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Degradation of radiation grafted anion exchange membranes tethered with different amine functional groups via removal of vinylbenzyl trimethylammonium hydroxide

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**Highlights**  
- AEMs using mono-quaternised amines exhibit similar IEC loss of ca. 5% per month.  
- Degradation of AEMs is mainly attributed to peroxide and hydroxide radical attacks.  
- Vinylbenzyl trimethylammonium and Benzyl peroxide are the main degradation products.  
- Under nitrogen, oxygen and 3 wt% H2O2 AEM shows the same degradation products.  
- Three-fold increase in the degradation rate in D2O under oxygen compared to nitrogen.

**Abstract**  
Low-density polyethylene (LDPE)-based anion exchange membranes (AEMs) with 65% degree of grafting of vinylbenzyl chloride (VBC) were tethered with different amine functionalities namely, trimethyl amine (TMA), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1-azabicyclo[2.2.2]octane (ABCO) and N-methylpiperidine (NMP), and were subjected to degradation test by immersing the OH− exchanged AEMs in deionised water at 60 °C, a condition analogous to fuel cell and electrolyser environment. All the quaternised membranes, regardless of the tethered amine functional group, exhibited similar degradation loss of ca. 5% IEC per month. Benzyl peroxide was detected in the degradation solution in all the tested AEMs. The observed degradation of the OH− exchanged AEMs was mainly attributed to peroxide and hydroxide radical attacks on the ternary (benzylic) carbon resulting in the release of vinylbenzyl trimethylammonium hydroxide (VBTMA) as a whole which was also detected. The degradation test performed on TMA-functionalised membrane under nitrogen, oxygen and 3 wt% H2O2 showed similar degradation products namely benzyl peroxide and VBTMA suggesting that the degradation mechanisms under these three conditions are similar. The over three-fold increase in the degradation rate under oxygen saturated solution compared to nitrogen is due to the higher peroxide concentration produced from oxygen reduction to superoxide via ylide.

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1. Introduction

The development of solid anion exchange membrane (AEM) as an alternative to liquid KOH solution as electrolyte paved the way for the renewed interest in alkaline fuel cell and electrolyser applications. Alkaline AEMs are solid polymer electrolytes that contain positive ionic groups, typically quaternary ammonium groups, =N3+(CH3)3, and mobile negatively charged anions, usually OH− [1,2]. Membranes based on quaternary ammonium groups are still the most studied AEMs for fuel cell and electrolyser applications. The use of alkaline AEMs offers the following advantages compared to proton-exchange membrane fuel cells (PEMFC), namely, (a) faster oxygen reduction reaction (ORR) kinetics under alkaline conditions thereby providing lower activation losses [3,4], (b) opportunity of using non-noble metal catalysts [5–7], and (c)

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lower cell components and membrane cost due to less corrosive operating conditions [3,6,8].

AEMs can be prepared through radiation grafting wherein the base film is subjected to high energy radiation (electron beam source, ultraviolet or Co gamma rays) to produce activated polymer backbone and by either step-wise or mutual grafting with the desired monomer to produce the chain grafts copolymer [9–11]. The functionalisation of the copolymer with the desired quaternary amine and subsequent anion exchange to mobile OH ions produce the AEM. We have previously reported that the radiation dose rate has a significant influence on the stability of the resulting AEM; applying higher radiation dose rate during grafting leads to a more chemically and thermally stable membrane [12]. This is due to the fact that using higher radiation dose rate will result in shorter and more uniformly distributed grafted chains with higher degree of cross-linking, thus resulting in a lower ion exchange capacity (IEC) loss per radical attack. AEMs fabricated using low density polyethylene (LDPE) as base polymer and vinylbenzyl chloride (VBC) as graft monomer have been established to be highly stable in fuel cell environment [13,14]. LDPE has a high degree of branching resulting in more uniform grafting and structural stability due to enhanced chain entanglement (via cross-linking) during radiation grafting. This strengthens the use of LDPE as base polymer for a more stable and cost-effective AEM.

The chemical and thermal stability of AEM are very important criteria in the design and synthesis of membranes for fuel cell and electrolyser application. The main concern for alkaline AEM is that it relies on OH− ion, a relatively strong base and nucleophile, for conductivity. With the use of a stable polymer backbone, the stability and degradation of AEMs then rest chiefly on the cation stability. There are three pathways of AEM degradation in alkaline media and elevated temperature widely reported in literature, namely, Hofmann elimination, nucleophilic substitution and formation of ylide intermediates [15,16]. Hofmann elimination is an E2 reaction involving the attack of OH− ions leading to the simultaneous removal of a β-proton and formation of a tertiary amine [17,18]. Nucleophilic substitution (SN2) proceeds either (1) by OH− ion attack on the benzylic carbon of the ammonium group resulting in the formation of a benzylic alcohol with consequent release of a tertiary amine (Fig. 1, reaction A), or (2) attack on the α-carbon of the cation transforming the ammonium group to a tertiary amine with release of an alcohol [19,20] (Fig. 1, reaction C). Lastly, the ylide formation pathway involves the abstraction of a proton from the benzylic methylene group leading to the formation of a ylide intermediate that subsequently converts to tertiary amine and water [21,22] (Fig. 1, reaction B). These ylide intermediates can potentially undergo further rearrangement reactions through Stevens or Sommelet-Hauser mechanism [23,24]. These three degradation pathways can occur in parallel and can lead to a combination of degradation products, although Hofmann elimination is preferred in the presence of β-hydrogens over nucleophilic substitution or the reversible reaction of ylide formation [15,22,25].

We have recently reported that, in close to neutral and low alkalinity solutions, typical of that in anion exchange membrane fuel cell (AEMFC) and water electrolyser (AEMWE), AEM degradation in terms of IEC loss was not mainly due to OH− ion attack on the trimethylamine (TMA) functional groups proposed above, but mainly due to the removal of the vinylbenzyl trimethylammonium (VBTMA) group as whole [12]. The loss of IEC due to the detachment of the VBTMA groups was attributed to the formation of superoxide (from oxygen in the presence of ylides) and other radicals (under nitrogen atmosphere) that attack the vulnerable tertiary carbon connecting the benzyl trimethylammonium hydroxide group to the LDPE backbone (Fig. 1, reaction E) resulting in graft chain scissions (VBTMA removal) (Fig. 1, reaction G). The rate of AEM degradation due to oxidation in the presence of OH− ions was...
also observed to increase when exposed to higher oxygen concentration and was explained by oxygen reduction to superoxide through ylide by Parrondo et al. but was assigned to backbone degradation from the formed superoxides attack [26]. The OH⁻ ions were also suggested to attack the quaternary carbon groups of the polymer backbone of polysulfone-based AEM via hydrolysis (Fig. 1, reaction D) that leads to membrane degradation [16] and an analogous reaction might occur for LDPE-VBTMA-OH leading to the formation of benzyl alcohol. Furthermore, the rate of AEM degradation was reported to accelerate in the presence of oxygen [27], wherein AEM degradation rate in terms of decrease in ionic conductivity (due to IEC loss) was 4 times faster in 100% humidified stream of oxygen than in nitrogen [14].

The use of TMA to impart functionality to AEMs is considered to give the most chemically stable products [28]. This is due to the absence of longer subgroups (e.g. ethyl or propyl) that introduce β-hydrogens making the AEM susceptible to degradation via the Hofmann elimination mechanism [29,30]. Studies of the ionic conductivity and fuel cell performance of several benzyl ammonium and sulfonium head groups for AEMs found that TMA-functionalised ionomers showed superior oxygen reduction reaction (ORR) performance and higher ionic conductivities in comparison to other studied head groups including 1,4-diazabicyclo[2.2.2]octane [2,13].

The use of other head groups such as, 1-azabicyclo[2.2.2]octane (ABCO) and 1,4-diazabicyclo[2.2.2]octane (DABCO), for AEM was introduced owing to their cyclic bulky structure that can provide chemical and thermal stability. This is because the rigid structures of ABCO and DABCO render them non-susceptible to Hofmann elimination [30–32]. Unlike the TMA-functionalised membranes, the combination of ABCO or DABCO with VBC results in the presence of β-carbons. However, their structures do not allow the stereoelectronics necessary for a Hofmann elimination mechanism [28,32] since the anti-periplanar arrangement, which is a requisite for Hofmann elimination to proceed is not possible [19,33]. Thermogravimetric analysis demonstrated [32] that DABCO-functionalised membrane exhibits better thermal stability than its TMA-based AEM counterpart. Stoica et al. [34] and Sollogou et al. [35] fabricated and characterised AEM incorporating both cyclic diamines onto an epichlorohydin-based polymer matrix, but not as separately functionalised AEM. The use of ABCO alone as a cation functional group for AEM application did not gain considerable interest due to its higher cost (harder to synthesise than DABCO) and toxicity [19].

Parrondo et al. [36] compared the stability of TMA and ABCO functionalities tethered to polyethylene oxide (PEO) base film via hexyl spacers and both were found to undergo degradation in 1 M KOH solution at 60 °C. DABCO unlike ABCO, has two nitrogen which provide a better stabilising effect wherein the positive charge can balance the overall charge and therefore, mono- or diquaternised DABCO-membrane is preferred [32,37]. It is expected that a mono-quaternised DABCO-based membrane will exhibit better chemical stability than ABCO-functionalised AEMs. However, both the quaternised ABCO and mono-quaternised DABCO still undergo a nucleophilic displacement reaction causing the release of ABCO or DABCO to the solution [28,38].

If both the DABCO nitrogens are quaternised, DABCO would act as a cross-linker (between the two chloromethylated styrene) resulting in a lower membrane water uptake and consequently lower ionic conductivity. Furthermore, the bis-quaternised DABCO converts into a piperazine structure which is less stable due to rapid elimination mechanism. At 160 °C in 2 M KOH solution under nitrogen atmosphere, the half-life (t1/2) of bis-quaternised DABCO drops to 2.3 min compared to 42 min (t1/2) for the mono-quaternised DABCO [28]. Therefore, the combined faster degradation and decrease in IEC rendered it inferior to mono- and diquaternised DABCO and unsuitable for fuel cell and electrolyser application.

N-Methylpiperidine (NMP) is another cycloaliphatic quaternary ammonium group used to functionalise AEMs. Dang and Jannasch [39] investigated the use of quaternary piperidinium group for AEMs using PPO base polymer film placing heptyl spacers in between. Thermogravimetric data indicated that NMP-based AEMs offer slightly better thermal stability than TMA-functionalised AEMs at the same IEC. The same study also indicated insignificant degradation in terms of IEC loss under alkaline stability test using 1 M NaOH solution at 90 °C for 8 days. Degradation of NMP-functionalised AEM is due to OH⁻ ion attack through nucleophilic substitution. NMP-based AEMs also degrade by ring-opening elimination and ring-opening substitution. Among the three possible pathways of NMP-functionalised AEM degradation, nucleophilic substitution is considered to be dominant [40].

In order to accurately assess cation stability, it is imperative to compare several amine functionalities tethered to the same polymer backbone and subject to the same degradation test conditions. Previous attempts to investigate AEM degradation used density functional theory (DFT) [21,41,42] and model compounds [40,43-45] instead of grafted or synthesised AEMs. In this research, LDPE-based AEMs were used and the investigation was extended to include the effect of employing other functional groups aside from TMA to the resulting stability of the functionalised membrane, namely, DABCO, ABCO and NMP immersed in deionised water. Furthermore, degradation studies reported in literature were all performed in highly alkaline media and elevated temperatures, which are test conditions very far from the actual operating environments of low-temperature AEMFC and AEMWE (i.e. deionised water). The investigations of the degradation of hydroxide-exchanged AEM reported herein were performed in water/deuterated water media with very low alkalinity in order to mimic the real operating conditions of fuel cells/electrolysers and so that the degradation by-products can be conveniently and directly analysed by 1H NMR spectroscopy.

2. Experimental

2.1. Materials

Commercial low-density polyethylene films were sourced from British Polythene Industries plc and were used as received. Poly(-vinylbenzyl chloride) (60/40 mixture of 3- and 4-isomers, M₀ = 55,000, Mₙ = 100,000), vinylbenzyl chloride (mixture of 3- and 4-isomers, 97%), trimethylamine (45 wt % in water), N-methylpyrrolidine and 1,4-diazabicyclo[2.2.2]octane were all procured from Sigma-Aldrich while 1-azabicyclo[2.2.2]octane was purchased from Alfa Aesar. Deuterium oxide (99.8 atom % D) was purchased from Acros Organics. Toluene, tetrahydrofuran, potassium hydroxide pellets, acetone, sulfuric acid, methanol and sodium chloride were all analytical reagent grade and were used as received.

2.2. Anion exchange membrane preparation

The AEMs were synthesised as previously reported [10,14] using low-density polyethylene (LDPE) as base polymer with vinylbenzyl chloride (VBC) as the graft monomer. The LDPE-g-VBC copolymer was prepared by immersing the LDPE films in nitrogen-purged 1:3:6.43 ratios by volume VBC/toluene/methanol solution and were secured in a screw-cap vial. The samples were sent to Synergy Health plc (Wiltshire, UK) for mutual gamma radiation grafting, carried out with total radiation dose of 20 kGy under radiation dose
rate of 2000 Gy h\(^{-1}\). The grafted copolymers obtained were washed thoroughly with toluene to completely remove VBC homopolymers and finally washed with acetone. To produce the AEM, a selection of amines were utilised to impart functionality to the LDPE-g-VBC copolymer (Table 1).

2.3. Membrane stability tests

2.3.1. Stability test of PVBC–TMA polymer

The stability of the TMA-functionalised PVBC polymer was initially assessed prior to stability test of the grafted LDPE polymers. The PVBC polymer film was produced from solution casting of PVBC-tetrahydrofuran (THF) solution which was allowed to dry to remove traces of THF solvent prior to immersion in TMA solution of 45% in water for 72 h. The VBTMA-Cl polymer was then allowed to remove traces of THF solvent prior to immersion in TMA solution of the PVBC polymer initially assessed prior to stability test of the grafted LDPE polymers.

2.3.2. Stability test of OH\(^{-}\) exchanged AEM functionalised with different head groups

Functionalised AEMs were treated with 1.0 M KOH solution for 20 min. The solution was replaced with fresh 1.0 M KOH solution and the process was repeated until a total OH\(^{-}\) exchange time of 1 h was achieved to ensure complete exchange of chloride ions to hydroxide ions. The membrane was then washed with copious amount of deionised water to remove residual hydroxide ions. Removal of excess OH\(^{-}\) ions was confirmed with pH paper. OH\(^{-}\) exchanged membranes were then immersed in D\(_2\)O in sealed polypropylene bottles and were placed inside a water bath at 60 °C for 2 months, wherein sample for each month interval were submitted for analysis. The initial solid Poly VBTMA-Cl polymer was set aside for comparison.

2.3.3. Stability of OH\(^{-}\) exchanged AEM under oxygen and nitrogen gas feed and peroxide

The OH\(^{-}\) exchanged TMA-functionalised AEM was immersed in D\(_2\)O in a polypropylene bottle fitted with reflux and under continuous flow of high-purity oxygen gas. The setup was secured in water bath at 60 °C. A similar setup was prepared but fed with nitrogen gas instead. After the stability test for 2 months, both the membrane and the D\(_2\)O solution were analysed. For comparison, OH\(^{-}\) exchanged TMA-functionalised AEM was immersed in 3 wt% H\(_2\)O\(_2\) solution in H\(_2\)O placed inside a sealed polypropylene bottle secured in water bath at 60 °C for 48 h.

2.4. Characterisation of the membrane and the degradation products

2.4.1. Measurement of the ion-exchange capacity (IEC)

The OH\(^{-}\) exchanged membranes were immersed in a known volume of 1.0 M NaCl solution and were left to stand overnight. The liberated hydroxide ions were titrated with 0.10 M H\(_2\)SO\(_4\) solution using a Titrette GMBH bottle-top digital burette and the endpoint was determined visually using methyl red indicator. After titration, the membranes were washed with deionised water to completely remove the salt and dried using a MTI Model DZF-6020-FP vacuum oven. Measurements of the weight were performed until no change in the dry weight remained. The IECs were computed using the amount of OH\(^{-}\) ions neutralised, expressed in mmol OH\(^{-}\), divided by the dry weight of the membranes, in grams.

2.4.2. Measurement of the ionic conductivity

The through-plane ionic conductivity of each of the functionalised membranes was measured following the same procedure previously reported [12,14] using the following formula:

\[
\sigma = \frac{4L}{R \pi d^2}
\]

where \(\sigma\) is the hydroxide ion conductivity, \(L\) is the membrane thickness, \(R\) is the resistance derived from the impedance value at zero-phase angle and \(d\) is the diameter of the membrane test area.

2.4.3. Solid-state nuclear magnetic resonance spectroscopy

Solid-state \(^{13}\)C and \(^{15}\)N NMR spectra of the membranes before and after degradation were obtained employing cross-polarisation magic-angle spinning (CP-MAS) NMR with two-pulse phase-modulated (TPPM) decoupling and neat tetramethylsilane (TMS) and nitromethane as chemical shift references, respectively, using a Varian VNMR S spectrometer at the EPSRC National Solid-state NMR Service in Durham University, UK.

2.4.4. Solution nuclear magnetic resonance spectroscopy

The \(^1\)H and \(^{13}\)C NMR spectra of the degradation solutions were obtained using a Bruker 500 Avance III HD NMR spectrometer operating at 500 MHz for \(^1\)H and 125 MHz for \(^{13}\)C with TMS as the chemical shift reference. All NMR spectra were processed using MestReNova 11.0 (Mestrelab Research S.L.) software.

3. Results and discussion

3.1. Stability of VBTMA polymer

The stability of the TMA-functionalised PVBC (VTBMA) polymer (without the LDPE base polymer) dissolved in D\(_2\)O mild alkaline solution was investigated using \(^1\)H NMR spectra of the aged polymer after 1 and 2 months as shown in Fig. 2. The \(^1\)H solution-NMR spectra showed similar sets of resonances before (OH\(^{-}\) untreated i.e. Cl\(^{-}\) form) and after (OH\(^{-}\) exchanged) the degradation test.

The peaks corresponding to the aromatic H can be seen in the...
6.25–7.25 ppm region [46]. The 4.25 ppm peak (9) is attributed to that of H attached to the benzylic carbon, evidence of VBTMA. The H attached with the secondary carbon (1) and (benzylic) tertiary carbon (2) can be seen around 1.5 and 2.8 ppm, respectively. Small magnitude peaks were present in the range of 3.0–3.25 ppm and 7.5–8.0 ppm and were seen in the original and degraded samples which might suggest they are due to impurities or small amount of TMA N-oxide for the 3.2 ppm resonance [47].

In the degraded solution in addition to the peaks observed above, the following new peaks can be seen: a weak peak at 8.4 ppm (#) and peak at 2.17 ppm (●) which can be attributed to the benzylic hydroperoxyl proton (O–O–H) [48] suggesting that peroxy radicals are the most likely initiator of membrane degradation [49]. These two peaks can be associated with the degradation product(s) as their intensities were observed to increase with degradation time. The 2.17 ppm (●) resonance coupled with the peaks at 1.25, 3.2 and 7.5 ppm can suggest the possible formation of N,N-dimethyl-1-phenylethylamine [16] representing the product of Stevens rearrangement (ylide degradation pathway) as shown in Fig. 1 (reaction B). However, the mentioned peaks at 1.25, 3.2 and 7.5 ppm cannot be confirmed due to overlap with other peaks discussed above.

This suggests that the degradation reaction due to SN2 substitution (Fig. 1, reactions A and C) is negligible under these tested neutral pH solutions as no 1H NMR peaks for methanol at 3.35 and 4.8 ppm, or for benzyl alcohol at 2.3 and 4.6 ppm could be detected. If methanol was indeed a degradation product and would have reacted with benzyl alcohol to form benzyl methyl ether (in the presence of oxygen), the latter was not detected either at 3.37 and 4.44 ppm. If any produced benzyl alcohol would have gone dehydration reaction to produce benzyl ether, peaks at 4.54 and 7.4 ppm should have been seen, which is not the case here. Finally, if benzyl alcohol would have gone oxidation to benzoic acid, peaks at 7.5 and 8.12 ppm would have been seen, again is not the case herein.

3.2. Effect of different head-groups

The synthesised LDPE-based membranes prepared previously [14] have a degree of grafting (DOG) of 65%. The DOG is the measure of the extent of polymerisation of the radiation grafted membranes, which is defined as the percentage mass of the grafted component in the final grafted film product [50]. The prepared membranes were functionalised with different head groups (Table 1) in order to determine the most stable head group among the amines investigated towards peroxy radicals attacks that are taking place when membranes are immersed in close to neutral pH solution. Fig. 3 shows the IEC profile of the membranes with different head groups after 1 and 2 months degradation time.

Among the different functional groups, TMA showed the highest initial IEC, primarily due to the ease of which TMA can effectively penetrate and functionalise the LDPE-g-VBC copolymer unlike that of the bulkier cyclic structures of DABCO, ABCO and NMP. All the membranes investigated showed a decrease in IEC through the 2-month degradation period indicating the loss of functional groups from the AEM. The degradation rates of TMA- and DABCO-based membranes in terms of % IEC loss after two month are 9.0 and 15.5%, respectively, indicating that TMA functionality provides better stability than DABCO-based AEM under these test conditions which we have reported previously [12]. ABCO and NMP, however, exhibited comparable degradation rates of 9.4 and 10.6% IEC loss, respectively. The order in increasing AEM stability in terms of % IEC loss is TMA > ABCO > NMP > DABCO. All the quaternised membranes, regardless of the tethered amine functional group, exhibited similar degradation loss of ca. 5% IEC per month. The slightly higher degradation rate in DABCO could be due to the difficulty in obtaining 100% mono-quaternisation and the presence of small amount of bis-quaternised DABCO which converts into a piperazine less stable structure as discussed previously.

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3.3. Ionic conductivity of the initial and aged membrane

Table 2 shows the through-plane ionic conductivity of the membranes tethered with different amine functionalities after degradation test at 60 °C and their respective membrane codes. AEM degradation in terms of IEC loss (Fig. 3), resulted in a decrease in the through-plane ionic conductivity (Table 2) for each month interval for all membranes investigated. It was expected that T-AEM would exhibit the highest ionic conductivity due to its higher initial IEC and the high basicity of TMA (pKb = 4.19). The observed decrease in ionic conductivity is in agreement with the observed decrease in IEC (Fig. 3) from the degradation test. T-AEM exhibited lower decrease in ionic conductivity at 60 °C after 2 months (16%; 101 to 85 mS cm⁻¹) compared to D-AEM (33%; 70 to 47 mS cm⁻¹) as shown in Table 2. A-AEM and N-AEM also showed evidence of degradation in terms of ionic conductivity loss due to the observed decrease in their respective IECs after 2 months degradation test. The loss in ionic conductivity cannot be directly compared with the loss of IEC as it is dependent on the distribution of IEC loss. In other words, the IEC loss is expected to occur initially at the membrane surface where the membrane interface with water and oxygen and at slower rate inside the membrane due to diffusion restrictions. The higher possible %IEC loss at the membrane interface could result in the observed large conductivity percentage decrease in comparison to the average %IEC loss recorded.

<table>
<thead>
<tr>
<th>Membrane Code</th>
<th>Functional Group</th>
<th>Initial IEC (mS cm⁻¹)</th>
<th>After 2 months IEC (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-AEM</td>
<td>TMA</td>
<td>101 ± 5</td>
<td>85 ± 4</td>
</tr>
<tr>
<td>A-AEM</td>
<td>ABCO</td>
<td>87 ± 4</td>
<td>71 ± 3</td>
</tr>
<tr>
<td>N-AEM</td>
<td>NMP</td>
<td>75 ± 3</td>
<td>65 ± 3</td>
</tr>
<tr>
<td>D-AEM</td>
<td>DABCO</td>
<td>70 ± 3</td>
<td>47 ± 2</td>
</tr>
</tbody>
</table>

Fig. 3. IECs of LDPE-based membranes (65% DOG) functionalised with different head groups after degradation test in deionised water at 60 °C.

3.4. NMR analysis of the aged membranes and the degradation products

The original and aged membranes (after 1 and 2 months degradation period) tethered with different amine functionalities were subjected to 13C and 15N CP-MAS NMR analysis to verify the loss of the chemical groups observed for each month while the degradation solutions (D₂O solution where the AEM was immersed during degradation test) were analysed using 1H solution NMR. The 13C CP-MAS NMR spectra obtained were normalised against LDPE peak since the base polymer was found to be stable and did not participate in the degradation reactions [12].

3.4.1. 15N CP-MAS NMR analysis

The 15N CP-MAS NMR spectra of T-AEM, A-AEM and N-AEM (Figs. S1–S3, Supplementary information) are essentially having the same single quaternised nitrogen peak at ~330 ppm [51], present in both the original and the degraded membrane. However, in the case of D-AEM, since DABCO having 2 Nitrogen atoms, two peaks can be seen: a resonance at ~330 ppm consistent with quaternised nitrogen and a resonance at ~368 ppm associated with the non-quaternised nitrogen [52], both present in the original and degraded membrane (Fig. S4, Supplementary information). If DABCO was bis-quaternised then only a single peak at ~330 ppm should be seen, if DABCO is mono-quaternised then two peaks showed be observed at ~330 and ~368 ppm, respectively. The intensities of the signals are not directly proportional to the number of equivalent 15N atoms (unlike 1H NMR) due to the low sensitivity of 15N-CP-NMR test. Therefore, no accurate quantification of mono to bis substituted DABCO can be made. It can however be said that there is a mixture of both mono and bis-substituted DABCO with mono-quaternised DABCO majority. Furthermore, in all the 15N CP-MAS NMR spectra, no other additional resonance peaks were observed suggesting that no other nitrogen-containing by-products have formed on the membrane at concentration high enough to be
detected by $^{15}$N CP-MAS NMR.

3.4.2. $^{13}$C CP-MAS and $^1$H NMR analysis

Fig. 4a shows the $^{13}$C CP-MAS NMR spectra of the original and aged T-AEM. The aromatic carbons give the resonances between 125 and 150 ppm. The signals between 180 and 210 ppm are spinning sidebands associated with the benzyl group. The CH−CH$_2$ groups resonate at 40−50 ppm, N(CH$_3$)$_3$ at 53 ppm and LDPE aliphatic carbons around 25−35 ppm. The 69 ppm resonance is assigned to the −CH$_2$N [53–55]. Comparison of the spectra of the initial and aged membranes revealed a decrease in the intensity of the benzyl group and the TMA head group which indicates decrease in the amount of these particular groups in the membrane structure.

The $^1$H NMR spectra of the degradation solution of T-AEM (Fig. 4b) confirms the removal of aromatic benzene ring (6.25−7.25 ppm region) [46] and TMA (2.9 ppm) [56] from the base polymer chain. The calculated molar ratio of benzene to TMA in the degradation solution from $^1$H NMR is 1:1 after 1 and 2 months of degradation as shown later in Table 3. In addition to this, the presence of the 4.25 ppm peak (9) also suggests that the majority of TMA seen in the solution was lost as VBMTA (detached from the polymer backbone as a whole) [57].

Aside from the expected functional groups and chemical components (i.e. benzene and TMA) seen and reported for VBMTA earlier, the $^1$H NMR spectra of the degradation solution of T-AEM revealed new peaks at 1.85 ppm (singlet), 8.4 ppm (singlet) and clusters of peaks in the 3.0−3.8 ppm region (Fig. 4b). The observed new peaks were detected after 1 and 2 months degradation indicating the presence of identical degradation products. The down-field resonance at 8.4 ppm (#) can be attributed to the formation of benzylic hydroperoxy proton (O−O−H) with the possible corresponding O−H signal at 1.85 ppm (׳) [48], or other aromatic compounds that contains O, which conforms with the 194 ppm peroxide peak in the previously reported $^1$O solution-NMR spectra [12]. The presence of benzylic peroxide (and possibly TMA N-oxide) suggest a peroxide radical formation and attack on the vulnerable tertiary carbon causing the release of the whole VBMTA group as we have previously proposed [12] (Fig. 1, reactions E, F and G).

The benzylic peroxide can undergo decomposition releasing OH radicals which in turn cause further radical attacks (propagation). The peaks between 3.0 and 3.25 ppm can be assigned to imidazoles or the 3.2 ppm (♦) resonance can be associated with TMA N-oxide [47] as discussed previously. While the additional peaks between 3.5 and 3.8 ppm were not observed previously in the original Poly VBMTA $^1$H NMR spectra and can be due to degradation products, the absence of other $^1$H NMR peaks make their assignment difficult.

Fig. 5a shows the $^{13}$C CP-MAS NMR spectra of the initial and aged D-AEM. Similar to T-AEM, the aliphatic carbon peaks of LDPE at 25−35 ppm and the aromatic carbons between 125 and 150 ppm, are present. There are two strong signals at 46 and 53 ppm associated with the carbons attached to the un-quaternised and quaternised nitrogen, respectively [58]. The marked decrease in the intensity of DABCO loss from initial, to month 1 and to month 2 degradation, compared to that of aromatic loss agrees with the observed loss of benzene and DABCO in the $^1$H NMR spectra of the degradation solution shown in Table 3.

The $^1$H NMR spectra of the degradation solution of D-AEM (Fig. 5b) reveals removal of both the benzene (6.25−7.25 ppm region) and DABCO head group (at 2.7 ppm for protons neighbouring the non-quaternised nitrogen) [59]. Both spectra of degradation samples showed the same set of resonances, indicating similar degradation products were produced and increased in concentration, after the longer degradation test as evidenced by the increased intensity of resonances from month 1−2. The mono-quaternised DABCO is suggested to offer an AEM with improved stability as the non-quaternised nitrogen balances the positive charge of the other nitrogen [37] making it less susceptible to nucleophilic substitution through OH− ion attack [32]. However, due to the presence of 2 Nitrogen atoms in DABCO, there is the tendency for DABCO to form crosslinks with the two Nitrogen atoms (bis-quaternised) [19] that converts into a less stable piperazine structure [28,38] as suggested by the presence of 2.5 ppm peak (♦) in the degradation products (Fig. S5, Supplementary information) thereby further contributed to the additional loss of head group and could explain the higher degradation rate observed.

The calculated ratio of benzene to DABCO loss in the solution is 1.08 after both 1 and 2 months of degradation (Table 3). As discussed previously, the removal of the VB−DABCO group is evident from the presence of 4.25 ppm peak (9, Fig. 5b) via attack of benzylic peroxide radicals associated with the peaks at 8.34 (♦) and 1.81 ppm (♦) [48]. If the diamine DABCO was only mono-quaternised then a ratio of benzene to DABCO of 1:1 is expected in the solution for VB-DABCO, similar to the earlier observation seen for the other studied amines. If DABCO was bis-quaternised a ratio of 1:0.5 is expected. The lower ratio seen of 1:0.8 instead of the theoretical 1:1 ratio is explained by the presence of amounts of bis-quaternised DABCO in addition to the majority of mono-quaternised DABCO as concluded earlier in $^{13}$N-CP-NMR section. Furthermore, there are new peaks detected in both spectra aside from the expected VBC and DABCO resonances, namely, 3.38 and 3.65 ppm indicating the presence of other degradation products similarly observed in TMA-based AEM degradation.

Fig. 6 shows the $^{13}$C CP-MAS NMR spectra of the original and aged A-AEM and the $^1$H NMR spectra of its degradation solution. ABCO has similar structure to that of DABCO but with only mono-quaternised nitrogen present, thus the only difference in the $^{13}$C CP-MAS NMR spectra is the additional intense CH$_2$−CH$_2$ peaks at 25 ppm (Fig. 6a). Being only mono-quaternised, A-AEM is expected to offer better stability than D-AEM which agrees well with the slower degradation rate of A-AEM in terms of % IEC loss (Fig. 3) and % ionic conductivity loss (Table 2) than D-AEM.

Fig. 6b shows the $^1$H NMR spectra of the degradation solution of A-AEM. Similar to the $^1$H NMR spectra of the degradation solutions of T-AEM and D-AEM, there is an observed loss of both the benzene and the ABCO head group from the membrane in both 1 and 2 months degradation. The two spectra are identical, indicating similar species are present after 1 and 2 months degradation. The spectra after 2 months degradation showed increased intensity of peaks, indicating more loss of both benzene and ABCO. Upon integration of the peaks from the spectra, the ratio of benzene to ABCO loss was found to be approximately 1:1 for both 1 and 2 months degradation test (Table 3). The similar ratio of benzene to ABCO loss is therefore can be due to their removal as a whole which is also evidenced by the 4.0 ppm peak shown in the spectra (9, Fig. 6b). Aside from the expected spectra of benzene and ABCO, there is evidence of the presence of benzylic peroxide radicals that are associated with the peaks at 8.34 (♦) and 1.81 ppm (♦). There is also a resonance at 2.1 ppm and unsymmetrical splitting pattern in the 3.4−3.8 ppm which could not be assigned and were detected in the same region regardless of the head group investigated as observed in previous spectra (Figs. 4a and 5a).

The $^{13}$C CP-MAS NMR spectra of the original and aged N-AEM and the $^1$H NMR spectra of its degradation solution are shown in Fig. 7. Similar to previous spectra, the aromatic benzene exhibited a down-field resonance at 7.25 ppm region) [46] and TMA (2.9 ppm) [56] from the base polymer backbone. However, due to the presence of 4 Nitrogen atoms making it less susceptible to nucleophilic substitution through OH− ion attack [32]. The lower ratio seen of 1:0.8 instead of the theoretical 1:1 ratio is explained by the presence of amounts of bis-quaternised DABCO in addition to the majority of mono-quaternised DABCO as concluded earlier in $^{13}$N-CP-NMR section. Furthermore, there are new peaks detected in both spectra aside from the expected VBC and DABCO resonances, namely, 3.38 and 3.65 ppm indicating the presence of other degradation products similarly observed in TMA-based AEM degradation.
**Fig. 4.** The (a) $^{13}$C CP-MAS NMR spectra of the original and aged T-AEM and (b) $^1$H NMR spectra of its degradation solution.
The $^1$H NMR spectra of the degradation solution of the N-AEM is shown in Fig. 7b. Similar to those observed in previous spectra, the resonances after 1 and 2 months degradation are identical suggesting the presence of similar degradation products and there is an observed increase in peak intensity after the degradation test is prolonged to 2 months. The amount of benzene and NMP detected from the $^1$H NMR spectra of the degradation solution was relatively small in comparison to the other studied head groups, hence the ratio of benzene to NMP loss was not computed (Table 3). This could be due to the low solubility of VB–NMP and requires further investigation. The observed decrease in IEC (Fig. 3) and ionic conductivity (Table 2) for N-AEM can still be explained by the radical attack on the tertiary carbon from the observed benzyl peroxide groups peak at 8.4 and 1.81 ppm.

All the AEMs investigated exhibited loss of benzene and head group as a whole, evidenced by the presence of peak associated with the benzylic carbon attached to the head group (9). The similarity between the degradation products detected from the studied head groups and similarities in the %IEC loss confirms that the degradation reaction is not chiefly influenced by the head group. Instead, it seems to be caused by radicals detected from benzylic peroxide groups peak at 8.4 ppm as well as the strong dependence reported previously on the surrounding oxygen concentration.

### 3.5. Degradation test under nitrogen and oxygen atmospheres

In order to investigate the effect of oxygen gas feed (oxidation) on the degradation of the membrane, OH$^-$ exchanged T-AEM was subjected to 2 months degradation test with continuous high-purity oxygen gas feed under D$_2$O reflux. A similar membrane was subjected to the same degradation test but with nitrogen gas feed for comparison. Immediately after the degradation test, both membranes were immersed in 1.0 M NaCl solution (without prior OH$^-$ ion exchange) for IEC measurement.

Table 4 shows a decrease in IEC of the membranes after the degradation test wherein from an initial 2.78 mmol g$^{-1}$, the IEC dropped to 2.0 and 2.53 mmol g$^{-1}$ with oxygen and nitrogen gas feed, respectively. The degradation under nitrogen environment (absence of oxygen) of the T-AEM could initially be explained by a similar report [16] wherein OH$^-$ ions attack the quaternary carbon of polysulfone-based AEM via hydrolysis or in this case, the ternary carbon with respect to the trimethylammonium hydroxide group causing the release of VBtMA as a whole (Fig. 1, reaction D). However, the presence of benzylic peroxide groups peak at 8.4 ppm even under nitrogen atmosphere and the similarity of the $^1$H NMR spectra of the degradation products under oxygen and nitrogen suggest that the attack is caused by peroxide radicals which can form from the re-combination of two OH$^•$ radicals rather than OH$^-$ ions as suggested by Arges and Ramani [16] since no benzylic alcohol peaks (2.3 and 4.6 ppm) were detected.

Fig. S8 shows $^{13}$C CP-MAS NMR spectra of the aged T-AEM under oxygen gas feed. The ratio of benzene to head group loss is very close to 1:1 for the degraded membranes both under nitrogen and oxygen gas feed, which is consistent with TMA-functionalised AEM as previously discussed. The $^1$H NMR spectra of the degradation products of T-AEM under oxygen and nitrogen atmospheres after stability tests are shown in Fig. 8b and were compared to that of T-AEM degraded under 3 wt% peroxide for 48 h (Fig. S6, Supplementary Information). The $^1$H NMR spectra revealed similar resonances under both oxygen and nitrogen gas feeds as well as peroxide indicating presence of the same soluble degradation products as discussed earlier.

The higher % IEC loss over 2 months of the T-AEM in D$_2$O under oxygen saturated atmosphere (30%) indicates over three-fold increase in degradation rate compared to only 9% IEC loss of the membrane in D$_2$O with nitrogen gas feed (Table 4) which suggests that the accelerated AEM degradation is caused by higher peroxide concentration produced from oxygen reduction to superoxide via ylide (Fig. 1, as suggested by Parrondo et al.) and consequently faster radical attacks through reaction E (Fig. 1). This was also seen from the rapid observation of the same degradation products within 48 h of peroxide immersion (Fig. S6, Supplementary Information). These observed benzylic peroxide in the degradation product solution (and possibly TMA-N-oxide) as well as evidence of peroxo radicals from $^{17}$O NMR spectra we previously reported [12], could be the result of peroxide (and possibly OH$^•$ radicals) attack on the benzylic ternary carbon causing the release of VBtMA which leads to the observed decrease in IEC [12] (Fig. 1, reactions E, F & G). The formed benzylic peroxide could decompose (Fig. 1, reaction F) to produce hydroxyl radicals propagating further radical attacks that further reduce the IEC due to VBtMA loss.

Therefore, this study suggests that in deionised water at 60 °C, an environment analogous to fuel cells and electrolyser, the degradation of AEM is chiefly driven by peroxide radical attack which occurs predominantly and was independent of the head groups studied, while degradation caused by head group loss from SN2 attack was not detected. This study hereby reports the importance of radical oxidation in the degradation process and recommends that future research on AEM degradation should be shifted from head group degradation in high alkaline/high temperature condition towards deionised water or close to neutral pH solutions under oxygen-saturated and peroxide environments. The stability of AEM towards radical attacks can be improved by: (1) removing the vulnerable proton attached to the ternary benzyl carbon by using for example, alpha-methylstyrene derivatives or eliminating the ternary/quaternary benzylic carbon all together such as the use of chloromethylated polyphenylene, (2) use of radical scavengers in par with the use of cerium oxide in Nafion, and (3) substituting the vulnerable proton in the alpha position with respect to the head group in order to suppress ylide formation and consequently the rate of oxygen reduction to superoxide.

### 4. Conclusion

The assessment of the chemical stability of LDPE-based anion exchange membrane (AEM) functionalised with different amine head groups namely, TMA, DABCO, ABCO and NMP, was performed. In this research, grafted or synthesized AEMs were utilised and subjected to the degradation tests in solutions close to neutral pH at 60 °C. All the quaternised membranes, regardless of the tethered amine functional group, exhibited similar degradation loss of ca. 5%
Fig. 5. The (a) $^{13}$C CP-MAS NMR spectra of the original and aged D-AEM and (b) $^1$H NMR spectra of its degradation solution.
Fig. 6. The (a) $^{13}$C CP-MAS NMR spectra of the original and aged A-AEM and (b) $^1$H NMR spectra of its degradation solution.
Fig. 7. The (a) $^{13}$C CP-MAS NMR spectra of the original and aged N-AEM and (b) $^1$H NMR spectra of its degradation solution.
IEC per month. The slightly higher degradation rate in DABCO could be due to the difficulty in obtaining 100% mono-quaternisation and the formation of a less stable piperazine structure from bi-substituted DABCO.

The stability assessment of Poly VBTMA-OH (without the LDPE base film) revealed polymer degradation through the formation of benzylic peroxy. The benzylic peroxy was also observed in the degradation solution of T-AEM along with vinylbenzyl trimethylammonium group (VBTMA) with VB to TMA ratio of 1:1. It is suggested that peroxy radical attacks the ternary benzylic carbon resulting in the formation of benzylic peroxy and the subsequent observed release of VBTMA as whole from the membrane. The formed benzylic peroxy could decompose to produce hydroxyl.

<table>
<thead>
<tr>
<th>Gas Feed</th>
<th>IEC (mmol g⁻¹)</th>
<th>Initial</th>
<th>After 2 months</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>2.78 ± 0.2</td>
<td>2.0 ± 0.1</td>
<td>2.53 ± 0.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4
The IEC of TMA-functionalised membranes immersed in D₂O supplied with different gas feeds at 60 ºC.

Fig. 8. The (a) ¹³C CP-MAS NMR spectra of the original and aged T-AEM under oxygen gas feed after 2 months and (b) ¹H NMR spectra of its degradation solution.
radicals propagating further radical attacks to reduce further the IEC from VBTMA loss. Such loss of vinylbenzyl and head group as a whole was similarly observed in other amine functionalities investigated (i.e. DABCO, ABCO and NMP) suggesting that the predominant degradation mechanism of the AEM in deionised water environment is through free radical attack.

The stability test performed on T-AEM under oxygen and nitrogen gas feed revealed over three-fold increase in the degradation rate under saturated oxygen environment compared to nitrogen. The analysis also confirmed that the degradation products under oxygen, nitrogen and 3 wt% H2O2 were the same VBTMA and benzyl peroxide. The accelerated AEM degradation seen under oxygen is caused by higher peroxide concentration produced from oxygen reduction to superoxide via ylide and consequently faster radical attacks on the tertiary carbon and loss of VBTMA.

It is therefore recommended that future tests on AEM stability should be conducted in deionised water in oxidative environment (oxygen/peroxide) with main strategies to improve the AEM stability, namely, addition of radical scavengers and the substitution or removal of vulnerable protons of benzyl carbons (in alpha position to head group and tertiary carbon).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2017.07.074.

References


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