



Effect of hydroxide and carbonate alkaline media on anion exchange membranes

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ABSTRACT

The effect of hydroxide and carbonate alkaline environments on the chemical stability and ionic conductivity of five commercially available anion exchange membranes was investigated. Exposure of the membranes to concentrated hydroxide environments (1 M) had a detrimental effect on ionic conductivity with time. Over a 30-day period, decreases in conductivity ranged from 27% to 6%, depending on the membrane. The decrease in ionic conductivity is attributed to the loss of stationary cationic sites due to the Hofmann elimination and nucleophilic displacement mechanisms. Exposure of the membranes to low concentration hydroxide (10^{-4} M) or carbonate/bicarbonate (0.5 M Na_2CO_3 /0.5 M NaHCO_3) environments had no measurable effect on the ionic conductivity over a 30-day period. ATR-FTIR spectroscopy confirmed degradation of membranes soaked in 1 M KOH. Apparition of a doublet peak in the region between 1600 cm^{-1} and 1675 cm^{-1} confirms formation of carbon–carbon double bonds due to Hofmann elimination. Membranes soaked in mild alkaline environments did not show formation of carbon–carbon double bonds.

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1. Introduction

Anion exchange membrane (AEM) fuel cells have recently received considerable attention due to their potential advantages over the proton exchange membrane (PEM) fuel cell. First, the kinetics for both fuel oxidation [1,2] and oxygen reduction [3,4] is enhanced in alkaline media compared to the acidic media, allowing the use of non-precious metal electrocatalysts in the cell. The fuel oxidation does not require water, allowing alcohol versions to operate on pure fuel, unlike the PEM fuel cell where water takes part in the electrochemical reaction and the fuel must be diluted. Also, during operation, the anion moves from cathode to anode and the resulting electrosmotic drag suppresses fuel crossover. Since water is produced in the anode and partially consumed at the cathode, water management is potentially simplified and could lead to prevention of electrode flooding. Recently, there have been promising results of hydroxide exchange membrane fuel cells (HEMFCs) using hydrogen, methanol and ethanol as the anode fuel [5–14].

However, the HEMFC still faces a pressing limitation: the degradation of the electrolyte by hydroxide, which is produced at the cathode through the following reaction:



The origin of the instability is normally considered to be the displacement of the cationic ammonium groups by hydroxide anions,

which are an excellent nucleophile. The three main mechanisms for degradation are: (i) a direct nucleophilic displacement; (ii) a Hoffman elimination reaction through β -hydrogen sites; and (iii) displacement of methyl groups by hydroxide ions, forming tertiary amines and methanol [15]. These modes of degradation involve the loss of the cationic sites, which reduces anion transport through the membrane. Therefore, as degradation progresses, the ionic conductivity of the membrane decreases. This is a significant issue with HEMFCs since the role of the cathode catalyst is to produce hydroxide anions with limited kinetic resistance and the role of the electrolyte is to transport those ions with limited ohmic resistance.

Currently, there is a significant ongoing effort to find anion exchange membranes with good stability at high pH. One approach to improving AEM stability is the elimination of β -hydrogens in the substituent groups of the cationic site, thereby preventing the Hofmann elimination mechanism. Most of the AEMs for fuel cells contain methyl-substituted ammonium groups as the cationic site, which contain no β -hydrogens. However, the benzyltrimethyl ammonium group still degrades in basic environments since trimethylammonium is easily cleaved by nucleophilic attack. Recently, numerous polymeric materials have been investigated as potential candidates for AEMs including, poly(vinyl alcohol) [13], polysulfones [16,17], poly(phenylene) [18], poly(epichlorhydrin) [19], among others. Although significant progress has been made concerning improvements in ionic conductivity, chemical degradation in the presence of hydroxide is still a major drawback for all materials studied. This is especially true in the HEMFC, where production of hydroxide in the cathode leads to pH values close to 14.

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Although the investigation of different chemical structures has the potential to lead to highly stable membranes, another approach consists of using a different mobile anion in the AEM fuel cell. A considerable improvement in AEM stability could be achieved by the use of the carbonate anion, which will diminish the pH in the electrodes and electrolyte. Also, the carbonate anion is expected to have a diminished tendency to attack AEMs through Hoffman elimination or nucleophilic displacement because it is a weaker nucleophile compared to hydroxide. In turn, this could open a whole new direction for the study of low temperature electrochemical devices operating on the carbonate cycle. Operation of the AEM fuel cell on the carbonate cycle could lead to a considerable increase in device operational lifetime. It has been shown that the presence of carbonate does not affect the kinetics of the oxygen reduction reaction [20] and fuel cells operating in the carbonate cycle at low temperature have been demonstrated [20–22]. The room temperature carbonate fuel cell can also act as a CO₂ pump.

The purpose of this study is to elucidate the effect of hydroxide and carbonate/bicarbonate on the ionic conductivity and chemical stability of commercially available anion exchange membranes. This was done by soaking the membranes in solutions with different concentrations of hydroxide or carbonate/bicarbonate for different times. Subsequently, ionic conductivity was measured using AC impedance and bond formation/reorganization was observed using ATR-FTIR spectroscopy.

2. Experimental

Five commercially available anion exchange membranes were used in this study to determine ionic conductivity and chemical stability in different alkaline environments. The membranes under study were: AMI-7001S (Membranes International), AMB-SS (ResinTech), Ralex AMH-PAD (Mega a.s.), Excellion I-200 (SnowPure) and MA-3475 (Lanxess Sybron). All membranes were received in the chloride form and were ion exchanged to either hydroxide or carbonate form prior to experimentation by soaking them for 24 h in 1 M KOH or 0.5 M Na₂CO₃/0.5 M NaHCO₃. For the stability tests, KOH, Na₂CO₃ and NaHCO₃ (ACS reagent grade) were dissolved in 18 MΩ Millipore water to make solutions of the following compositions: (a) 1 M KOH; (b) 10⁻⁴ M KOH; and (c) 0.5 M Na₂CO₃/0.5 M NaHCO₃. Three sample membranes were soaked in each solution for 1, 2, 5, 10, 20 and 30 days and were then exposed to conductivity measurements and attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR).

Conductivity measurements were performed in a custom built two compartment glass cell (Pine Instruments) using 5 mm diameter polycrystalline platinum disk electrodes separated by 6 cm. A schematic for the conductivity cell is presented in Fig. 1. Prior to experimentation, the cell and electrodes were rinsed with deionized water and fresh electrolyte solution. All conductivity experiments were thermostated at 25 ± 0.1 °C. The membrane and solution were held at the experimental temperature for at least 20 min prior to experimentation to ensure thermal equilibrium. AC impedance measurements were performed with an Autolab PGSTAT302N potentiostat using frequency ranges from 0.1 Hz to 300 kHz and alternating potential amplitude of 10 mV. Fully hydrated membranes were placed in the conductivity cell and the cell was filled with either 1 M KOH or 0.5 M Na₂CO₃/NaHCO₃. The resistance of the membrane and solution was measured (R_{total}). The resistance of the solution was measured without the membrane present ($R_{solution}$). Membrane resistance (R_{mem}) was obtained from the difference of the measured resistances ($R_{mem} = R_{total} - R_{solution}$). The thickness of the membrane was measured with a digital micrometer by placing the membrane between two 1 mm thickness glass slides to ensure both a planar surface and limited compres-

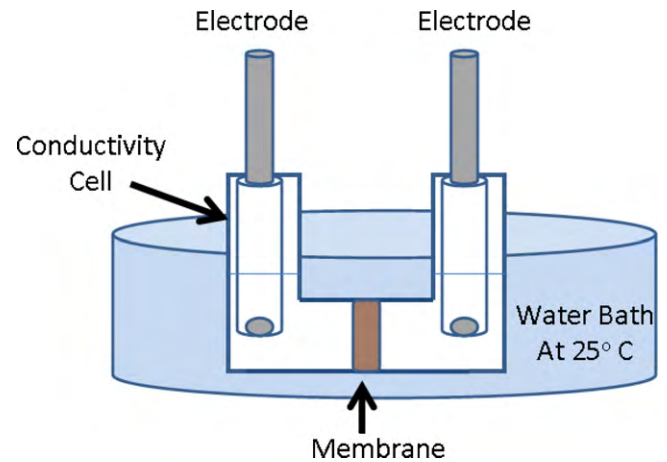


Fig. 1. Schematic of the conductivity cell.

sion of the film during measurement. Ionic conductivity, σ , was obtained using the following equation:

$$\sigma = \frac{l}{R_{mem}A} \quad (2)$$

where l is the membrane thickness and A is the membrane surface area exposed to the electric field. The conductivity of each commercial membrane was obtained using all the 3 samples in solutions a–c at 1, 2, 5, 10, 20 and 30 days. The average value for each condition is reported here.

ATR-FTIR was performed with a Nicolet iS10 spectrometer (Thermo Scientific). All samples were analyzed in absorption mode using an ATR element with a 2 mm diameter diamond crystal. A spectrum was obtained in three different locations for each sample to ensure even chemical composition.

3. Results and discussion

3.1. Physical changes

All membranes as received were either white or light colored and very flexible. However, various physical changes were observed during soaking, and were dependent on the solution and soaking time. These include variations in color, physical appearance and flexibility of the membrane.

The AMI-7001S, MA-3475 and AMB-SS membranes soaked in 1 M KOH underwent severe color change, which was observed in as little as 5 min. With time, the color would progressively change to dark brown, dark red and dark brown, respectively. This phenomena has been observed by other groups for anion exchange membranes soaked in highly alkaline solutions (pH ~14) and has been attributed to deterioration of the chemical structure [5,6]. The I-200 and AMH-PAD membranes did not change color during the 30-day period. However, all membranes became stiff and brittle with increased soaking time and even slight bending would cause the membranes to crack. In addition, the MA-3475 membrane soaked in 1 M KOH lost portions of its polymer and the inner supporting cloth was exposed after being in solution for 30 days. MA-3475 was observed using a Hirox KH-1300 optical microscope (2100× magnification) which confirmed the presence of the cracks and the exposure of the inner supporting cloth.

None of the membranes soaked in 0.5 M Na₂CO₃/NaHCO₃ exhibited any color change over the 30-day period, suggesting negligible chemical deterioration. Similar results were obtained with membranes soaked in 10⁻⁴ M KOH, where no change in color was observed for any soaking time period. After experimentation, the membranes remained flexible and would not crack when bent.

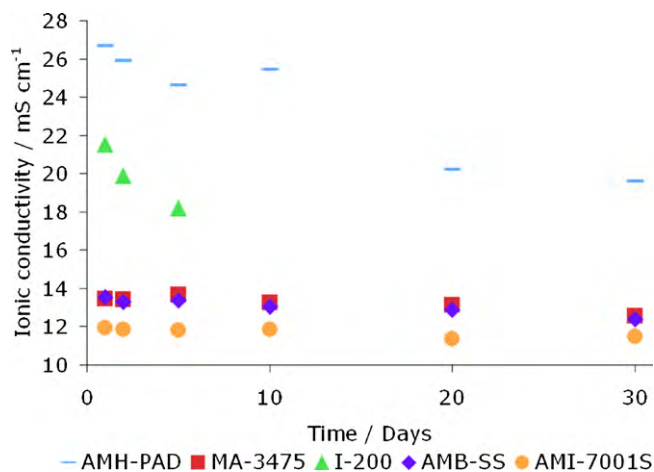


Fig. 2. Ionic conductivity decline for all studied membranes soaked in 1 M KOH.

3.2. Conductivity measurements

Membrane conductivity was measured in concentrated alkaline solutions. Fig. 2 shows ionic conductivity as a function of soaking time for the commercially available membranes soaked in 1 M KOH. Clearly, the conductivity of the AMH-PAD and I-200 membranes rapidly decrease with time. The effect is less pronounced for MA-3475, AMB-SS and AMI-7001S, though a more focused plot, Fig. 3, reveals a distinct decline in the ionic conductivity of the remaining membranes with increased soaking time. Although the AMH-PAD membrane has the highest initial conductivity, it also undergoes the greatest decrease in conductivity, 27%, over the 30-day period. AMI-7001S had the smallest decrease in conductivity, 6%, over 30 days of soaking in 1 M KOH. This might appear to be a small decrease; however, it would prevent any long term use of the membrane. For example, in the hydroxide exchange membrane fuel cell, even a 6%/month decrease would significantly limit device operating lifetime.

Fig. 4 shows ionic conductivity as a function of soaking time for membranes soaked in 10^{-4} M KOH. The absolute values of the conductivities observed are a bit lower than in Fig. 2. This is caused by the lower concentration of hydroxide (4 orders of magnitude) at the membrane/electrolyte interface, which decreases overall transport and, consequently, the ionic conductivity. Of the membranes tested, AMH-PAD was the only sample that showed a measurable decrease in conductivity, 2%, over the 30-day testing period. This is expected as the membrane was highly unstable in 1 M KOH. All of

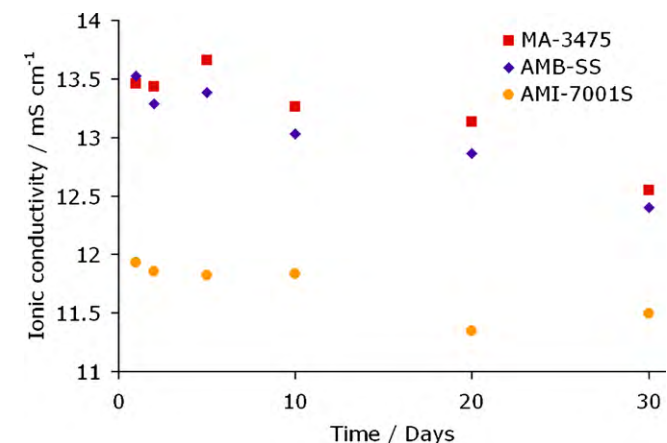


Fig. 3. Focused plot for MA-3475, AMB-SS and AMI-7001S membrane conductivity soaked in 1 M KOH.

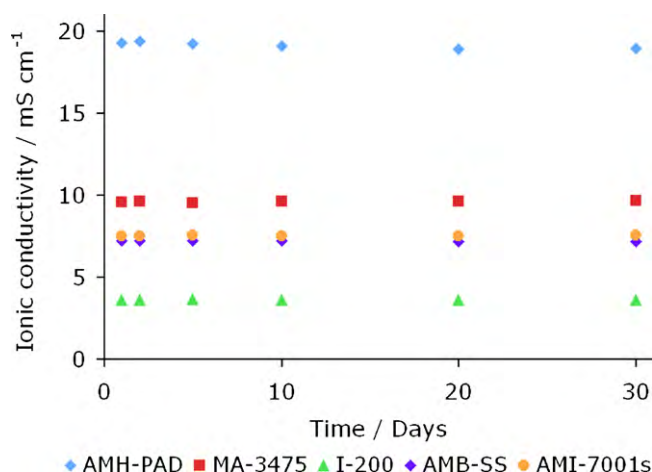


Fig. 4. Ionic conductivity vs. time for all studied membranes soaked in 10^{-4} M KOH.

the other membranes investigated in this study did not show any measurable conductivity at any time in 10^{-4} M KOH.

Fig. 5 presents the ionic conductivity of the commercially available membranes as a function of soaking time for membranes exposed to 0.5 M Na_2CO_3 /0.5 M NaHCO_3 . The behavior in carbonate/bicarbonate solution is similar to the 10^{-4} M KOH solution, which is expected since both have similar pH (~ 10). For all membranes, the initial conductivity (day 1) was the same as the final conductivity (day 30) within $\pm 0.1 \text{ mS cm}^{-1}$. The carbonate/bicarbonate electrolyte had no adverse effect on membrane chemical stability in the time studied, as observed by conductivity measurements. This behavior has been previously observed for a polysulfone anion exchange membrane at 50°C in carbonate only solutions compared to hydroxide only solutions. In the presence of hydroxide, the ionic conductivity abruptly decreased while it stayed constant in the presence of carbonate [22]. Therefore, prolonged membrane performance is expected in low temperature electrochemical devices with carbonate anions due to increased stability in their ionic conductivity compared to their hydroxide counterparts.

Figs. 6–8 summarize the behavior of AMH-PAD, MA-3475 and I-200 by plotting the ionic conductivity (S) over initial ionic conductivity (S_0) versus the soaking time for each solution in three membranes. Solutions of carbonate/bicarbonate and dilute hydroxide did not affect the ionic conductivity over a period of 30 days in any of the membranes, while 1 M KOH always lead to significant reduction in the ionic conductivity with time. AMH-PAD (Fig. 6)

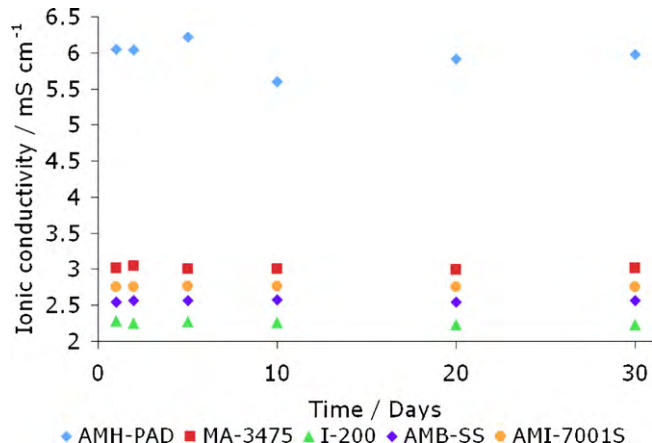


Fig. 5. Ionic conductivity vs. time for all membranes soaked in 0.5 M Na_2CO_3 /0.5 M NaHCO_3 .

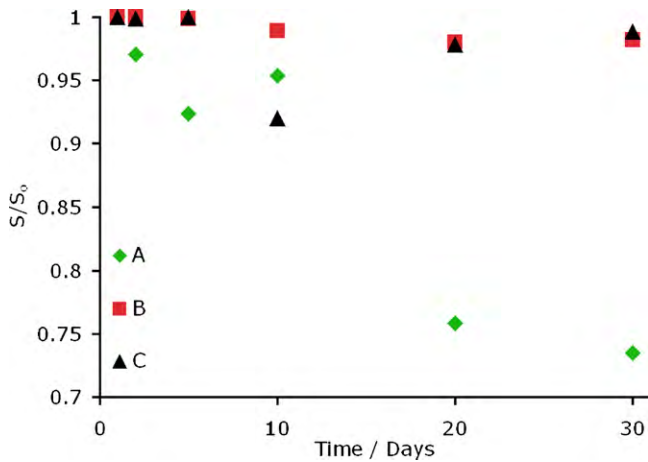


Fig. 6. Conductivity degradation comparison for AMH-PAD membrane soaked in (A) 1 M KOH, (B) 10^{-4} M KOH and (C) 0.5 M Na_2CO_3 /0.5 M NaHCO_3 .

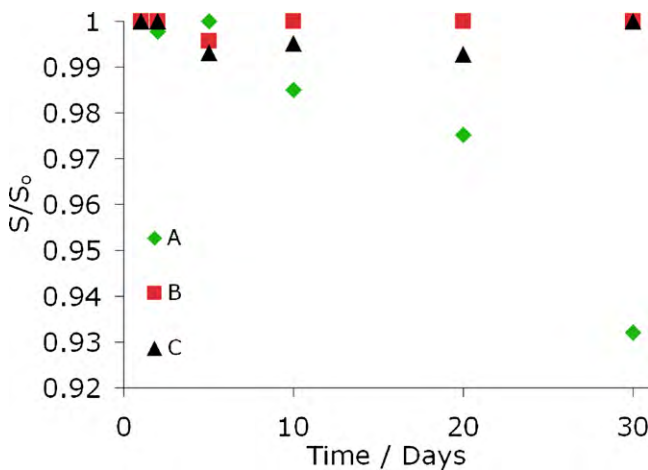


Fig. 7. Relative conductivity degeneration for MA-3475 membrane soaked in (A) 1 M KOH, (B) 10^{-4} M KOH and (C) 0.5 M Na_2CO_3 /0.5 M NaHCO_3 .

had a decrease of over 25% over a 30-day period in 1 M KOH, while MA-3475 (Fig. 7) has a decrease of 7% in the same time period. I-200 underwent an ionic conductivity decrease of 16% in only 5 days (Fig. 8). Unreliable conductivity measurements were obtained after 5 days for the I-200 membrane, suggesting considerable degrada-

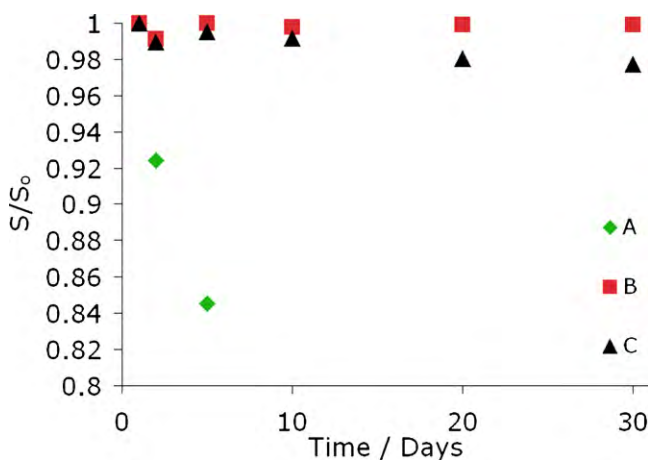


Fig. 8. Conductivity deterioration with time for I-200 membrane soaked in (A) 1 M KOH, (B) 10^{-4} M KOH and (C) 0.5 M Na_2CO_3 /0.5 M NaHCO_3 .

tion of this membrane in 1 M KOH. This suggests that the mild pH (~ 10) of the soaking environment had a negligible effect on the membrane cationic sites and overall chemical stability due to the low amount of strong nucleophiles present in the electrolyte. This finding supports the hypothesis of this study, which is that a less caustic environment will lead to reduced electrolyte degradation.

One drawback for carbonate-based devices is the lower mobility of the anion compared to OH^- , which limits ionic conductivity. The initial (day 1) conductivity for the membranes exchanged to carbonate/bicarbonate is considerably smaller than for membranes exchanged to hydroxide. This is caused by the significantly larger size of the carbonate anion (2.7 Å) compared to hydroxide (1.7 Å) [24], which reduces its mobility, and thus, its conductivity. However, the conductivity is not reduced by as much as might be expected by size alone due to the fact that the degree of hydration depends on the surface charge density which decreases with increasing ionic radius. The hydration radius is generally used as a measure of the combined ion and hydration layers size. Hydration radius for solvated hydroxide has been reported as 3 Å, while for solvated carbonate it is 3.94 Å [24] and for solvated bicarbonate it is 5.6 Å [25].

Therefore, the major contributor to the conductivity decrease is most likely the bicarbonate ion since its hydrated radius is considerably larger than hydroxide (1.9 \times) and it has the same valence. The carbonate anion, on the other hand, has a valence of 2, which will partially compensate for the decrease in mobility due to size. As in simple aqueous electrolytes, the ion mobility is inversely related to the radius. However, a mean mobility should be considered which accounts for the solvent present in the membrane pore. Also, for hydrodynamics and electrostatic reasons, the mobility of the ions inside the membrane pore will be lower than in simple electrolytes [26]. Therefore, it is not fitting to directly relate the expected conductivity decrease for dilute electrolytes to the measured membrane conductivity. Conductivities measured in the presence of carbonate only, have been reported as considerably closer to hydroxide [22,23]. In this work, an AMH-PAD membrane was exchanged to only carbonate and AC impedance performed with a carbonate only electrolyte. The ionic conductivity of the membrane was 10.1 mS cm^{-1} , a 70% increase compared to the membrane exchanged to carbonate/bicarbonate.

3.3. FTIR measurements

The membranes studied have different polymer backbones which were determined using ATR-FTIR. Three polymer backbones were found: polyethylene (AMH-PAD), polypropylene (I-200) and polystyrene (AMI-7001s, AMB-SS, MA-3475). Fig. 9 shows the ATR-FTIR spectra of the AMH-PAD membrane soaked in deionized water. The broad peaks at 3370 cm^{-1} and 1630 cm^{-1} correspond to water contained in the membrane. The small peak at around 1200 cm^{-1} corresponds to the nitrogen-carbon bond stretch. Peaks corresponding to the polyethylene backbone can also be seen. Strong peaks between 2800 cm^{-1} and 3000 cm^{-1} are assigned to CH_2 symmetric and asymmetric stretching, respectively; while the peak at 1473 cm^{-1} corresponds to bending deformation [27].

The instability of the polymer electrolytes in the presence of high concentrations of hydroxide ions is due to degradation by nucleophilic attack and Hoffman elimination [15]. The Hoffman reaction involves the release of lower coordinated amines and the formation of a carbon-carbon double bond in the polymer electrolyte. The C=C bond has an FTIR response at $1600\text{--}1650 \text{ cm}^{-1}$. For quaternary groups undergoing nucleophilic attack, a R-C-OH functional may be left behind. Though the dominant OH stretch is

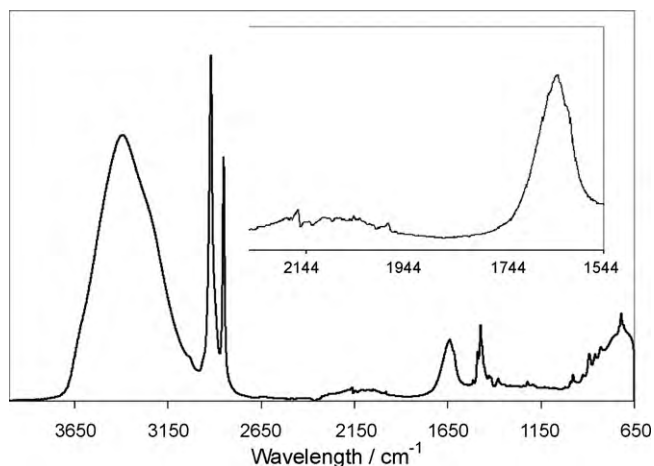


Fig. 9. ATR-FTIR spectra for AMH-PAD membrane soaked in deionized water.

present around 3200 cm^{-1} and overlap with the water peak, there is also a weak response at $1700\text{--}1750\text{ cm}^{-1}$. Therefore, degradation through both nucleophilic attack and Hoffman elimination should be observable using FTIR. In this work, AMH-PAD was used for ATR-FTIR studies due to its pronounced degradation.

Fig. 10 shows the ATR-FTIR spectra for AMH-PAD soaked in 1 M KOH for 2 and 30 days. The membrane soaked for 2 days contains only a single peak which corresponds to water at around 1640 cm^{-1} . However, the membrane soaked for 30 days shows two clear differences. First, a secondary peak, slightly overlapping with water appears at 1615 cm^{-1} forming a doublet peak. This peak is consistent with the formation of carbon–carbon double bonds during degradation, which suggests that the Hoffman elimination reaction is active on the AMH-PAD membrane. Similar spectra were obtained when the samples were analyzed in different locations of the membrane, ensuring even chemical decomposition. A second new peak is observed around 1760 cm^{-1} . The location of this new peak is extremely close to that expected from the R–C–OH functional, which is consistent with nucleophilic attack. When the AMH-PAD membrane was soaked in 0.5 M Na_2CO_3 /0.5 M NaHCO_3 for 30 days, neither additional peak is observed. This agrees well with both the conductivity data and observed physical changes, suggesting that negligible chemical degradation occurs when the membranes are exposed to carbonate environments.

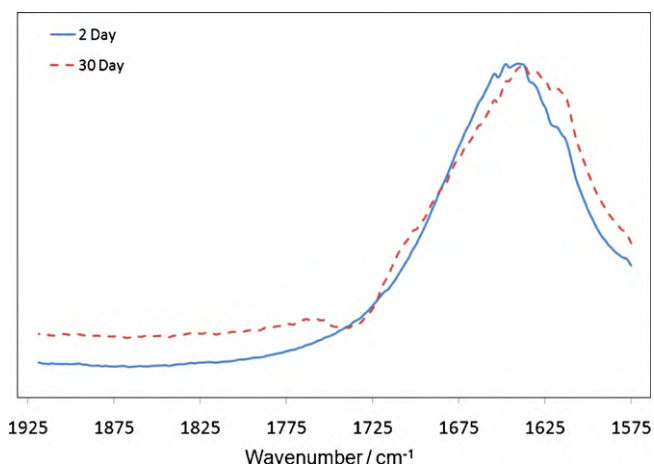


Fig. 10. ATR-FTIR spectra for AMH-PAD membrane soaked in 1 M KOH for (A) 2 days and (B) 30 days.

4. Conclusions

The effect of hydroxide and carbonate alkaline environments on chemical stability and ionic conductivity was investigated in commercially available anion exchange membranes. Highly alkaline environments caused a considerable ionic conductivity decrease, believed to be due to the nucleophilic attack and Hoffman elimination mechanisms. A mild hydroxide alkaline environment had no effect on membrane ionic conductivity; the low concentration of strong nucleophiles diminishes the possibility of stationary cation sites being degraded. The presence of carbonate and bicarbonate decreases the ionic conductivity due to the larger size of these anions compared to hydroxide. However, these weak nucleophiles create a low pH environment that does not cause chemical degradation, as observed by the constant ionic conductivity over time. Therefore, a local decrease in pH will increase electrolyte durability.

This work suggests that the AEM fuel cell operating on the carbonate cycle is a promising alternative to the traditional HEMFC fuel cell. The carbonate anion provides a lower localized pH than hydroxide, extending the operational lifetime of commercially available anion exchange membranes. However, there are still issues to overcome for efficient operation of room temperature AEM fuel cells operating on the carbonate cycle. First, the conductivity of carbonate in solid electrolytes needs to be increased. Second, electrocatalysts that allow for the selective formation of carbonate over hydroxide at the cathode under fully hydrated conditions must be attained, since hydroxide formation is preferred on all known catalysts under humidified conditions. Finally, it is unclear what effect the carbonate anions will have in the H_2 oxidation in the AEM fuel cell.

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