa and an elongation at break of 22%). Utilizing this AEM in a water electrolyzer results in higher electric current densities (2.2 A cm⁻² at 2.0 V) and exceptional durability when assembled with Ni–Fe and Ni–Mo foam electrodes.

Introduction

Hydrogen is essential for decarbonization and sustainability.¹,² Water electrolysis employing anion exchange membranes (AEMs) as the diaphragm has emerged as a particularly promising technology to produce green hydrogen,³–⁵ because this technology does not rely on expensive palladium group metal catalysts but can directly couple with renewable energy such as wind or solar energy.⁶–¹⁰ The AEM is the crucial component of an AEM water electrolyzer; however, the scarcity of AEMs with comprehensive excellent performance hampers the commercial implementation of this hydrogen production technology.¹¹,¹² Excellent performance AEMs require high alkaline stability, high dimensional stability, and high conductivity, but in practice, the increase in conductivity upon increasing the ion exchange capacity (IEC) is often accompanied by a rise in the rate of water uptake (WU) and swelling ratio (SR).¹³ Another way to increase the conductivity of AEMs while maintaining high dimensional stability is to induce microphase separation and construct efficient ion channels,¹⁴ e.g., increasing the volume of structural units can effectively alleviate the chain stacking and reduce the OH⁻ transport resistance, thus enhancing the conductivity.¹⁵

Polyarylpiperidine-based AEMs perform well at low temperatures and in low concentration alkali solutions but are not sufficiently stable at elevated temperatures and in high concentration alkali solutions,¹⁶–¹⁹ because the piperidinium group is easily degraded by the attack of hydroxide ions. Of course, low concentrations of lye cause less pollution, and therefore polyaryl piperidinium AEMs are still a good choice if there are highly active enough catalysts to match.

Currently, there are no commercially proven highly active catalysts in low-concentration lye or pure water. However, there are commercially proven catalysts at high temperature and in high-concentration lye.²⁰,²¹ Therefore, if we can directly find membranes that are resistant to high-temperature and high-concentration lye, AEM water electrolyzers (AEMWEs) can be industrialized in one go. In addition, high-temperature and high-concentration lyes result in other benefits: faster oxygen precipitation kinetics, higher ionic conductivity, and more CO₂ resistance (OH⁻ + CO₂ → HCO₃⁻).²²

Since 2022, we have first established a new AEM system based on poly(aryl quinuclidinium), which is super stable in highly concentrated alkaline solution, even at elevated temperatures.²³–²⁵ Our poly(aryl quinuclidinium) AEM has been purchased by many companies and academic institutions, including Sun from Westlake University in 2023. In 2024, Sun also confirmed the high alkaline stability of our patented²³ branched poly(aryl quinuclidinium) AEM.²⁶ To improve the ionic conductivity of the poly(aryl quinuclidinium) AEM but retain its high dimensional stability, herein we introduce a dinaphthyl unit into the polymer backbone. Unlike p-terphenyl, the dinaphthyl unit has a distorted dihedral angle between the two naphthyl planes due to steric hindrance, and the angle (74°) is larger than that of the terphenyl (Fig. S1 and
This increases the free volume inside the AEM, which improves ionic conductivity (Fig. 1).27,28

**Results and discussion**

Trifluoromethanesulfonic acid (TFSA) catalyzed the synthesis of poly(binaphthyl-co-terphenyl quinolinium) (PBTQ) through the reaction of $p$-terphenyl, binaphthyl, and 3-quinuclidine. Subsequently, PBTQ was quaternized with iodomethane to yield poly(binaphthyl-co-terphenyl quinuculidinium) iodine (PBTQ-I) (Fig. 2a). The involvement of binaphthyl in different equivalents was denoted by suffixes, e.g. PBTQ-OH-5 indicates the ratio of binaphthyl in the total equivalents of $p$-terphenyl and binaphthyl is 5% in poly(binaphthyl-co-terphenyl quinuclidinium)hydroxide (PBTQ-OH).

Six different solvents were chosen to test the solubility of PBTQ (unquaternized) and PBTQ-I (quaternized), which are $n$-methyl-pyrrolidone (NMP), CHCl$_3$, dimethyl sulfoxide (DMSO), $N,N$-dimethylacetamide (DMAc), $N,N$-dimethylformamide (DMF), and tetrahydrofuran (THF). PBTQ is insoluble in CHCl$_3$ and THF but soluble in the other four solvents. In the dissolution process of PBTQ, the dissolution results after adding trifluoroacetic acid (TFA) were the same as those without TFA; PBTQ-I is soluble in DMSO and NMP, but insoluble in the other four solvents. From these results, both PBTQ and PBTQ-I have the best solubility in DMSO solvent, so it is the most

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**Fig. 1** Design of the poly(aryl quinuclidine) AEM with high conductivity and high dimensional stability by introducing a twisted structural unit.

**Fig. 2** (a) Synthetic procedure of polymers based on PBTQ; $^1$H nuclear magnetic resonance (NMR) spectrum of (b) PBTQ and (c) PBTQ-I, respectively.
appropriate to choose DMSO as the solvent in the process of membrane casting.

The chemical structures of both PBTQ and PBTQ-I were elucidated through nuclear magnetic resonance (NMR) spectroscopy. To mitigate interference from water peaks, a small quantity of TFA was incorporated into the NMR samples. In the $^1\text{H}$ NMR spectrum of PBTQ, prominent peaks referring to terphenyl are observed in the range of 7.77 to 7.31 ppm, while weak peaks attributed to binaphthyl appear in the range of 8.42 to 7.77 ppm. Additionally, a broad peak is evident at 4.30 ppm, along with a minor peak at 3.53 ppm, two peaks at 3.21 ppm and 3.12 ppm, and two peaks at 1.95 ppm and 1.78 ppm. These peaks correspond to the a-H, b-H, c-H, and d-H protons, and their integration is in substantial agreement with the anticipated theoretical ratio of 12 : 2:1 : 4 : 4. The NMR spectrum of PBTQ-I further reveals the successful quaternary methyl peak at 3.18 ppm, with the remaining peaks exhibiting consistency with those observed in the NMR spectrum of PBTQ (Fig. 2b and c).

The preparation of PBTQ-I films employs a casting method. Initially, PBTQ-I powder is dissolved in DMSO, and the resulting solution is cast onto a glass substrate. Subsequently, the cast sample is subjected to heat drying. The dry film is easily detached by immersing it in pure water. The surface of PBTQ is smooth and dense, the color of the film changes to pink due to the addition of naphthalene, and the overall appearance is a transparent pink film (Fig. 3a). The incorporation of the binaphthyl group enhances the rigidity of the polymer backbone while maintaining the IEC. This leads to a notable enhancement in the dimensional stability and anion conductivity of the AEM when compared with PPTQ (Table 1). For example, the SR decreases from 7.41% to 6.78%, and from 9.26% to 7.13% at 20 °C and 80 °C for PBTQ-OH-10 and PPTQ-OH, respectively. With higher binaphthyl content PBTQ-OH-x shows a greater decrease of WU (Fig. 3c) and SR (Fig. 3d), which may be attributed to the increased rigidity of the polymer backbone, resulting in improved dimensional stability of the AEM.

Morphological analysis conducted through scanning electron microscopy (SEM) and atomic force microscopy (AFM) reveals that the surface of PBTQ-I exhibits a smooth and featureless profile, devoid of grooves and protrusions (Fig. S3 and S4†). In the thermogravimetric analysis (TGA) data profile, a notable mass loss is evident at 100 °C, which is ascribed to the volatilization process of undried water. Additionally, a significant weight loss within the temperature range of 180 °C to 240 °C indicates the potential occurrence of a thermal decomposi

PBTQ-OH-5 exhibits a tensile strength of 35.5 MPa with an elongation at break of 13%, while PBTQ-OH-10 displays
a tensile strength of 35.5 MPa with an elongation at break of 22.5%. However, too much binaphthalene causes deterioration of the mechanical performance, e.g. PBTQ-OH-15 demonstrates a lower tensile strength of 22.8 MPa with an elongation at break of 2% (Fig. 3b). Young’s modulus of the films increases with the increase in the content of binaphthalene. We also measured the intrinsic viscosity of PBTQ-OH-x (Table 2). The lower intrinsic viscosity of PBTQ-OH-15 indicates a lower molecular weight than the other two films. The degradation of the mechanical properties of PBTQ-OH-15 may be a combination of increased brittleness due to Young’s modulus surge and low molecular weight.

The AFM phase diagram (Fig. S3†) unambiguously illustrates the presence of uniformly distributed ion channels within PBTQ-OH. Furthermore, it is established that PBTQ-OH possesses the capability of microphase separation as evidenced by SAXS (Fig. 4a). The incorporation of a large number of naphthalene-based units into the polymer backbone of PBTQ reduces chain stacking and thus improves ionic conductivity compared to our previous studies. Specifically, the conductivity of PBTQ-OH in pure water increases with increasing temperature in the range of 30–80 °C. Notably, the conductivity achieves a noteworthy value of 170.21 mS cm\(^{-1}\) at 80 °C (Fig. 4b and S6†), representing a substantial enhancement compared to our previous studies (PPTQ-OH 139.12 mS cm\(^{-1}\)).

### Table 1 IEC, WU, SR, and hydration number (\(\lambda\)) of PBTQ-OH-10 and PPTQ-OH AEMs

<table>
<thead>
<tr>
<th>AEM</th>
<th>IEC/mmol g(^{-1})</th>
<th>WU/%</th>
<th>SR/%</th>
<th>(\lambda)</th>
<th>(\sigma) [mS cm(^{-1})]</th>
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<tr>
<td></td>
<td>Theoretical</td>
<td>Titration</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>PBTQ-OH-10</td>
<td>(Br(^{−}))</td>
<td>(Br(^{−}))</td>
<td>(OH(^{−}))</td>
<td>20 °C</td>
<td>80 °C</td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>2.42</td>
<td>2.85</td>
<td>10.28</td>
<td>18.18</td>
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<td>PPTQ-OH</td>
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<td>2.40</td>
<td>2.83</td>
<td>20.25</td>
<td>25.95</td>
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### Table 2 Young’s modulus and intrinsic viscosity of PBTQ-OH-x

<table>
<thead>
<tr>
<th>AEM</th>
<th>Young’s modulus/MPa</th>
<th>Intrinsic viscosity/dL g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBTQ-OH-5</td>
<td>877.55</td>
<td>1.64</td>
</tr>
<tr>
<td>PBTQ-OH-10</td>
<td>1160.11</td>
<td>1.85</td>
</tr>
<tr>
<td>PBTQ-OH-15</td>
<td>1396.73</td>
<td>1.55</td>
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![Fig. 4](image-url) (a) SAXS and (b) conductivity of PBTQ-OH-x membranes; (c) the Arrhenius plots of the different membranes used for calculating activation energies; (d) comparison plot of conductivity versus SR of different AEMs.\(^{29–58}\)
conductivity of PBTQ-OH-5 also reaches 143.00 mS cm\(^{-1}\) at 80 °C. The conductivity of PBTQ-Cl-10 is 114.31 mS cm\(^{-1}\) at 80 °C. The Arrhenius curve (Fig. 4c) of the AEM shows that the activation energy of PBTQ-OH-10 (13.04 kJ mol\(^{-1}\)) is lower than that of PPTQ-OH (13.30 kJ mol\(^{-1}\)) which is consistent with the difference in conductivity between the two. PBTQ-OH-10 has a higher conductivity than most other membranes while maintaining a lower SR (Fig. 4d and Table S2†).

In practical applications, the chemical structure of AEMs is often compromised by alkaline corrosion, rendering them unsuitable for prolonged use, as observed in the case of piperidine-based AEMs.\(^{15}\) Conversely, quinuclidium has exhibited commendable stability in alkaline environments. Specifically, PBTQ demonstrates remarkable resistance to degradation and negligible alteration in anion conductivity (Fig. 5c) even after 2556 h of immersion in 1 M, 5 M, and 10 M NaOH solutions at 80 °C (Fig. 5a and b and S7†). This observation suggests that the introduction of the binaphthyl unit doesn’t sacrifice the alkaline stability but enhances the AEM’s conductivity. PBTQ-OH-10 immersed in 10 M NaOH lye became less soluble in DMSO over time and was almost completely insoluble after 1000 h. It seems that some cross-linking occurs, which still needs to be further investigated.

Following a 7 day immersion in three distinct concentrations of NaOH solutions, a comparative analysis of the results reveals trends in WU and SR concerning concentration variations. WU displays a decrease with increasing alkalinity, and SR demonstrates the same relationship (Fig. S8†). Following a 2556 h immersion in three distinct concentrations of NaOH solutions, the mechanical characterization of the immersed membrane indicates varying degrees of decline. Importantly, higher alkaline concentrations are associated with a lesser reduction in membrane mechanical properties. For instance, in a 10 M NaOH solution, the membrane exhibits an 11.66% reduction of elongation at break, whereas, in a 1 M NaOH solution, a more substantial reduction in the mechanical properties of the membrane is observed (Fig. 5d and Table S1†).

It is interesting to note that the tensile stress of PBTQ in 10 M NaOH solution increases rather than decreases. This higher mechanical stability in 10 M NaOH can be attributed to lower SR and WU (Fig. S8†).

To assess the practical application performance of the AEM, a water electrolysis test platform was established. This platform involves sandwiching PBTQ-OH-10 between NiFe foam as the anode and NiMo foam as the cathode, creating a precious metal-free electrolyzer by compacting the three components.\(^{40}\) An alkaline solution of 5 M KOH was employed as the electrolyte, which exhibits a current density of 2.2 A cm\(^{-2}\) at 2.0 V when the temperature increases to 80 °C (Fig. 6a). We also tested the water electrolysis performance of PBTQ-OH-10 at 1 M KOH (Fig. S9†), which shows a much lower current density (<0.25 A cm\(^{-2}\)) at 2 V. This difference indicates that AEMWE working at higher alkaline concentrations has its advantage.

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Fig. 5  (a) \(^1\)H NMR spectra variation of the PBTQ AEM after alkaline treatment in 1 M NaOH at 80 °C and (b) in 5 M NaOH at 80 °C for 2556 h; (c) the variation of OH\(^{-}\) conductivity and (d) mechanical properties of the membrane after alkaline treatment in 1 M and 5 M NaOH solutions at 80 °C for 2556 h.
The stability test was conducted with a 6 M KOH electrolyte at 60 °C. The electrolyte was cycled by a peristaltic pump. The electrolysis was continued for a certain period and paused for 2 h to refresh the electrolyte. The electrolyzer’s voltage exhibited a gradual increase under a fixed current density of 0.5 A cm\(^{-2}\). Subsequently, the voltage was stabilized at about 1.9 V with minimal fluctuation in a 500 h test, followed by a 100 h stability test at 1 A cm\(^{-2}\), where the current density increased and the voltage stabilized at about 2.22 V (Fig. 6c). This shows that the AEM has high stability. After 600 h of stability test, PBTQ-OH-10 still did not show degradation (Fig. 6b), which further supports the super alkaline stability of our membrane. These results indicate that our AEMWE has good current density and stability without precious metals.

**Conclusions**

In this study, we propose a binaphthalene-modified AEM incorporating N-methylquinuclidinium cationic groups. This AEM exhibited remarkable stability when subjected to high alkali concentration conditions (5 M at 80 °C) for 2556 h, demonstrating no chemical degradation, and OH\(^-\) conductivity did not decrease. The introduction of binaphthalene is effective in reducing chain stacking to increase anion conductivity, leading to an OH\(^-\) conductivity of 170.21 mS cm\(^{-1}\) at 80 °C, but with minimal impact on alkaline stability and mechanical strength.

In the water electrolyzer water device utilizing Ni–Fe and Ni–Mo electrodes, the current density achieves 2.2 A cm\(^{-2}\) at 2.0 V under conditions of 5 M KOH and 80 °C. Furthermore, the device exhibited high durability during a constant current density stability test for a duration of 600 h. This research introduces a useful approach for developing high-performance AEMs based on polyaryl quinuclidinium).

**Data availability**

The data supporting this article have been included as part of the ESI.

**Author contributions**

Ming Li: methodology, supervision, access to funding, project management and writing. Hongbo Zhang: investigation, experimentation, writing, data organization, and analysis. Xianying He: water electrolysis. Hanhua Feng: morphology testing. Cheng Li: assisting with experiments.

**Conflicts of interest**

There are no conflicts to declare.
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