



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

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

Richard Espiritu ^{a, b}, Bernard T. Golding ^c, Keith Scott ^a, Mohamed Mamlouk ^{a, *}

^a School of Chemical Engineering and Advanced Materials, Merz Court, Newcastle University, Newcastle Upon Tyne NE1 7RU, United Kingdom

^b Department of Mining, Metallurgical and Materials Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines

^c School of Chemistry, Bedson Building, Newcastle University, Newcastle Upon Tyne NE1 7RU, United Kingdom

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 Benzylic 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.

ARTICLE INFO

Article history:

Received 10 May 2017

Received in revised form

17 July 2017

Accepted 22 July 2017

Available online xxx

Keywords:

Anion exchange membrane

Membrane degradation

Radical attack

Peroxide radicals

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. Benzylic 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 benzylic 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.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

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, $-N^+(CH_3)_3$, 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)

* Corresponding author.

E-mail address: mohamed.mamlouk@ncl.ac.uk (M. Mamlouk).

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 ^{60}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 ($\text{S}_{\text{N}}2$) 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

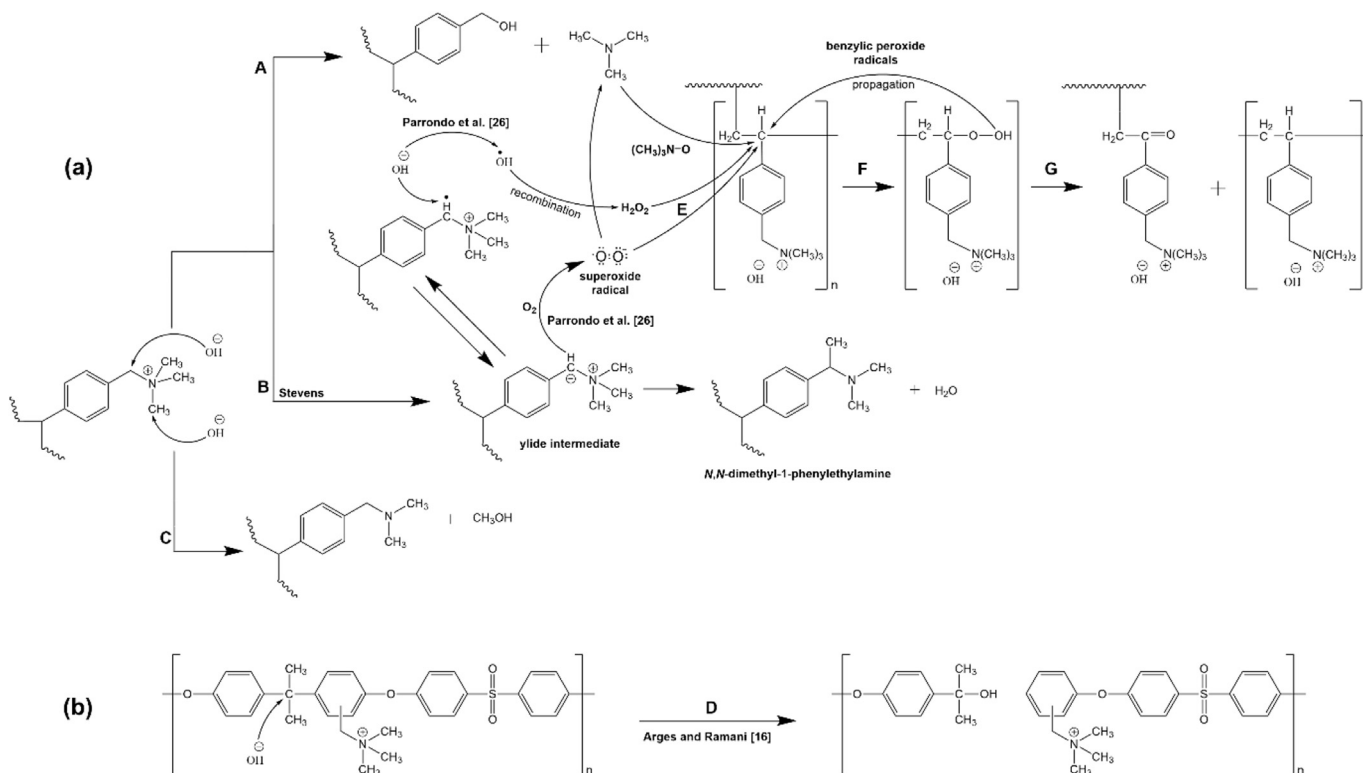


Fig. 1. The possible degradation mechanisms of TMA-functionalised AEM immersed in close to neutral pH water medium.

Download English Version:

<https://daneshyari.com/en/article/7726163>

Download Persian Version:

<https://daneshyari.com/article/7726163>

[Daneshyari.com](https://daneshyari.com)