



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Alkaline anion exchange membrane degradation as a function of humidity measured using the quartz crystal microbalance

V.J. Bharath^a, R. Jervis^a, J. Millichamp^a, T.P. Neville^{a,b}, T. Mason^a,
B. Tjaden^a, P.R. Shearing^a, R.J.C. Brown^c, G. Manos^a, D.J.L. Brett^{a,*}

^a Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, Torrington Place, London, WC1E 7JE, UK

^b Centre for Nature Inspired Engineering, University College London, Torrington Place, London, WC1E 7JE, UK

^c Environmental Division, National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK

ARTICLE INFO

Article history:

Received 15 September 2016

Received in revised form

7 January 2017

Accepted 26 January 2017

Available online xxx

Keywords:

Fuel cells

Hofmann elimination

QCM

In-situ degradation

Thin film

ABSTRACT

The solid polymer electrolyte (SPE) alkaline anion exchange membrane (AAEM) fuel cell exhibits facile oxygen reduction reaction (ORR) kinetics and has the ability to utilise non-precious metal electrocatalysts. However, the AAEM is reported to suffer from increased instability within the alkaline media (degradation) via a number of routes, including nucleophilic elimination when operated at temperatures above 60 °C, somewhat eliminating the kinetic advantage of operating at higher temperatures. Nonetheless, modelling studies have indicated that the membrane hydration could show improved resistance to alkaline instability and subsequent degradation when operated at elevated temperatures. This investigation uses the quartz crystal microbalance (QCM) to examine the thermal stability of a commercial AAEM as a function of humidity. The results show that hydration improves ionomer resistance to degradation, as the ions within the system (namely the OH⁻ nucleophile and cationic headgroups) become less reactive. In-line mass spectrometry data confirms that the ionomer degrades during the elevated temperature excursions used in this study.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Alkaline anion exchange membrane (AAEM) fuel cells have the potential to replace the traditional acidic proton exchange membrane (PEM) fuel cells for low temperature applications. With more facile oxygen reduction reaction (ORR) kinetics than traditional PEM fuel cells, the alkaline medium allows implementation of lower cost, non-precious metal

electrocatalysts [1,2], compared to the more resilient precious metals (e.g. Pt) required in acidic media [3–5].

AAEMs contain positively charged (cationic) headgroups that have been suggested to dissociate more weakly than the sulphonic acid groups found in Nafion; coupled with the inherently lower electrochemical mobility of OH⁻ ions compared to protons, means that AAEMs typically have ionic conductivities approximately a quarter of those for PEMs [6]. Many AAEMs include more cationic groups along the polymer

* Corresponding author.

E-mail address: d.brett@ucl.ac.uk (D.J.L. Brett).

<http://dx.doi.org/10.1016/j.ijhydene.2017.01.158>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

backbone to improve ion exchange capacity (IEC) and thus the ionic conductivity; however, the increased fixed charge concentration can lead to deterioration of the AAEMs' mechanical properties [7–9].

The most common cationic group in AAEMs is quaternary ammonium, $[R_4N^+]$ [10], which is often used as it has higher stability within alkaline media compared to phosphonium or sulphonium groups [11]. However, it has been well documented that AAEMs can also suffer from chemical instability in alkaline environments [11–13], with chemical degradation stemming largely from nucleophilic attack by hydroxide ions on the cationic fixed charged sites; a process accelerated by operation at elevated temperatures.

For example, the quaternary ammonium group is susceptible to cleavage in the presence of hydroxide ions, leading to the E2 elimination reaction (the Hofmann elimination) shown in Fig. 1.

During E2 elimination, hydroxyl ions attack β -hydrogens, leading to the formation of an alkene, an amine and a water molecule. Most work to date has suggested that Hofmann elimination is negligible below 60 °C, but much faster at higher temperatures, resulting in significant membrane degradation [14–16]. This is an obvious limitation for current alkaline membranes as the kinetic benefit of operating at higher temperatures is unobtainable.

The other key mode of ionomer degradation is direct nucleophilic displacement at the cation site; this can occur through two possible reaction pathways for quaternary ammonium charge sites, as shown below in Figs. 2 and 3. In these cases, the hydroxide ions attack at either the methyl group, forming methanol, or at the C–C bond between the alpha and beta carbons to cleave the cation site (S_N2 reaction) [12]. These mechanisms are further discussed elsewhere [17,18]. Other degradation routes presented within the literature include deprotonation of the $[R_4N^+]$ headgroups to produce nitrogen ylide intermediaries [19,20] and specific studies on the degradation of the polymer backbone put forward by Arges et al. [21,22], Chen and Hickner [23] and Mohanty et al. [24]. The consequence of these degradation mechanisms is a loss in the number of ion-exchange groups and a subsequent decrease in OH^- conductivity, with consequences for fuel cell performance.

As with most SPEs, AAEM hydroxyl conduction improves with hydration as the ionomer channels solvate and subsequently swell [25,26]. There is a balance between improved membrane conductivity through hydration and the deleterious effects on performance seen in fuel cells caused by the formation of liquid water blocking reactant channels and gas diffusion layer pores. Recent published work [17,20,27] on formulated headgroups has added a new dynamic to this balance, indicating a correlation between ion solvation (and hence ionomer hydration) and ionomer degradation by nucleophilic attack.

The model presented by Chempath et al. [17] implements an untethered cationic head group, $[N(CH_3)_4]^+$, and shows that the degradation mechanisms appear more aggressive in a system with low water content. Work by Macomber et al. [20] reports a similar conclusion, where the thermal degradation of tetramethyl ammonium hydroxide is retarded by hydration. In both cases, the investigations explain that a dehydrated membrane exhibits more aggressive degradation, as both the hydroxyl ions and cations remain un-solvated and thus more reactive [17,20].

This investigation experimentally explores how specific hydration levels affect the alkaline instability and hence degradation mechanisms of a commercially available AAEM ionomer (Tokuyama, Japan) with tethered quaternary ammonium headgroups, using a quartz crystal microbalance (QCM). The QCM has proved to be a powerful *in-situ* mass monitoring technique for the study of polymer interactions at a solid interface, offering nanogram mass resolution [28–31]. *In-line* mass spectrometry is used alongside the QCM in this study to further elucidate the importance (and limitations) of cation and hydroxide ion solvation for the stability of an AAEM ionomer.

Experimental

Quartz crystal microbalance

The QCM is a bulk acoustic wave (BAW) resonator that is often used as an *in-situ* mass monitoring device with nanogram resolution [32,33]. With an applied voltage, the QCM oscillates at a specific frequency as a function of its dimensions and the amount of mass deposited on its electrodes. If the system under consideration undergoes a mass deposition or loss, the shift in frequency can be accurately measured and the analogous contacting mass change can be determined using the Sauerbrey equation:

$$\Delta f = \frac{-2f_0^2 \Delta m}{A\sqrt{\mu_q \rho_q}} \quad (1)$$

where Δf is the measured frequency shift, f_0 is the microbalance's fundamental frequency, A is the piezoelectric area, μ_q and ρ_q are the shear modulus and density of quartz respectively, and Δm is the corresponding mass change.

Aspects of the use of the Sauerbrey equation are well established and the reader is directed to [32–34] for further information. Studies often only consider the frequency shift of the QCM, limiting the extent of information accessible using the technique. Additional insight can be derived about viscoelastic changes in thin films by using crystal admittance spectroscopy (CAS). In the conventional (active) mode of operation, the QCM oscillates at its natural frequency and the

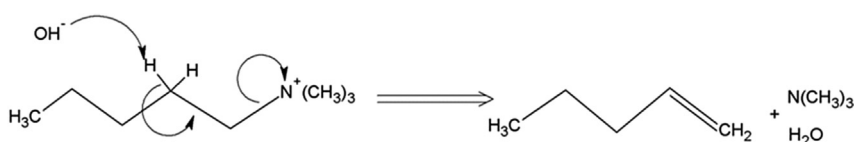


Fig. 1 – Hofmann (E2) elimination reaction mechanism.

Download English Version:

<https://daneshyari.com/en/article/5146831>

Download Persian Version:

<https://daneshyari.com/article/5146831>

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