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CRediT authorship contribution statement

**Huanhuan Li:** Writing-Original Draft, Conceptualization, Methodology. **Na Yu:** Writing-Original Draft, Formal analysis, Investigation. **Florian Gellrich:** Investigation, Conceptualization, Methodology. **Alexander Kappel Reumert:** Data Curation. **Mikkel Rykær Kraglund:** Investigation, Methodology. **Jianhao Dong:** Investigation, Methodology. **David Aili:** Writing-Original Draft, Writing - review & editing, Funding acquisition. **Jingshuai Yang:** Conceptualization, Writing-Original Draft, Writing - Review & Editing, Supervision, Project administration.
- 1M KOH @ 80°C
- Ni based electrodes
Diamine crosslinked anion exchange membranes based on poly(vinyl benzyl methylpyrrolidinium) for alkaline water electrolysis

Huanhuan Li,¹ Na Yu,¹ Florian Gellrich,² Alexander Kappel Reumert,² Mikkel Rykær Kraglund,² Jianhao Dong,¹ David Aili,²*, Jingshuai Yang¹*

¹ Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, China
² Department of Energy Conversion and Storage, Technical University of Denmark, Elektrovej, Building 375, 2800 Lyngby, Denmark

¹ These authors contributed equally to this work.

Abstract

New chemically crosslinked anion exchange membranes are prepared for water electrolysis based on high ion conductive poly(vinyl benzyl methylpyrrolidinium) and rigid polysulfone. Eight bifunctional tertiary amines are screened as crosslinking agents to optimize the properties of membranes. The fabricated crosslinked membranes exhibit excellent chemical resistance towards radicals, and meanwhile possess improved decreased swelling, enhanced mechanical stability, suitable conductivity and improved alkali resistance stability. As typical candidates, membranes crosslinked by $N,N,N',N'$-tetramethyl-1,6-hexanediamine, 4,4’-trimethylene-bis(1-methylpiperidine) and 1,4-bis(2-methylimidazol-1-yl)butane are down-selected for water electrolysis in 1 M KOH at 80 °C, and display current densities of 500 mA cm$^{-2}$, 400 mA cm$^{-2}$ and 600 mA cm$^{-2}$ at 1.9 V using nickel alloys as

*Corresponding author: larda@dtu.dk (D. Aili), yjs@mail.neu.edu.cn (J. Yang)
electrodes without ionomer, respectively. Furthermore, the durability profile for the cell over one week at 500 mA cm\(^{-2}\) illustrates the potential of membranes working in mildly alkaline conditions. 

*Keywords:* anion exchange membrane; crosslinked membranes; methylpyrrolidinium; poly (vinyl benzyl chloride); water electrolysis

1. **Introduction**

Sustainable hydrogen production by water electrolysis is a cornerstone in the green transition [1]. The acidic proton exchange membrane (PEM) electrolysis progress combines high rate capability with high efficiency [2], but the scope of application is limited by the usage of precious metals such as iridium and platinum [3,4]. Critical raw materials can be completely avoided in alkaline environment, and recent development is therefore directed towards alkaline electrolyzers, which could dynamically operate and reach good cell performance without compromising energy efficiency [5-6]. Towards this target, anion exchange membrane (AEM) electrolyzers have been intensively explored during the last decade. An alkaline AEM cell concept analogous to the PEM technology allows for operation with a feed of pure water [7-10], but several studies show that a support electrolyte is advantageous from a performance point of view [7,11-13]. One of the reasons is that the overpotential for the H\(_2\) and O\(_2\) evolution reactions decreases if the pH is sufficiently high [14], but the support electrolyte also reduces the ohmic resistance of the membrane and at the membrane-electrode interface [6].

Mitigating the degradation of cationic functionalities by e.g. Hofmann elimination or nucleophilic substitution is a formidable challenge for AEMs, and a main driver for the development in this area [15]. Numbers of cationic functionalities have been explored in this context, including various quaternary ammonium chemistries [16,17], imidazolium [18-20], guanidinium [21,22], piperidinium [23], pyrrolidinium [24-28], phosphonium [29], permethylcobaltocenium [30] or Tröger’s base [31].
Among them, the pyrrolidinium cations appear particularly attractive because the degradation mechanism goes via a high-energy transition state [32-34]. The chemical resistance of pyrrolidinium cations has been determined by using model systems [24] as well as on the membrane level when grafting to a poly(phenylene oxide) (PPO) backbone, where no signs of degradation were observed after 348 h in 1 M NaOH at 90 °C [35].

Recently, the alkaline stability of the polymer main chain in AEMs has also attracted much attention. The traditional approach has been to use backbone chemistries of poly(arylene ether) type polymers, which are first chloromethylated or brominated, before the functional groups are installed by substitution. The electron withdrawing cationic functionalities may activate the backbone for nucleophilic attack by hydroxide ions and chain scission, which predominantly occur at the aryl ether linkages [36-38]. From a stability perspective, backbone chemistries free from aryl ether linkages are therefore of great interest. Our previous work shows that poly(vinyl benzyl chloride) (PVBC) is a suitable starting material for AEMs, since the chloromethyl groups allows for the installation of cationic groups while the aryl-ether free backbone provides good alkaline stability [39]. The $^1$H NMR data showed that PVBC grafted with methyl pyrrolidinium groups (PVBC-MPy) was highly stably in alkaline environment, but mechanically robust AEMs could not be obtained from the pure PVBC-MPy because of the excessive water absorption. To balance the water uptake, the PVBC-MPy was therefore blended with a mechanically robust polymer [39] or ionically crosslinked with a sulfonated secondary component [40].

In the present work, a series of new covalently crosslinked AEMs were fabricated from PVBC-MPy and polysulfone (PSF), meanwhile using eight bifunctional tertiary amines as crosslinking agents. The PVBC-MPy was responsible for ion conducting function, while the aromatic thermoplastic PSF with a low chloromethylated degree of around 33% was employed to provide additional mechanical
robustness due to its superior mechanical strength, excellent processing property and easy availability [36,41,42]. AEMs derived from eight different bifunctional tertiary amines were prepared, including short-chain and long-chain aliphatic structures as well as five- and six-membered (un)saturated heterocyclics. The novel AEMs were thoroughly characterized with respect to physicochemical properties, and three membrane chemistries were selected for electrolysis testing, showing excellent performance stability over 170 h.

2. Experimental

2.1 Materials

PVBC (a 60/40 mixture of 3-and 4-isomers with number average molecular weight $M_n$ of 55,000 g mol$^{-1}$) was obtained from Sigma-Aldrich Chemistry. $N,N,N',N'$-Tetramethylethylenediamine (1#), $N,N,N',N'$-tetramethyl-1,6-hexanediame (2#), 1,4-dimethylpiperazine (3#), 4,4'-trimethylene-bis(1-methylpiperidine) (4#), 1,3-bis(4-pyridyl)propane (7#), 4,4'-vinylenediprydine (8#) and 1-methylpyrrolidine (MPy) were purchased from Adamas Reagent Ltd. 1,4-Bis(imidazolyl)butane (5#), and 1,4-bis(2-methylimidazol-1-yl)butane (6#) were synthesized as described elsewhere [43,44]. Chloromethylated polysulfone (CMPSF) was synthesized from polysulfone (PSF, Sigma-Aldrich Chemistry) as described elsewhere [41], which had a chloromethylatation degree of around 33%. $N,N$-Dimethylacetamide (DMAc), K$_2$CrO$_4$ and NaNO$_3$ were obtained from J&K Scientific. KOH and AgNO$_3$ were supplied by Tianjin Damao Chemical and Tianjin Fengchuan Chemical (China), respectively.

2.2 Polymer synthesis and membrane fabrication

PVBC, MPy, CMPSF and the different bifunctional tetraamines (crosslinker) were dissolved separately in DMAc to obtain solutions with a solid content of about 2 wt.%. At room temperature
(RT), the PVBC/DMAc and MPy/DMAc solutions were mixed ultrasonically for 15 minutes at a molar ratio of 1:0.8 (based on the PVBC repeating units) to achieve an uniform and transparent mixture. Subsequently, the CMPSF/DMAc and crosslinker/DMAc solutions were added to the (PVBC+MPy)/DMAc mixture according to a fixed -CH$_2$Cl / -N(CH$_3$)$_2$ molar ratio of 1:1, and ultrasonicated for 0.5 h at RT to achieve a homogenous solution. This implies that the weight ratio of PVBC to PSF of the finished membrane was 0.53:1. Each membrane-casting solution was poured into a Petri dish (the diameter: 6.5 cm), and dried at 80 °C for 12 hours. The schematic procedure for preparing membranes is shown in Fig. 1. The obtained membranes were washed thoroughly in deionized water to remove the residual solvent in the membrane sample. Finally, uniform and transparent membranes were obtained with the theoretical cross-linking degree of 20%.
Fig. 1 The schematic fabrication procedure and chemical structure of various covalently cross-linked membranes. The membranes are referred to the bifunctional tetramine crosslinker used for the AEM fabrication.

2.3 Characterization

The Bruker VERTEX70 spectrometer with an attenuated total reflection (ATR) accessory was used to record the Fourier transform infrared (FT-IR) spectra. X-ray photoemission spectroscopy (XPS) spectra were measured using an American Thermo escalab 250XI surface analysis system, and the detector equipped with an Al X-ray source operating at 150 W (1.486 keV) and 1.6A using the carbon (C1s) line at 284.8eV as the reference. The surface imaging was carried out using a SU-8010 scanning electron microscope (SEM) after sputtering platinum on the surface of samples. Fenton test was employed to investigate the oxidative stability of membranes. The Fenton’s reagent was firstly produced by 3 wt.% H₂O₂ and 4 ppm Fe²⁺ (added as (NH₄)₂Fe(SO₄)₂·6H₂O). Samples were immersed in Fenton’s reagents at 60 °C for a certain period of time, and then taken out, washed in distilled water and dried in an oven at 80 °C until the weight of membranes kept constant. Whereafter, membranes were put back to fresh Fenton’s reagents for sequential testing. The water absorption and dimensional swellings of membranes were determined based on mass and dimensions changes of membranes between the wet and dry states. After blotting the surface of membranes with wetted paper, the weight and dimensions of the water-saturated membranes were recorded quickly. Then membranes were dried at 80°C for 24 hours, whose dry weight and dimensions were measured accordingly. The ion exchange capacity (IEC) of the prepared AEMs was determined by Mohr titration [45]. The dried sample was accurately weighted, and then submersed in 0.5 M NaNO₃ solution (aq.) for 24 h to exchange Cl⁻ ions from membranes. By using K₂CrO₄ as the indicator, the amount of released Cl⁻ was determined by
using 0.1 M AgNO\textsubscript{3} standard solution. The IEC was calculated according to Equation 1, where $V_{Ag^+}$ is the consumed volume of AgNO\textsubscript{3} solution and $m_{dry}$ is the mass of the membrane in Cl\textsuperscript{-} form.

$$
IEC = \frac{V_{Ag^+} \times C}{m_{dry}} \times 100\% \quad (1)
$$

The mechanical properties were measured on a tensile strength instrument (CMT2000, SHIJIN Company, China) under ambient atmosphere at a crosshead speed of 5 mm min\textsuperscript{-1}. Membranes were cut into the dumbbell shape with a width of 4 mm and a length of 25 mm. The through-plane ion conductivity of the membrane (in chloride form) was determined by a two-electrode system in purified water as previously reported [39]. The OH\textsuperscript{-} conductivity of membranes was measured in 1 mol L\textsuperscript{-1} KOH as described elsewhere [46]. The AC impedance spectroscopy was collected on the Princeton electrochemical workstation (VersaSTAT 3) ranging from 100 Hz to 100 kHz. The alkali resistance of AEMs was measured in 1 M KOH solution at 60 °C and 80 °C by determining the change in conductivities of membranes with the immersing time.

2.4 Electrode preparation

Nickel felt (Bekaert) with a sheet thickness of 220 µm and fiber diameter of 14 µm, were die cut into circular electrodes substrates with a diameter of 36 mm (10 cm\textsuperscript{2}). The electrode substrates were thereafter ultrasonicated in 1 M HCl for 5 min followed by washing in water and ethanol before the subsequent steps. The NiMo cathodes were prepared via a hydrothermal synthesis followed by a reduction step in line with recent publications [47 - 49]. Ni(NO\textsubscript{3})\textsubscript{2}\cdot6H\textsubscript{2}O (40 mM) and (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}\cdot4H\textsubscript{2}O (10 mM) were dissolved in Milli-Q water (18 MΩ cm\textsuperscript{-1}) and transferred to a PTFE lined autoclave along with the cleaned electrode substrate. The PTFE liner was prior to synthesis cleaned under sonication (room temperature) in HCl (10 wt.%, aq.) for 5 min, boiled in H\textsubscript{2}SO\textsubscript{4} (40 wt.%, aq.) for 60 min, and finally washed with water repeatedly. The autoclave was placed in a furnace...
at 150 °C for 6 h, and left to cool to RT. The electrode was removed from the autoclave, rinsed with water, and placed in a tube for reduction. Heating was performed at 15 °C min\(^{-1}\) under Ar-atmosphere. The reduction was carried out under an atmosphere of 4 vol.% H\(_2\) and 96 vol.% Ar at 650 °C for 3 h.

The NiFe anodes were prepared similar to common procedures using hydrothermal procedure, but followed by an ex-situ electrochemical conditioning step \([50, 51]\). Ni(NO\(_3\))\(_2\)·6H\(_2\)O (7 mM), Fe(NO\(_3\))\(_3\)·9H\(_2\)O (3 mM) and urea (40 mM) were dissolved in water and transferred to a PTFE lined autoclave with the electrode substrate. The PTFE liner was cleaned as described above. The autoclave was heated to 120 °C for 12h and cooled to RT naturally. After removal, the electrodes were washed in water and ethanol. Conditioning was carried out by electrochemically cycling the anodes in 1 M KOH (aq.) for 20 cycles from 1.0-1.65 V (after iR-correction) against a RHE reference electrode at 50 mV s\(^{-1}\). The conditioned electrodes were rinsed with water and stored until use.

2.5 Electrolysis testing

Electrolyzer tests were carried out at 80 °C using 1 M KOH (aq.) as electrolyte. The membranes were stored in the electrolyte overnight at room temperature for pre-equilibration prior to cell test, and were cut to size just before assembly. The cell house was all nickel with an active area of 10 cm\(^2\). 250 mL electrolyte was circulated on both anode and cathode side at 75 mL min\(^{-1}\). Water was added every 2-3 days to compensate for consumed water. Polarization curves and galvanostatic electrochemical impedance spectroscopy (GEIS) were performed after an initial break-in at 100 mA cm\(^{-2}\) for 1 h, and after 1 week at 500 mA cm\(^{-2}\) before the end of test. Power was supplied by an Elektro Automatik PS-5040-40 A and polarization was carried out stepwise for 60 s with data being the averaged over the last 30s. GEIS was recorded using a Biologic VSP-300 from 100 kHz to 0.05 Hz at 15 ppt/decade at 50, 100, 200, 400 and 800 mA cm\(^{-2}\) using and amplitude of 10% of the setpoint up to 10 mA cm\(^{-2}\).
3. Results and discussion

3.1. Fabrication and properties of crosslinked membranes

As a low-cost commercially available polymer with excellent organo-solubility, PVBC was chosen to be the skeleton of AEMs. Since the PVBC repeat unit contains the chloromethyl group, the normal chloromethylation step in the AEM fabrication could be eliminated [15]. Furthermore, the lack of ether linkages and strongly electron drawing groups is expected to govern the chemical resistance. The quaternization was carried out by employing the Menschutkin reaction, and partially crosslinked AEMs were obtained by adding MPy together with a series of different bifunctional tertiary amines. A smaller fraction of CMPSF (with a molar ratio of 0.2:1 between the ClCH\textsubscript{2}- group in CMPSF to PVBC), which was readily quaternized by tertiary amines, was added to provide additional mechanical robustness and to benefit the membrane fabrication of the AEMs. The AEM fabrication process is illustrated schematically in Fig. 1, together with the structures of the bifunctional tertiary amines used for the preparation of the different membranes (hereafter referred to as M-1# to M-8#).

Fig. 2 shows optical photographs and surface SEM images of the as-prepared M-1# to M-8# membranes. All the membranes were transparent and uniform. The M-1# to M-6# membranes were colorless, while M-7# and M-8# membranes crosslinked by the dipyridine compounds displayed light brown color, which is probably related to the pyridine structure of the crosslinking agents. SEM imaging showed that all the membranes exhibited uniform, smooth, dense and non-porous microstructure. No apparent signs of phase separation could be observed. In addition, the energy dispersive spectroscopy (EDS) was used to investigate the element dispersion in membranes. Fig. S1 (in Supporting Information) shows the element mappings of N, S and Cl of the M-2#, M-4# and M-6# membranes. It can be seen that N, S and Cl elements were distributed throughout the whole area,
indicating the sufficient contact between PVBC-MPy and CMPSF with different crosslinking agents without macroscopic phase separation [52]. Thus, the homogenous structures of the crosslinked M-x# membranes were achieved.

![Photographic and surface SEM images of various covalently crosslinked membranes.](image)

Fig. 2 Photographic and surface SEM images of various covalently crosslinked membranes.

The FTIR-ATR spectra of various membrane M-1# to M-8# in the Cl⁻ form are shown in Fig. 3.
The characteristic peak at 675 cm\(^{-1}\) is related to the C-Cl stretching vibration of PVBC, while the characteristic peaks at 2918 cm\(^{-1}\) and 2850 cm\(^{-1}\) result from the symmetrical and asymmetric -CH\(_2\)-stretching [53,54]. The characteristic C-Cl peak at 675 cm\(^{-1}\) disappeared in the spectra of PVBC-MPy and different crosslinked membranes, supporting quantitative quaternization of the chloromethyl groups. Meanwhile, the spectra of PVBC-MPy and crosslinked membranes display a wide and strong absorption band at 3730-3192 cm\(^{-1}\), which is attributed to the stretching vibration of -OH groups, originating from the absorbed water [18,27]. Pure PVBC and CMPSF are highly hydrophobic, but the introduction of highly hydrophilic quaternary ammonium functionalities resulted in significant water uptake from ambient air as evidenced by the characteristic -OH band in their IR spectra. In addition, characteristic peaks at 1153 cm\(^{-1}\) and 1242 cm\(^{-1}\) appeared in the spectra of CMPSF and different crosslinked membranes, corresponding to the asymmetric and symmetrical stretching vibrations of O=S=O groups [55,56]. These results demonstrate that covalently crosslinked membranes have been successfully obtained.
Fig. 3 FTIR-ATR spectra of PVBC, CMPSF, PVBC-MPy, and M-1# to M-8#. All AEMs were in the Cl⁻ form.

XPS was employed to further investigate the chemical structure of different membranes. As depicted in Fig. 4A, a Cl₂p absorption peak at 200 eV was observed from all the measured membranes [57]. Meanwhile an N₁s absorption peak appeared at 400 eV in the spectra of PVBC-MPy, M-2#, M-4# and M-6# membranes [56,58], indicating the successful substitution of the chloromethyl groups in PVBC and CMPSU by MPy and crosslinkers. The above conclusion was further supported by Cl₂p spectra, as shown in Fig. 4B. In the Cl₂p spectra of PVBC and CMPSF, the doublet peaks at 200.3 and 201.9 eV were ascribed to the Cl₂p₃/₂ and Cl₂p₁/₂ signals of the Cl atom in the chloromethyl group of PVBC and CMPSF, respectively [59]. As to the PVBC-MPy, the above two Cl₂p peaks shifted to lower binding energies (196.8 and 198.4 eV), probably resulting from the electronegative Cl⁻ attached to the methylpyrrolidinium group [59]. In addition, in the N₁s XPS spectrum of PVBC-MPy (Fig. S2),
only one peak at 402.1 eV was found, which was due to the N atom in the pyrrolidinium group. However, there were two N1s peaks at 402.0 and 400.0 eV for M-2#, M-4# and M-6# membranes. One peak resulted from the pyrrolidinium group, while the other was ascribed to the nitrogen containing crosslinkers [52, 60, 61]. However, it should be noted that the chemical structure of crosslinked membranes was complex, and it is difficult to precisely determine the bifunctional tertiary amines react with both PVBC and CMPSU or with only PVBC/CMPSU. More investigations such as solid state NMR could be done to further determine the accurate chemical structure of crosslinked AEMs.

![Fig. 4 Wide-survey XPS spectra, Cl2p spectra of PVBC, PVBC-MPy, CMPSF, M-2#, M-4# and M-6# membranes.](image)

Table 1 lists the IEC, water uptake, hydration number (λ) and dimensional swellings of PVBC-MPy and M-1# to M-8# membranes. As previously reported [39,40], pure PVBC-MPy showed high IEC (3.60 mmol g⁻¹) and significant water absorption (600%). Although the high IEC and water uptake values govern ion conductivity, dimensional stability and mechanical strength are compromised. By combining crosslinking with bifunctional tetraamines in combination with CMPSF reinforcement, the IEC, water uptake and swellings of covalently crosslinked membranes were largely reduced. The
chemical structure of the crosslinker was found to have a big impact on the water uptake. Among all the crosslinked membranes, AEMs with diamine compounds as the crosslinker (i.e. M-1# and M-2#) exhibited the highest water uptake, while M-7# and M-8# membranes crosslinked by the bis-pyridyl compounds (i.e. M-7# and M-8#) displayed the lowest water uptake. Dai et al. [62] also observed that triethylamine quaternized poly(styrene-block-(ethylene-co-butylene)-block-styrene) (SEBS) membranes crosslinked with N,N,N’,N’-tetramethyl-1,6-hexanediamine and N,N,N’,N’-tetramethylethlenediamine achieved superior water uptake. Meanwhile, membranes with a similar type crosslinker displayed comparable water uptake and λ value, suggesting that the similar crosslinkers in the present work had a little effect on the water uptake.

Table 1 IEC, water uptake, hydration number (λ) and swellings at RT of the covalently crosslinked membranes in form of Cl⁻.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (mmol g⁻¹)</th>
<th>Water uptake%</th>
<th>λa</th>
<th>Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Measured</td>
<td></td>
<td>Area%</td>
</tr>
<tr>
<td>PVBC-MPy</td>
<td>4.21</td>
<td>3.60</td>
<td>--b</td>
<td>--</td>
</tr>
<tr>
<td>M-1#</td>
<td>2.27</td>
<td>1.97±0.2</td>
<td>26.0±1.3</td>
<td>7.4±1.1</td>
</tr>
<tr>
<td>M-2#</td>
<td>2.20</td>
<td>2.02±0.3</td>
<td>28.5±2.1</td>
<td>8.1±1.8</td>
</tr>
<tr>
<td>M-3#</td>
<td>2.26</td>
<td>1.79±0.4</td>
<td>15.3±3.4</td>
<td>5.2±1.9</td>
</tr>
<tr>
<td>M-4#</td>
<td>2.16</td>
<td>2.01±0.3</td>
<td>19.8±1.9</td>
<td>5.7±1.4</td>
</tr>
<tr>
<td>M-5#</td>
<td>2.20</td>
<td>1.88±0.2</td>
<td>20.7±2.1</td>
<td>6.3±1.3</td>
</tr>
<tr>
<td>M-6#</td>
<td>2.17</td>
<td>1.97±0.4</td>
<td>21.5±3.1</td>
<td>6.5±2.2</td>
</tr>
<tr>
<td>M-7#</td>
<td>2.20</td>
<td>1.76±0.3</td>
<td>13.4±2.7</td>
<td>4.5±1.6</td>
</tr>
<tr>
<td>M-8#</td>
<td>2.21</td>
<td>1.72±0.4</td>
<td>12.2±2.3</td>
<td>4.4±1.8</td>
</tr>
</tbody>
</table>
The degree of hydration is defined as the number of water molecules per cationic group.

Not available.

In addition, the area and volume swellings of different membranes were also shown in Table 1. It can be clearly seen that the dimensional swellings accompanied with the water uptake result, which means that the membranes with longer crosslinkers displayed higher swelling capacity. Comparing with our previous results, the covalently crosslinked membranes in the present work exhibited lower area swelling when they had the same PVBC-MPy matrix and comparable water uptake. For example, the blend membrane (e.g. PVBC-MPy/45%PEK-cardo) with the water uptake of around 22% displayed an area swelling of 26% [39]. The ionically crosslinked membrane (e.g. PVBC-MPy/10% sPEEK) exhibited a water uptake of around 20% and area swelling of 15%. In a word, above results indicate that chemical crosslinking can play a positive role in maintaining the dimensional stabilities and occupying high water absorption together, which provides a greater possibility for the prepared cross-linked AEMs for the water electrolyzer or fuel cell.

As discussed above, the significant water uptake of the PVBC-MPy membrane resulted in insufficient mechanical integrity for being tested. However, the mechanical strengths of the eight crosslinked membranes were significantly improved, obviously resulting from the formed crosslinking structures and the introduced rigid enhanced material of PSF. The tensile strength of hydrated M-1# to M-8# membranes were measured as depicted in Fig. 5A. The chemical structure of the cross-linker had a big impact on the mechanical properties of crosslinked membranes. The M-2# membrane exhibited the lowest tensile strength (9.5 MPa) among all the investigated membranes, while the tensile strengths of the other membranes were higher than 20 MPa. Nevertheless, all the membranes displayed satisfied tensile strength for the assembly and testing of water electrolyzers. Above results reveal mechanical
properties of AEMs could be greatly improved through chemical crosslinking and introducing supporting materials.

Fig. 5 Mechanical properties (A) and ionic conductivities as a function of temperature (B) of various covalently crosslinked membranes (in Cl\(^-\) form).

The ion conductivity of M-1# to M-8# in the Cl\(^-\) form (when mounted in the conductivity cell), is shown in Fig. 5B as a function of temperature. The conductivity of M-2#, M-4# and M-6#, i.e. the membranes derived from crosslinkers with a longer chain length, were slightly higher than that of their shorter crosslinking chain counterparts (i.e. M-1#, M-3# and M-5#). This can partly be explained by the higher water uptakes. As shown in Table 1, M-2#, M-4# and M-6# membranes also exhibited higher water uptake than M-1#, M-3# and M-5# membranes. Among the whole investigated membranes, the M-2# membrane possessed the highest conductivity at each temperature, which also achieved the highest water uptake. Meanwhile, the M-7# and M-8# membranes crosslinked by dipydidyl compounds displayed the lowest conductivities accordingly. Meanwhile, Fig S3 shows the OH\(^-\) conductivity of the M-2#, M-4# and M-6# membranes. It can be seen that the OH\(^-\) conductivity of
each membrane was obviously higher than its Cl$^-$ conductivity, which might be due to the faster migration rate of OH$^-$ than Cl$^-$ \[11,13,15\]. These results show that the conductivity of crosslinked membranes can be adjusted structure of crosslinkers, and a suitable crosslinker should be considered in order to obtain advantageous comprehensive performance, i.e. high conductivity and suitable mechanical strength simultaneously.

3.2 Chemical stability

The Fenton reagent with Fe$^{2+}$ added in H$_2$O$_2$ solution is widely used in the polymer electrolyte literature to assess radical-oxidative stability of AEMs \[17,40\]. Recently, Dekel et al. and Ramani et al. separately employed the in-situ electron paramagnetic resonance (EPR) spectrometer and fluorescence spectroscopy to determine the generation of reactive oxygen species (mainly superoxide anion radical) in the operating AEM fuel cell \[63,64\]. Thus, the AEM should exhibit excellent oxidative resistance under harsh operating conditions. In this study, Fenton test was employed to evaluate the oxidative stability of PVBC-MPy and M-1# to M-8# membranes by determining the weight change of membrane samples in Fenton reagent at 60 °C. As seen from Fig. 6, the uncrosslinked highly swollen PVBC-MPy was completely degraded within 41 hours. In our previously work, it showed that methylimidazolium functionalized PSF membrane was unstable in the Fenton solution and broke into small pieces after 30 hours of Fenton test \[41\]. On the contrary, M-1# to M-8# exhibited significantly improved chemical stabilities and kept their initial physical shapes after Fenton test. For example, M-1# showed a remaining mass of 94% after 143 h in the Fenton test solution. The superior chemical stability of the crosslinked membranes was clearly attributed to the chemically crosslinked structure, which compacted membranes, reduced swellings and hindered the radical attack \[40\]. Nevertheless, it can also be seen that the membrane crosslinked with different bifunctional tetraamines displayed different chemical
stability. For example, by comparing M-1# and M-2# (which have a crosslinker length of 2 and 6 carbon atoms, respectively), it is seen that the membrane with a short length degraded slower than the corresponding membrane with a longer chain length. A similar trend for the M-3# and M-4# membranes could be seen. This is probably because the bifunctional tetramines with short aliphatic chains of the alkyl groups bonded to amine nitrogen would make the crosslinked membrane more compact and hinder the attack of radicals, resulting in better chemical stability. Moreover, the aromatic heterocyclic crosslinked membranes (M-5# to M-8#) displayed comparable chemical stability. Totally speaking, M-1# and M-3# exhibited superior chemical stability comparing with other crosslinked membranes.

Fig. 6 Chemical stability of various membranes (in form of Cl⁻) in Fenton’s reagent (3% H₂O₂ + 4 ppm Fe²⁺) at 60 °C.

As widely reported, the QA groups of AEMs are normally easy to degrade due to the OH⁻ attack, especially under high temperature and high OH⁻ activity conditions [15]. In this work, the alkaline
stability of M-1# to M-8# membranes was investigated by submerging them in 1 M aqueous KOH and kept at 60 °C and 80 °C, respectively. During the test, all the membranes remained tough and integral. As shown in Fig. 7A, the crosslinked membranes only displayed slightly decreased conductivities over duration of the measurement at 60 °C, which suggested that the crosslinking improved the alkaline stability of membranes. This is also in agreement with the findings by e.g. Wang et al. [65], who fabricated a crosslinked structure of SEBS and PPO using \( N,N',N',N'' \)-tetramethyl-1,6-hexanediamine, (i.e. the crosslinker for M-2# in the present work). It was reported that the crosslinked membrane lost initial conductivity of 33% after immersing in 1 M NaOH for 500 h at 80 °C. Dai et al. [62] also concluded that the chemical crosslinking can effectively maintain the performance of AEMs in the harsh alkaline conditions. Their reported crosslinked AEM maintained 76% of the initial conductivity after immersing in 2 M NaOH at 60 °C for 500 h, as compared with 19% for the un-crosslinked one.

As depicted in Fig. 7B, the conductivity decay rates of M-1#, M-2#, M-4# and M-6# in 1 mol L\(^{-1}\) aqueous KOH solution at 80 °C was similar to those in 1 M KOH at 60 °C, further confirming the chemical stability of the such crosslinked electrolyte systems. However, at 80 °C the M-3#, M-5#, M-7# and M-8# membranes degraded severely in 1 M KOH. For example, the conductivities of M-5# and M-7# decreased by 43% and 50%, respectively, which probably resulted from the poor alkali resistance of crosslinkers. As previously reported, methylimidazolium and pyridinium groups were not stable enough in aqueous basic conditions, e.g. 1-3 M KOH/NaOH [19,26,66]. Meanwhile, it is found that the conductivity loss of the membranes with similar crosslinkers upgraded when the crosslinker had a longer aliphatic chain, such as for M-1# and M-2#, M-3# and M-4#. Komkova et al. [42] observed the same phenomenon for various diamines crosslinked PSF membranes, and they attributed the different stability to the different electron density at the β-carbon. In addition, the tensile strengths of crosslinked membranes after aging in 1 M KOH solution at 60 °C at different time were also tested as
summarized in Fig. 7C. It is observed that the whole membranes exhibited less decline in mechanical strength, which possibly implied the limited backbone degradation.

Fig. 7 Changes in conductivity at 60 °C for various crosslinked membranes during ageing in 1 M KOH solution at 60 °C (A) and 80 °C (B) and tensile strengths of the different membrane after aging 1 M aqueous KOH at 60 °C for different durations (C).

3.3 Electrolysis testing

Among the investigated crosslinking agents, the M-2#, M-4# and M-6# membranes were due to their combination of high conductivity, good aging stability and adequate mechanical properties.
deemed the most promising candidates and down-selected for water electrolysis tests. Membranes were cast to a thickness of approximately 80 µm in their hydrated state. Electrolysis tests were conducted with 1 M KOH as supporting electrolyte using 3D electrodes, which circumvent the need for an ionomer. The ionomer is normally an essential part of the catalyst layers if cells are designed to work with pure water, but it has repeatedly been shown that the performance of AEM electrolysers is greatly enhanced when a supporting electrolyte is used [14,67,68]. This is likely due to the enhanced ionic transport in electrode layers mediated by the electrolyte, but it also positively affects the conductivity of the membrane. For 3D electrodes, unlike the catalyst layers in membrane electrode assembly approaches, the ionic transport is exclusively mediated by the electrolyte, since no ionomer is present. Thus the electrodes represent a simple way to assess different novel membranes without the need for individually optimized catalyst layers or the challenges faced when interfacing a specific ionomer with a different membrane. Polarization performance in 1 M KOH and 80 °C at the beginning of test (BoT) and at the end of test (EoT) is shown in Fig. 8A and 8B. At 500 mA cm$^{-2}$, the cells with M-2#, M-4#, and M-6# membranes show initial cell voltages of 1.91 V, 2.00 V, and 1.85 V. At around 1.9 V the current densities correspond to 500 mA cm$^{-2}$, 400 mA cm$^{-2}$ and 600 mA cm$^{-2}$ for above cells. The lower performance of the cell with M-4# is in line with the lower measured conductivity of this membrane compared to M-2# and M-6#. However, while the measured conductivity of M-2# is higher than M-6#, cell performance is the best for M-6#. While the cells showed some degradation, no large change in the slope of the ohmic part of the polarization curve was observed, indicating good membrane stability even under technical conditions. When using 3D electrodes, the slope is not only related to the resistance of the membrane, but also contains a contribution from the ionic transport within the 3D structure of the electrode. Even with thin felt electrodes (220 µm), the relative thickness remains much greater than the membrane (~80 µm), and at 1 M KOH a significant part of the ohmic part can
potentially be attributed to the electrodes. In addition, the tested cell performance is compared with recent published AEM electrolysis cell results by means of the current density at 1.9 V in Table S1. It can be seen that the water electrolysis cell in the present work displayed comparable or higher current densities at the same voltage of 1.9 V. Nevertheless, it is worth noting that the testing conditions and electrode materials vary greatly within the field of AEM based electrolysis, and much research remains to be done both on membranes and electrodes.

Fig. 8 Polarization curves recorded by beginning (A) and end of test (B) in 1 M KOH at 80 °C. Nyquist plots recorded at 100 mA cm\(^{-2}\) for each cell at beginning (C) and end of test (D).
To more closely assess the membrane contribution, EIS was carried out under galvanostatic conditions. Nyquist plots of impedance data recorded at 100 mA cm\(^{-2}\) at the beginning and the end of test is shown in Fig. 8C and 8D. The data was equipped with an L-R-Q-RQ equivalent circuit (shown with the line), with the objective of extracting the high frequency resistance (HFR). While the model might not accurately capture the electrode behavior, it is adequate to obtain accurate resistance values for the membrane. During the course of one week, we observed no increase in membrane resistance. Instead all cells showed a slight decrease in HFR. For M-6#, the HFR decreased rather insignificantly from 0.34 Ω cm\(^{-2}\) to 0.33 Ω cm\(^{-2}\), while the cells based on M-4# and M-2# showed a more substantial HFR decrease from 0.54 to 0.49 Ω cm\(^{-2}\) in the case of M-4#, and from 0.47 to 0.42 Ω cm\(^{-2}\) in the case of M-2#. For M-6#, assuming an effective membrane thickness of 80 µm inside the cell, the end of test HFR of 0.33 Ω cm\(^{-2}\) correspond to a specific conductivity of 24 mS cm\(^{-1}\), which is lower than the ex-situ data in Fig. 5B. Similar is observed for M-2# and M-4#. It is noted that the apparent conductivity of the three membranes appear lower during cell test, than the ex-situ values measured in Cl\(^-\) form. And in all cases, it is still significantly higher than the 0.08-0.15 Ω cm\(^{-2}\) generally seen in PEM electrolyzers [2,69,70], or the 0.10-0.20 Ω cm\(^{-2}\) demonstrated in some recent AEM work [68,71]. The apparent decrease throughout the test is likely a result of increased electrolyte uptake compared to initial conditions, and likely promoted by the higher temperatures in the cell. While this could be due to increased swelling due to partial decomposition of crosslinkers, it is not straightforward to determine based on the present experiments alone and warrants further study. Unlike ex-situ conductivity experiments conducted in water, where the loss of functionalized crosslinkers is detrimental to performance, cell tests are conducted under electrolyte flooded conditions. Therefore, some deviation from the ex-situ behavior is expected, although the general expectation would be an improved conductivity.
The durability profile for the cell with M-6# membrane is depicted in Fig. 9. The cell voltage primarily upgraded during the first 48 h, likely due to rapid initial degradation of the electrodes, after which the voltage remains more or less constant. Two distinct voltage jumps are observed when water was resupplied, perhaps due to disturbance in the established concentration gradients across the cell, which are slow to level out through the membrane. As shown by both the polarization curves and by the increase in the arcs of the impedance data presented in Figure 9, significant electrode degradation took place over the course of one week. By the end of tests, black precipitate was also observed in tubing of the anode electrolyte, suggesting that a substantial amount of Fe had leached from the applied NiFe catalyst. This supports that the cell degradation is primarily electrode related, although a deeper investigation into the electrodes is beyond the scope of this work. It is noted that all membranes slightly altered color during cell experiments, suggesting that some chemical changes might have taken place.

Fig. 9 Voltage profile of a cell with an M-6# membrane, operated at 500 mA cm$^{-2}$, in 1 M KOH at 80 °C. The asterisks denote when water was supplied.
4. Conclusions

A series of new chemically crosslinked AEMs for water electrolysis were prepared based on PVBC-MPy and PSF, using bifunctional tertiary amines as crosslinking agents. The PVBC-MPy was responsible for ion conducting function, while the aromatic thermoplastic PSF was used to provide additional mechanical robustness. Eight bifunctional tertiary amines were employed to construct the cross-linked network and optimize the properties of AEMs. FT-IR results proved the successful synthesized crosslinked M-1# to M-8# membranes. SEM revealed that all the membranes occupied uniform, smooth, dense and non-porous microstructure. No apparent signs of phase separation could be observed. Crosslinked AEMs with the crosslinker having longer molecular chain exhibited higher water absorption and ionic conductivity. The introduction of rigid PSF and crosslinked network significantly improved the dimensional, mechanical and oxidative stabilities of membranes. M-2#, M-4# and M-6# with N,N,N′,N′-tetramethyl-1,6-hexanediamine, 4,4’-trimethylene-bis(1-methylpiperidine and 1,4-bis(2-methylimidazol-1-yl)butane as the crosslinker, respectively, exhibited good alkaline robustness in 1 M KOH at 60 °C and 80 °C for 600 h, which thus were down-selected for water electrolysis in 1 M KOH at 80 °C. Cell polarization curves demonstrated that the M-2#, M-4# and M-6# membranes displayed pretty cell performance with a current density of 500, 400 and 600 mA cm⁻² at 1.91 V using nickel alloys as electrodes without ionomer. Furthermore, the durability profile for the cell with M-6# membrane over one week at 500 mA cm⁻² in 1 M KOH at 80 °C illustrates the feasibility of the membrane operating under mildly alkaline conditions.

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References


**Highlights**

1. Eight bifunctional tertiary amines are employed to fabricate crosslinked AEMs.
2. Crosslinked AEMs exhibit superior dimensional, mechanical, oxidative and alkaline stabilities.
3. AEMs exhibit excellent water electrolysis performance and stability using Ni alloy electrodes.
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: