



Contents lists available at ScienceDirect

Journal of Power Sources

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

A practical method for measuring the ion exchange capacity decrease of hydroxide exchange membranes during intrinsic degradation

Klaus-Dieter Kreuer^{a, *}, Patric Jannasch^b

^a Max-Planck-Institute for Solid State Research, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

^b Department of Chemistry, Polymer & Materials Chemistry, Lund University, SE-22 100 Lund, Sweden

HIGHLIGHTS

- A new method for quantifying IEC decrease of hydroxide exchange membranes.
- Degradation rate of HEMs depends on temperature, hydration number and total water content.
- Method could help to resolve debates about relative durability of various HEMs.

ARTICLE INFO

Article history:

Received 7 June 2017

Received in revised form

25 July 2017

Accepted 26 July 2017

Available online xxx

Keywords:

Hydroxide exchange membrane

AEM

Degradation

TGA

Fuel cell

ABSTRACT

In this work we present a practical thermogravimetric method for quantifying the IEC (ion exchange capacity) decrease of hydroxide exchange membranes (HEMs) during intrinsic degradation mainly occurring through nucleophilic attack of the anion exchanging group by hydroxide ions. The method involves measuring weight changes under controlled temperature and relative humidity. These conditions are close to these in a fuel cell, i.e. the measured degradation rate includes all effects originating from the polymeric structure, the consumption of hydroxide ions and the release of water. In particular, this approach involves no added solvents or base, thereby avoiding inaccuracies that may arise in other methods due to the presence of solvents (other than water) or co-ions (such as Na⁺ or K⁺). We demonstrate the method by characterizing the decomposition of membranes consisting of poly(2,6-dimethyl-1,4-phenylene oxide) functionalized with trimethyl-pentyl-ammonium side chains. The decomposition rate is found to depend on temperature, relative humidity *RH* (controlling the hydration number λ) and the total water content (controlled by the actual IEC and *RH*).

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The potential application of anion exchange membranes (AEMs) in their hydroxide (OH⁻) form (sometimes denoted by HEM) as separators in low temperature fuel cells is a matter of ongoing research. In contrast to acidic proton exchange membranes (PEM) that require the use of noble metal electro-catalysts to form a fuel cell electrode, the basic conditions under which HEMs operate allow less costly non-noble metal catalysts to be used [1]. OH⁻ conductivity values approaching the proton conductivity of PEMs (such as Nafion[®]) are common [2] for high levels of hydration, and bicarbonate (HCO₃⁻) formation from the reaction of OH⁻ with CO₂ present in air (used as oxidant in fuel cells) may be reduced by

using CO₂ absorbers and adequate electrochemical management (self-purging [3]).

The major problem stems from the mandatory presence of highly nucleophilic hydroxide ions as conducting ion. Quaternized ammonium (QA) groups are commonly used as positive countercharge within the polymeric structure; however, as typical leaving groups, QAs are well-known to react with OH⁻ through different energetically similar pathways [4] including nucleophilic substitution, β -elimination, and rearrangement reactions such as Stevens rearrangement in the absence of β -protons. As a consequence, HEMs inherently decompose, thereby losing ion exchange capacity (IEC) and ionic conductivity [5–10].

The degradation rate depends not only on the kind of QA but also on its environment within the polymeric structure. To deal with this complexity, we studied the degradation rates of a series of QA-salts in concentrated aqueous solutions of NaOH to identify

* Corresponding author.

E-mail address: kreuer@fkf.mpg.de (K.-D. Kreuer).

suitable candidates for ionic groups in HEMs [11]. In this small molecule study, we also investigated the effects of different types of attachment, e.g. benzylic attachment is found to be extremely critical with respect to stability which is consistent with the results of another small-molecule study showing higher stability for alkyl-substituted compared to benzylic-substituted cations [12]. In the end, however, it is critical to test the durability of membranes under conditions similar to those in an operating fuel cell.

These conditions differ from the conditions provided by aqueous solutions of NaOH (KOH) in various ways: i) within a HEM, OH⁻ counter ions are consumed in degradation reactions while the concentration (activity) of OH⁻ in excess NaOH solution is virtually unaffected by membrane degradation. ii) For high molarity, significant co-ion uptake (which corresponds to an uptake of excess NaOH) may affect the degradation rate through the presence of Na⁺ in the membrane. iii) The molar ratio [H₂O]/[OH⁻] in aqueous solutions of NaOH may be higher than for the low hydration conditions which may occur in running fuel cells. Especially the cathode side is expected to dry out as a result of electroosmotic water drag [13,14] from the cathode to the anode side at high ionic (OH⁻) current density.

Ion solvation (type of solvent and degree of solvation) actually affects degradation rates, and especially heavy hydration is known to strongly reduce the reactivity of the highly nucleophilic OH⁻ ion [11].

In a recent small-molecule NMR study, Dekel et al. [15] have quantified this effect in *ex situ* tests for hydration levels $\lambda = 0$ (dry) – 4 [H₂O]/[OH⁻] by adding defined amounts of water to dry solutions of QA and KOH in DMSO and following the degradation by ¹H NMR spectroscopy.

Here we present a gravimetric method which allows one to follow the IEC decay of HEMs at controlled temperature and hydration levels. The approach captures all effects that originate from the polymeric structure of the membrane, while avoiding possible inaccuracies arising from the unrealistic presence of solvents (other than water), co-ions (such as K⁺), or an excess of counter ions (OH⁻). Moreover, the method is straight-forward and requires only a thermogravimetric analyzer [16].

2. Basic idea

As generally observed for PEMs, also the hydration number ($\lambda = [\text{H}_2\text{O}]/[\text{ionic group}]$) for HEMs is approximately proportional to the IEC for a given temperature T and relative humidity RH ($RH < 65\%$ where hydration is exothermic). This approximately holds for different types of QA [data not yet published] and is especially true when a given type of ionomer with different concentration of a given type of QA is concerned. Therefore, also the difference of hydration numbers for two different values of RH ($\Delta\lambda$) is a good measure for the actual IEC. In the proposed method, degradation occurs under controlled T and RH conditions while continuously recording the sample weight. This decreases with time for two reasons:

- i) volatile reaction products may be set free,
- ii) hydration water is released because of decreasing IEC (degradation of ionic QA groups).

The first contribution depends on the kind of reaction products (alcohols, amines) and the polymeric host, degree of hydration and temperature determining the rate at which the degradation products are released. The second contribution, however, is mainly controlled by the decreasing IEC. Both contributions can easily be separated by intermittently measuring the hydration number for a higher RH . The increase of λ ($\Delta\lambda$) then is a measure of the actual IEC

at that time. In this way, the evolution of IEC during degradation is recorded as a function of time. From this, information about reaction order and reaction rate may directly be deduced.

Conceptually, the method works provided hydroxide ions merely react with QA functional groups (which is mostly the case). If hydroxide ions are also consumed in reactions with the polymer backbone, e.g. through nucleophilic attack of aryl-sulfones [17] or aryl-ethers [18], a decrease of $\Delta\lambda$ is expected as well because the reaction products (e.g. phenylates) are less hygroscopic than hydroxide ions. In order to exclude such reaction pathways, the IEC should be double checked at the end of the experiment by an independent method (see below). An IEC value higher than the one obtained from TGA would then be indicative for backbone degradation.

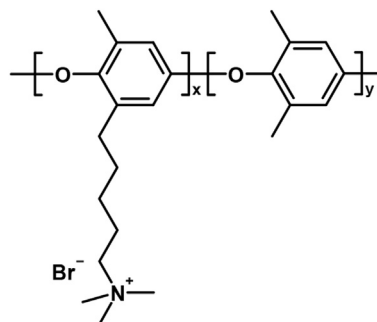
3. Experimental

All experiments were carried out with a HEM consisting of a poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) backbone functionalized with trimethyl-pentyl-ammonium side chains (Scheme 1).

Since there is no benchmark membrane for AEMs (like in the case of PEMs for which Nafion is generally used for benchmarking) we have selected this homemade membrane because its chemical structure is related to the chemical structures of several AEMs for which reasonable stability in aqueous NaOH solutions have been reported [19–22]. The ionomer has been prepared as described earlier [23] and membranes were formed from NMP solution at $T = 80^\circ\text{C}$.

The IEC of as-prepared membranes was determined in the Br⁻ form by displacing Br⁻ with NO₃⁻ (~100 mg membrane in 40 ml 0.2 M NaNO₃ for three days) and titrating the released Br⁻ with AgNO₃ using a silver-electrode. Membranes in their Br⁻ form were converted into the OH⁻ form by ion exchange in 1 M NaOH (200 mg membrane in 40 ml solution) where the solution was replaced five times every 24 h under CO₂-free conditions (in a homemade glove box [24]). This turned out to be necessary in order to reduce the Br⁻ content to less than 3% of the IEC. The residual Br⁻ content of OH⁻ exchanged membranes was actually determined by displacing Br⁻ with NO₃⁻ after each exchanging step and subsequent Br⁻ titration (see above) using small pieces of the membrane. For the ion exchange procedure, one should keep in mind that ionic association in the NO₃⁻, Br⁻ and especially the I⁻ forms of AEMs leads to a severe stabilization compared the OH⁻ form [2]. The hydroxide exchanged membranes were rinsed with deionized water until neutrality and then kept in pure water not longer than a few days before carrying out the stability experiments.

For this, a thermogravimetric balance with magnetic coupling is used (for details see ref. [13]) membrane samples (100–200 mg) were placed in a quartz crucible within the glove box and then



Scheme 1. PPO grafted with trimethyl-pentyl-ammonium cations.

Download English Version:

<https://daneshyari.com/en/article/7726149>

Download Persian Version:

<https://daneshyari.com/article/7726149>

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