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Practical *ex-Situ* Technique To Measure the Chemical Stability of Anion-Exchange Membranes under Conditions Simulating the Fuel Cell Environment

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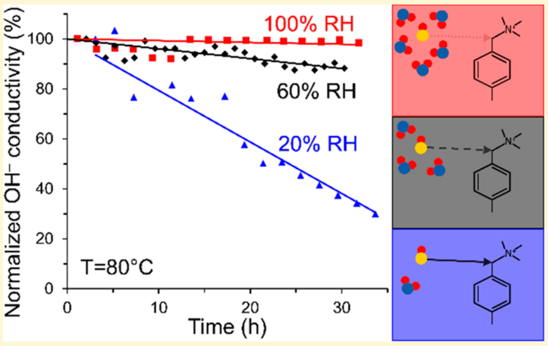
ABSTRACT: Anion-exchange membrane (AEM) degradation during fuel cell operation represents the main challenge that hampers the implementation of AEM fuel cells (AEMFCs). Reported degradation values of AEMs are difficult to reproduce as no standard methods are used. The present use of different techniques based on exposure of membranes to aqueous KOH solutions under different conditions and measuring different outputs during time does not allow for a reliable and meaningful comparison of reported degradation data of different AEMs. In this study, we present a practical and reproducible *ex-situ* technique to measure AEM degradation in conditions that mimic an *operando* fuel cell environment. In this novel technique, we measure the change of the true hydroxide conductivity of the AEM over time, while exposing it to different relative humidity conditions. The technique does not make use of liquid alkaline solution, thus simulating real fuel cell conditions and providing a good baseline for comparative degradation studies.



Anion-exchange membrane fuel cells (AEMFCs) have attracted growing attention during the past few years due to their rapid development and great potential to provide a low-cost and efficient power generation solution.[1−4] However, their commercial development is hampered by the chemical degradation of the anion-exchange membranes (AEMs) during cell operation.[5−7] The hydroxide anions (OH^-), while transported from the cathode to the anode, attack the positively charged functional groups in the polymer membrane (and ionomers in the electrodes), suppressing their anion and water transport capabilities, reducing in turn the effective hydroxide conductivity.[8−13]

To measure the chemical degradation of AEMs, many studies used model compounds that mimic the functional groups of the membranes. While this provides a good quantitative understanding of the chemical degradation of the cationic moieties in alkaline media, it does not necessarily represent the real behavior of the whole AEM.[14−17] Furthermore, AEMs functionalized with alkaline-stable cations are not necessarily alkaline-stable unless also the polymer backbones and its linkers to the cations are also stable.[18]

To measure the degradation of AEMs over time and to determine their stability in alkaline environments, different procedures have been used. All of them involve soaking of AEMs in liquid KOH (or NaOH) electrolytes, at different alkaline electrolyte concentrations, different temperatures, for different extended periods of time, to try to imitate the alkaline environment of the AEMFCs.[19,20,29,30,21−28] The AEMs are then washed with the aim of removing all the KOH electrolyte absorbed in the polymer matrix, after which the loss in conductivity as a function of soaking time is evaluated. Besides the lack of standard conditions that allows comparison between different results, several problems occur during measurement of the degradation of the anion conducting polymer.[31] Liquid KOH electrolyte absorbs differently in different AEMs, rendering a complete removal of the electrolyte from the polymer matrix of the membrane

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uncertain, thus affecting conductivity measurement and therefore degradation data. In addition, while trying to remove the remaining KOH from the AEM by washing with water, or during measurements of conductivity, carbonation (on any air exposure) may occur,[32−37] detrimentally affecting results. Already a short exposure to small traces of CO_2 in the atmosphere strongly impacts the composition of ions in the solid electrolyte.[33,38] Up to now, no single study may assure that all the remaining KOH was fully removed and that no (bi)carbonates were formed during the entire conductivity measurements.

In addition to these issues, all previous degradation studies on AEMs were carried out at high hydration conditions,[39−44] which do not simulate well the harsh conditions of AEMFC operations.[45] Just a few studies were conducted under low hydration conditions.[45−53] Dekel *et al.*[45] first reported that model cationic compounds degrade significantly faster at low hydration conditions. The authors also showed that decreasing the amount of water molecules in the medium decreases the activation energy of the nucleophilic attack of the OH^- with the cationic model molecules,[45] consistent with DFT predictions of Chempath *et al.*[54] In a subsequent study, using a thermogravimetric method, Kreuer *et al.* measured the ion-exchange capacity (IEC) of an AEM under controlled temperature and low relative humidity (RH) conditions.[51] They showed that the reduction of the IEC during time due to the chemical degradation of the membrane is higher as the RH is reduced.[51] The enhancement in the cation degradation exposed to low hydration medium was further confirmed in theoretical studies by Pusara *et al.*, who simulated the interactions between the quaternary ammonium cations and the OH^- solvated by different amount of water molecules.[46] The authors reported that when fewer water molecules are available in the medium, ammonium−hydroxide pairing occurs more frequently and with higher intensity, confirming then the cationic moieties in the AEM.[46]

All the mentioned methods include the use of an alkaline solution to measure the chemical degradation, which does not necessarily represent the real behavior of the entire AEM in the environment of an operating AEMFC, where OH^- ions are *in situ* generated in the cell, without any liquid electrolyte or solution (or excess K^+/Na^+ or OH^- ions). Consequently, the development of a standard, reliable technique is necessary to measure the true degradation of AEMs without the use of liquid KOH electrolyte at any step of the measurement. We present here a practical *ex-situ* technique to measure the degradation of an AEM in conditions that mimic the true environment of an AEMFC in operation.

The technique is based on our recently developed *ex-situ* method to measure the true OH^- conductivity in AEMs without the use of liquid electrolyte.[55] This method offers an opportunity to standardize conductivity measurements by determining the true OH^- conductivity simulating the real environment of an AEMFC during operation. In short, the method takes advantage of the reversibility character of the carbonation process[32,33,38,55,56] and exchange the (bi)carbonate anions by OH^- anions generated *in situ* by an external current. The applied current during the experiment causes the anions to move toward the anode, and the (bi)carbonates are released in the form of carbon dioxide.[55] This method was already adopted by several studies to characterize AEMs (see for instance, Varcoe *et al.* and others[50,52,57−60]), and recently by Holdcroft *et al.*[60] who showed visual effects of the anion-exchange process.

Using this method, we measured the anion conductivity during the decarbonation process of an LDPE-based radiation-grafted AEM as a function of time, until the plateau maximum value is reached (see Figure 1). This value is referred to as the true OH^- conductivity of the membrane.[55] At the plateau, the AEM is in its full OH^- form, and we measure the drop in the value of true hydroxide conductivity as a function of time. A similar test was already carried out by Varcoe *et al.*,[52] to show the stability of the AEM at a relative humidity of 100%; however, as already mentioned, at high hydration levels there is little or no degradation due to the water solvation effect around the OH^- ions.[45] For this study, we use the technique to investigate the impacts of different and harsher environmental conditions on the AEMs and present a method to measure the degradation of AEMs in an environment that mimics an operating AEMFC. In the proposed technique, we measure the drop in the value of true OH^- conductivity as a function of time at different (lower) relative humidity values. The resulting OH^- conductivity changes are then normalized to the initial conductivity values measured at different RH values, as shown in Figure 2.

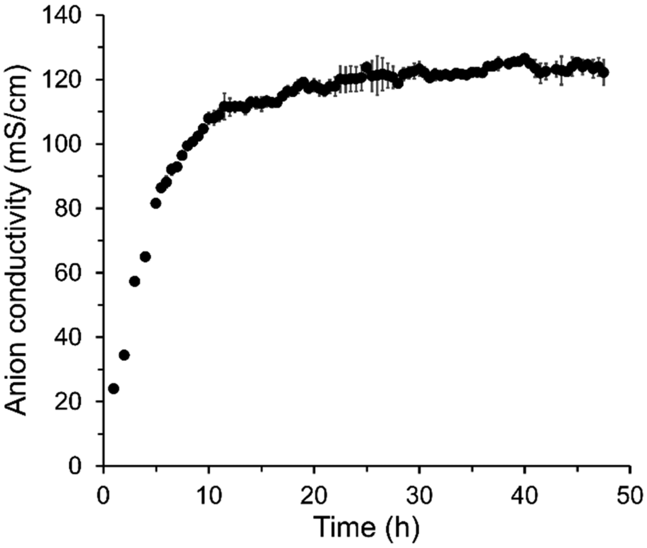

Figure 1. Decarbonation process of an AEM using Ziv and Dekel *ex-situ* method,[55] to measure the true OH^- conductivity of the membrane (55 μm thick low-density polyethylene radiation-grafted AEM functionalized with benzyl trimethylammonium (BTMA-LDPE) AEM[50,52,61]). The average and the standard deviations (shown by bars) of the conductivity are based on measurements of three different samples of the same AEM.

The drop in the normalized true OH^- conductivity over time measured in different relative humidity environments (Figure 2a) shows the relative stability of the AEM under flow of OH^- anions at different hydration levels. As can be seen, as RH decreases, the chemical degradation of the AEM increases. While at 100% RH the AEM is stable, showing a decay of normalized OH^- conductivity of only 0.07%/h, at 60% and 20% RH the conductivity decay is 0.40%/h and 2.06%/h, respectively. To confirm that this decay in conductivity is a result of polymer degradation, the final IEC values of the membranes after the test time were measured and shown in Figure 2b. It is clearly noticeable that the IEC decreases by

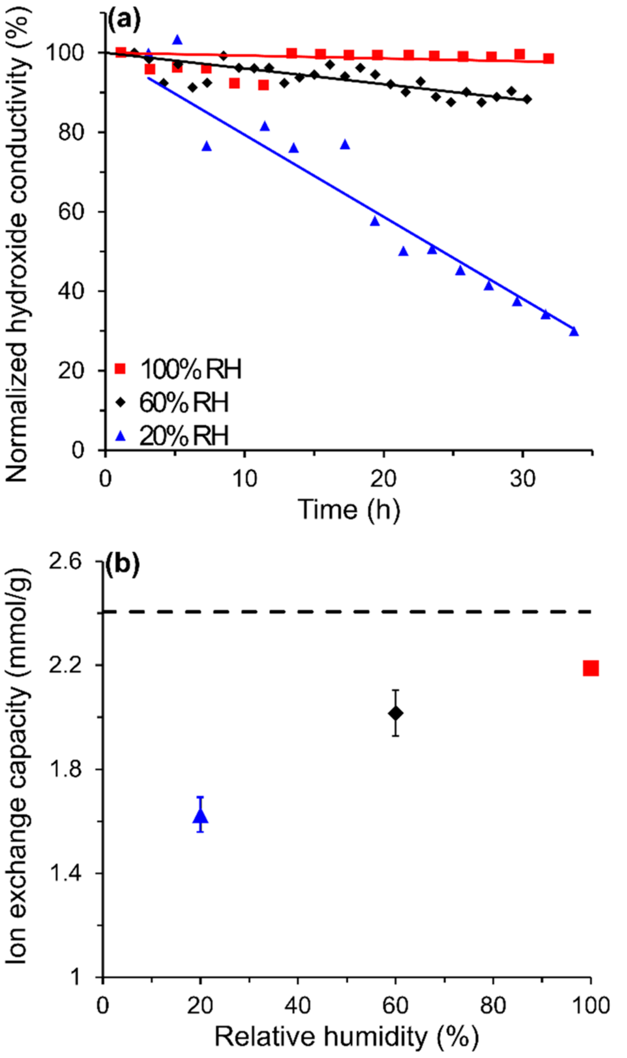

Figure 2. (a) Normalized true OH$^-$ conductivity of the BTMA-LDPE AEM as a function of test time (80 °C, 100 μA, and a nitrogen flow of 500 sccm/min) at different RH levels. (b) Final IEC of the AEMs measured after the degradation experiments shown in (a), as a function of the RH applied during the tests. The average and the standard error of the IEC are based on three measurements of the different samples of AEM. The dashed line marks the initial IEC of a fresh (non-degraded) membrane.

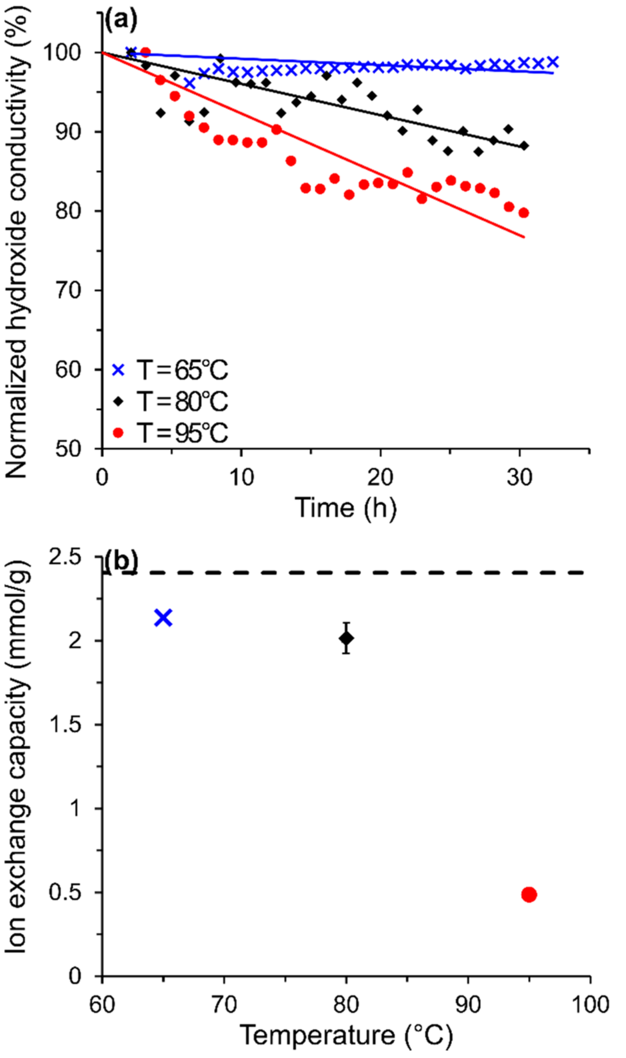

Figure 3. (a) Normalized true OH$^-$ conductivity of the BTMA-LDPE AEM as a function of time (60% RH, 100 μA, and a nitrogen flow of 500 sccm/min) at different temperatures. (b) Final IEC of the AEMs measured after the degradation experiments shown in (a), as a function of the temperature applied during the tests. The average and the standard error of the IEC are based on three measurements of the different samples of AEM. The dashed line marks the initial IEC of a fresh (non-degraded) membrane.

reducing the RH in the gas inlet of the cell. Consequentially, the decrease of the ionic conductivity is caused by a reduced number of functional groups in the AEM. Correlating the rate of decay of the normalized OH$^-$ conductivity (from slope of Figure 2a) at different RH values provides a practical and reliable way to characterize the chemical stability of AEMs. For instance, for the membrane measured in this study, BTMA-functionalized LDPE-based radiation-grafted AEMs, the calculated OH$^-$ stability relationship is 0.025%/h/RH. Using this parameter, which we call the "AEM degradation parameter", will help to standardize degradation results, allowing us to compare degradation properties of different AEMs to be used for AEMFCs.

The effect of temperature on the chemical stability of the AEM using this new technique is also studied. Figure 3 shows the change in normalized true OH$^-$ conductivity at 65, 80, and 95 °C measured at 60% RH, a representative humidity level at which the decrease in conductivity is largely noticeable. As expected, the degradation rate of the AEM increases with temperature.[47,62] While at 65 °C there is no evident degradation, at 80 and 95 °C the conductivity decay increases to 0.4%/h and to 0.7%/h, respectively. The IEC loss of the AEMs tested at different temperatures is shown in Figure 3b. The IEC dropped from 2.40 to 2.14 mmol/g at 65 °C, while it dropped to 2.02 and 0.49 mmol/g at 80 and 95 °C, respectively, confirming the increasing degradation caused by the increasing temperature of the proposed stability tests.

In conclusion, we present a practical, *ex-situ* method for measuring the chemical stability of AEMs in a fuel cell-like environment. With this method, we conducted tests showing the degradation rate of a relatively stable AEM (LDPE-BTMA radiation-grafted AEM) at different RH values and different temperatures. We propose to use a sole parameter to characterize the membrane stability to be used for AEMFCs, which we call the "AEM degradation parameter". For the

LDPE-BTMA membrane, for example, this parameter was calculated to be 0.025%/h/RH.

In comparison with all current methods to measure chemical degradation of AEMs, this technique offers excellent reliability and reproducibility, as no liquid electrolyte (with all the involved complications) is used at any time of the test. This also assures to mimic the in-operando fuel cell environment, measuring then the real stability behavior of an AEM during fuel cell operation.

Finally, this method, which only requires a four-probe conductivity instrumentation, can be easily standardized. By adopting this new liquid electrolyte-free stability measurement method to calculate the AEM degradation parameter of developed anion conducting polymers, the research community will finally be able to measure and compare the chemical stability between different AEMs in a reliable, reproducible, and comparable way. We strongly recommend the adoption of this method and the new degradation parameter as a standard for measuring and expressing the stability of AEMs.

■ EXPERIMENTAL SECTION

Anion-Exchange Membrane. For these experiments we used the low-density polyethylene-based radiation-grafted anion-exchange membrane functionalized with benzyltrimethylammonium cationic functional groups synthesized by Wang *et al.*[61] The BTMA-LDPE AEMs (55 ± 2.0 μm in thickness, received in Cl^- form) were first exchanged to bicarbonate form, by soaking them in 1 M $KHCO_3$ aqueous solution at room temperature for 48 h and then soaking in deionized water for 48 h at room temperature. Solution and water are renewed six times.

***In-Situ* Exchange to the Hydroxide Form and Chemical Degradation Measurement without Alkaline Solutions.** To exchange the AEMs from bicarbonate to their hydroxide form, the liquid electrolyte-free method from Ziv and Dekel is used.[55] The carbonated membranes were mounted in a four-electrode (two current and two potential sense) membrane test system (MTS 740, Scribner Associates Inc.) and exposed to pure nitrogen (99.999% N_2) with a continuous flow rate of 500 sccm/min. The RH is set to 100% and the temperature to 40 °C with a direct current flow between the current electrodes to release the bicarbonates at the anode (*in-situ* exchange them with OH^- inside the AEM). For the decarbonation process of the AEM the current is increased from 100 to 300 μA (Ivium-n-Stat, Ivium Technologies) for the first 6 h to accelerate the process and then is set to 400 μA. The resistance is measured every 2 h by using a standard four-probe technique.[63] After 400 μA is set, the resistance is measured every 30 min. The ionic conductivity of the membrane samples is calculated by[63]

$$\sigma = \frac{L}{R \cdot W \cdot d} \tag{1}$$

where L is the distance between the sensing electrodes (4.25 mm), R is the measured resistance of the membrane sample, W is the width of the sample, and d the thickness of the membrane, which is measured right after taking out of the deionized water from the washing process mentioned before. After a threshold of the conductivity is reached and the value does not change significantly, we assumed that the AEM is in the pure OH^- form. This procedure has been repeated for each membrane sample. For the degradation measurement, the RH is set to 60%, temperature to 80 °C, and the applied current to 100 μA, unless it is specified differently. The hydroxide conductivity is determined frequently (every 1−2 h) for around 100 h. By measuring the slope in change of hydroxide conductivity we determine the degradation of the membrane, and based on that data, the final AEM degradation parameter.

Ion-Exchange Capacity Measurement. The AEM is soaked in 1 M KCl aqueous solution and continuously shaken (TOS-4030PD, mrclab) for 48 h. The solution is renewed six times to make sure that enough ions are available for the ion-exchanging process. After this, the membrane samples are washed with deionized water for 48 h, followed by storing them in 1 M KNO_3 aqueous solution for 48 h. The KNO_3 solution with the membrane is titrated with 0.01 M $AgNO_3$, and the molarity of the chloride ions is measured (751 GPD Titrino, Metrohm). Finally, the membrane in nitrate form is washed in deionized water and dried for at least 8 h in a vacuum oven. The IEC is then calculated by[64,65]

$$\mathrm{IEC} = \frac{\Delta V_{\mathrm{AgNO_3}} \cdot c_{\mathrm{AgNO_3}}}{W_{\mathrm{NO_3}}(\mathrm{dry})} \tag{2}$$

where $\Delta V_{\mathrm{AgNO_3}}$ and $c_{\mathrm{AgNO_3}}$ are the volume and the concentration of the added titrant solution, respectively, and $W_{\mathrm{NO_3}}$ (dry) is the dry weight of the membrane. This procedure is repeated three times for each sample; average and standard deviations of the IEC measurement are determined.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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