



A practical method for measuring the true hydroxide conductivity of anion exchange membranes

Noga Ziv, Dario R. Dekel*

The Wolfson Department of Chemical Engineering and the Nancy & Stephan Grand Technion Energy Program (GTEP), Technion – Israel Institute of Technology, Haifa 3200003, Israel

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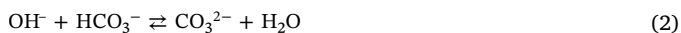
ABSTRACT

Hydroxide ions in anion exchange membranes (AEMs) are quickly exchanged for larger and less mobile anions (CO₃²⁻ and HCO₃⁻) when the membrane is exposed to ambient air. Therefore, reported conductivity values of AEMs in hydroxide form are difficult to reproduce, and existing conductivity measurement techniques are not always reliable. Up to now, comparison of reported data for the hydroxide conductivity of different membranes has not been possible because tests have been performed not just with different anions, but also under different conditions and using different methods. In this work we present a practical and reproducible ex situ method for measuring the true value of the hydroxide conductivity of AEMs.

1. Introduction

Anion exchange membrane fuel cells (AEMFCs) have attracted a lot of attention in recent years due to their potential as highly effective, clean, low-cost sources of energy [1]. In an AEMFC, hydroxide anions (OH⁻) are the dominant anions transported through the anion exchange membrane (AEM) from the cathode to the anode side of the cell [2].

The value of OH⁻ conductivity is therefore critical in distinguishing between different membranes and in determining those most suitable for use in a fuel cell. However, the true OH⁻ conductivity value is difficult to measure due to the fast reaction of OH⁻ with CO₂ (ca. 400 ppm in ambient air), which replaces OH⁻ with larger and less mobile anions – bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) (see reactions (1) and (2)) [3,4].



This carbonation process has significant effects on the AEM and the AEMFCs [5,6], which are not yet fully understood [7]. The reactions take place immediately upon exposing the membrane to ambient air and advance very quickly; it was found that during exposure to ambient air OH⁻ was fully replaced within 1 to 6 h [8–11], and a decrease of 60–70% in conductivity was measured in only 40–60 min [12–14]. Some early works have disregarded this problem and measured OH⁻ conductivity without CO₂ removal, and therefore the obtained results

might reflect the conductivity of a mixed anion form of AEM instead of the pure OH⁻ form [15,16].

To avoid these problems and measure the conductivity of an AEM in its pure OH⁻ form, many works have used gas-purged water during the exchange process [13] or during measurement [8,17–21]. However, this method might produce carbonated AEMs since exposure of the membrane to ambient air for even a few minutes is sufficient to exchange some of the OH⁻ with (bi)carbonate, and there might be some dissolved CO₂ in the water. Also, measuring the conductivity in water does not reflect the conditions in an operating fuel cell.

Another method that aims to overcome these challenges is the use of a glovebox containing an inert gas with ultra-low CO₂ levels, in which the ion-exchange process of the membrane and measurement take place [22–24]. Among the disadvantages of this method are the complexity of performing AEM conductivity measurements, inconsistency in gas composition (mainly CO₂ level) from one glovebox to another, and the problematic use of a large amount of degassed water inside the glovebox. In summary, the conditions which are currently used to measure the OH⁻ conductivity of AEMs are usually hard to reproduce and not stable, making it impossible to compare reported data.

This work provides a new, ex situ, practical method for measuring true OH⁻ conductivity. The method does not require the use of a complex glovebox, nor expensive fuel cell tests, neither does it involve chemical steps to convert the membrane into its hydroxide form.

* Corresponding author.

E-mail address: dario@technion.ac.il (D.R. Dekel).

2. Experimental

2.1. Anion exchange membranes

We used PBI-based membranes in their carbonate form (HMT-PMBI 89.3% dm (degree of methylation), supplied by Holdcroft's group, Simon Fraser University, Canada). The preparation and characterization of the PBI-based AEMs have been reported elsewhere [25]. The AEM has a reported thickness of ca. 50 μm and an ion exchange capacity (IEC) of 2.5 meq g^{-1} . The hydroxide conductivity at room temperature (while immersed in liquid water) was reported to be 23 mS cm^{-1} [13,25].

2.2. Hydroxide conductivity measurement method

The membrane samples in their carbonate form were mounted in a membrane test system (MTS 740, Scribner Associates Inc.). The samples were exposed to a continuous 500 sccm min^{-1} gas flow containing nitrogen (99.999% N_2) or nitrogen with an ambient concentration of CO_2 (99.999% N_2 with 400 ppm CO_2), under constant 90% relative humidity at 40 °C. A constant direct current of 100 μA (SP-300 potentiostat, Bio-Logic) was applied to the membrane (see Fig. 1).

Every 10 to 30 min, the ionic resistance of the membrane was measured using a standard 4-probe technique [26], and the in-plane anion conductivity was then calculated using the equation:

$$\sigma = \frac{L}{R \cdot W \cdot d} \quad (3)$$

where L is the distance between the two inner sensing electrodes (4.25 mm), R is the membrane's resistance (measured by voltage scanning between ± 100 mV), W is the sample width (ca. 10 mm) and d is the membrane's thickness (measured under wet conditions).

3. Results and discussion

Fig. 2 shows the in-plane conductivity values measured in the AEM over a period of time. In the first stage, the membrane is left under experimental conditions without applying any current in order to reach an equilibrium. During this stage the conductivity changes slightly before reaching a relative stable value of ca. 15 mS cm^{-1} . The slight changes in anion conductivity in this first stage are believed to be a result of water exchange between the gas environment and the membrane, and the increase in the measurement cell's temperature from room temperature to 40 °C.

As can be seen in Fig. 2, when a current of 100 μA is applied through the membrane, its conductivity starts to increase at an apparently exponential rate. This significant increase in measured anion conductivity is explained by the electrochemical reactions taking place at the electrodes. At the positive electrode (cathode), OH^- is produced according to:

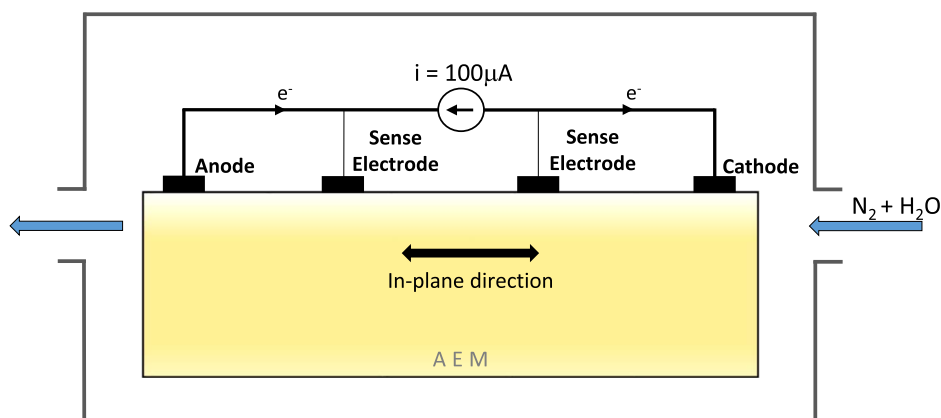


Fig. 1. Schematic illustration of the experimental setting.

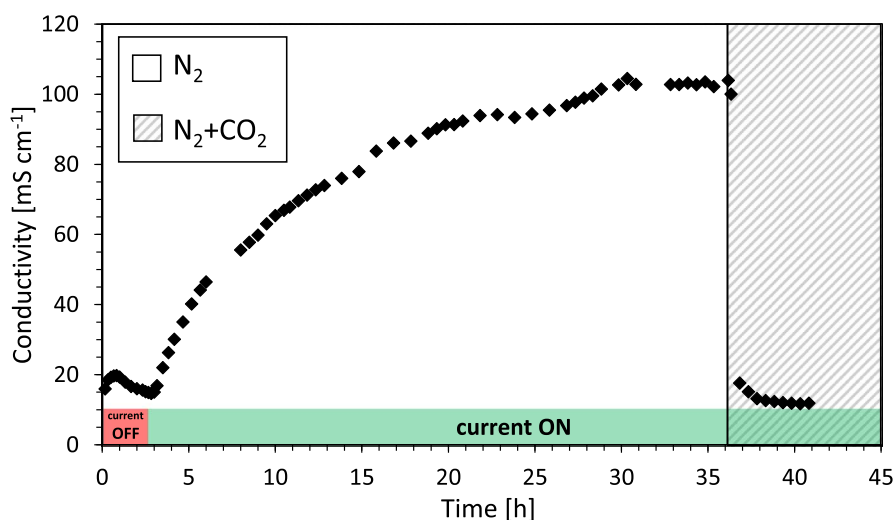


Fig. 2. Changes in AEM conductivity before, during and after applying 100 μA direct current, with a change in the ambient gas after 36 h. Test conditions remained constant at 90% RH and 40 °C.

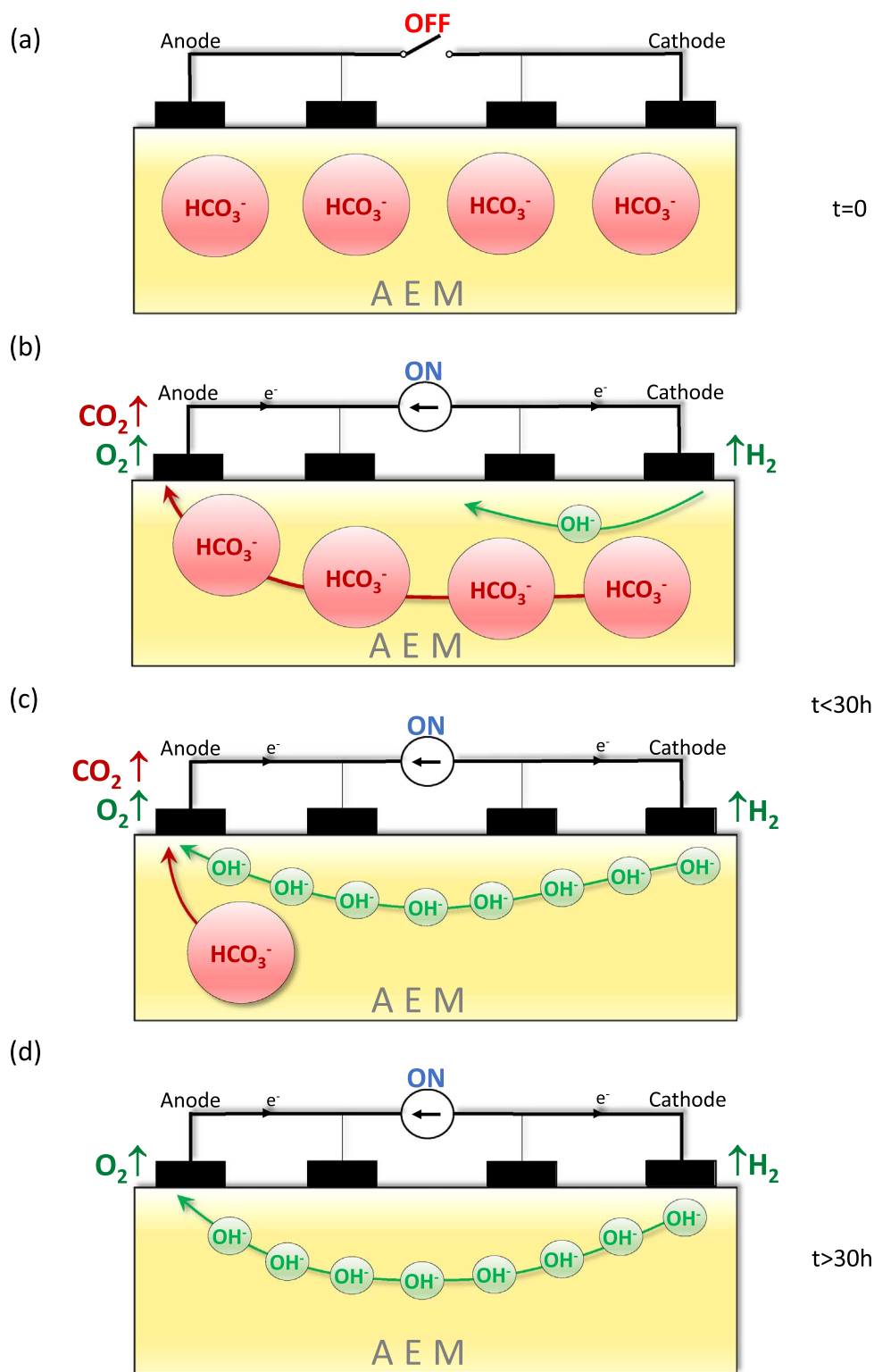


Fig. 3. Schematic illustration of the processes taking place in the AEM while applying the direct current under the conditions of our conductivity test.

The amount of water supplied with the humidified ambient gas is about ten orders of magnitude higher than the amount consumed in reaction (4), so water does not limit the electrochemical reaction. As a result of the current, the anions initially present in the membrane ($\text{HCO}_3^-/\text{CO}_3^{2-}$) move towards the negative electrode (anode), where CO_2 is released via the following reactions [7]:



As a result of these reactions, the relative amount of OH^- in the membrane continuously increases at the expense of the $\text{HCO}_3^-/\text{CO}_3^{2-}$ concentration, thus increasing the measured anion conductivity values (see Fig. 2). Similar behavior was observed by Kimura et al. [27], but the authors did not continue their tests over a long period, and no stabilization in the conductivity readings was reached in that case. In our tests, we continued the measurements for approximately 30 h, until

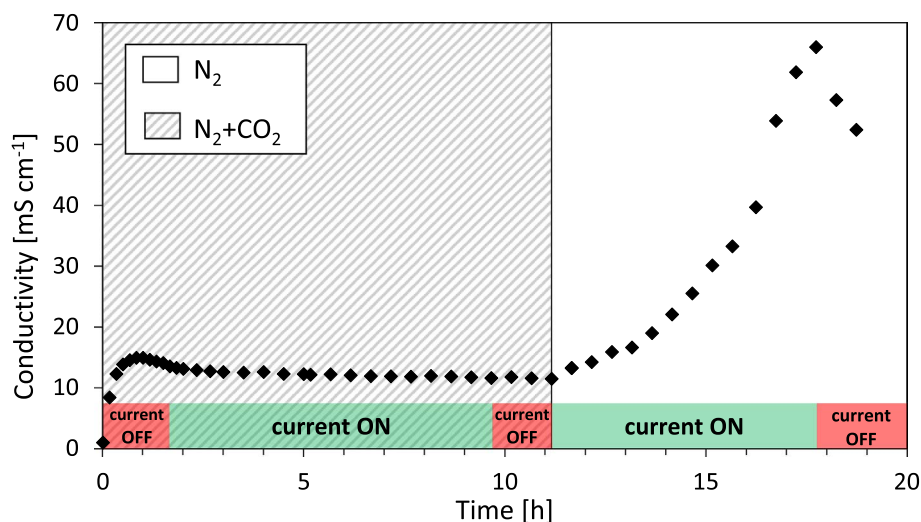


Fig. 4. Changes in the measured conductivity of the AEM while applying current and changing the ambient gas: first, N_2 containing 400 ppm CO_2 , then pure N_2 .

all the carbonate anions were replaced by OH^- . At this asymptotic value the measured conductivity reaches its maximum value, around 103 mS cm^{-1} . We call this value the “true hydroxide conductivity” of the AEM, as it was obtained when all the carbonate anions had been replaced by the hydroxide, and therefore the membrane was in its pure OH^- form.

The process described above is represented schematically in Fig. 3. Before any current is applied, Fig. 3(a), the membrane contains large HCO_3^- and CO_3^{2-} anions (for simplicity only HCO_3^- anions are shown). Once the current is switched on, Fig. 3(b), OH^- begins to form at the cathode and HCO_3^-/CO_3^{2-} anions begin to move towards the anode, while gases are generated at the electrodes according to reactions (4), (5) and (6). After ca. 2 h, Fig. 3(c), OH^- is transported to the anode, the concentration of HCO_3^-/CO_3^{2-} decreases due to the release of CO_2 and the conductivity significantly increases. Finally, after ca. 30 h of applying $100 \mu\text{A}$, Fig. 3(d), all the HCO_3^-/CO_3^{2-} have been removed from the membrane, OH^- anions continue to be transported through the membrane and its conductivity is stable, and at its maximum value – its true hydroxide conductivity.

In order to confirm that the AEM is entirely in its OH^- form after the point when the membrane reaches its maximum conductivity, we switched the gas inlet from nitrogen to nitrogen containing 400 ppm of CO_2 (gray area in Fig. 2) at ca. 36 h. Fig. 2 shows that after CO_2 is introduced into the atmosphere, the conductivity immediately decreases to a value close to its initial value. This is a result of the immediate reaction of OH^- with CO_2 to create HCO_3^-/CO_3^{2-} through reactions (1) and (2), which causes a decrease in conductivity, even though the current is still applied. This decrease confirms that OH^- is produced during application of current, that it is responsible for the increase in conductivity, and that once the membrane is back in contact with CO_2 , the conductivity corresponding to the fully carbonated form is obtained.

To further confirm that the increase in conductivity results from the electrochemical removal of CO_2 from the membrane, a similar (although inverse) procedure was carried out using N_2 with 400 ppm CO_2 as the ambient gas, and the results are presented in Fig. 4. In the presence of CO_2 , OH^- anions produced in reaction (4) will immediately react to create HCO_3^- and CO_3^{2-} via reactions (1) and (2). The conductivity therefore remains constant at the initial value corresponding to the AEM in its HCO_3^-/CO_3^{2-} form. When the flowing gas is switched to pure nitrogen (without CO_2), the conductivity increases since OH^- is not neutralized by CO_2 and its concentration in the membrane can increase. This clearly proves that OH^- is formed, and HCO_3^- and CO_3^{2-} are removed from the membrane while the current is applied, causing the increase in conductivity values.

It should be remarked that the true hydroxide conductivity value found in this work using the proposed method, 103 mS cm^{-1} , is twice as high as the conductivity value of the same membrane measured after the common practice of aqueous KOH soaking followed by water washing in a CO_2 -free chamber ($\sim 50 \text{ mS cm}^{-1}$). Also, using our proposed method, we succeed in showing an increase in conductivity of ca. 6 times for the final OH^- form compared to $\sim 15 \text{ mS cm}^{-1}$ for the initial air-equilibrated AEM containing HCO_3^- and CO_3^{2-} . This ratio is significantly higher than the ratio obtained in the literature using conventional glovebox-based methods [7]. This strengthens the conclusion that our method can indeed be used to measure the true hydroxide conductivity value of an AEM.

4. Conclusions

We present a novel, practical, ex-situ method for measuring the true value of the hydroxide conductivity of AEMs. The method is based on forcing the release of the larger (bi)carbonate anions as CO_2 gas by applying an external electric current through the membrane. The current forces electrochemical reactions in the AEM at the electrodes so that OH^- is formed at one electrode, and HCO_3^-/CO_3^{2-} are purged as CO_2 at the other electrode, until all the anions in the membrane are exchanged in situ to OH^- . This method offers excellent reproducibility compared with the methods currently used to measure OH^- conductivity. Finally, the method involves relatively simple instrumentation and configuration, and conditions closer to those found in an operating fuel cell.

By adopting this new anion conductivity measurement method the research community will finally be able to compare hydroxide conductivity between different AEMs in a reliable and reproducible way. We strongly recommend the adoption of this method for measuring the hydroxide conductivity of AEMs.

Declarations of interest

No conflict of interest.

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