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Influence of different parameters on total fluoride concentration evaluation in ex-situ chemical degradation of nafion based membrane

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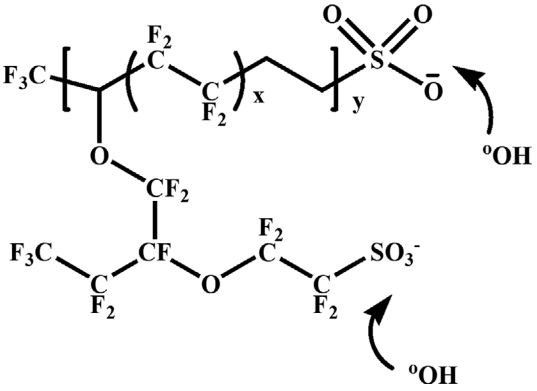
Abstract−The impact of different parameters on the chemical degradation of the Nafion polymer electrolyte membrane was investigated in detail under different concentrations of Fenton solution. As a consequence of chemical degradation, the performance and durability of the perfluorosulfonic acid-based electrolyte membrane in fuel cells was studied. Quantitative estimation of fluoride emitted after chemical degradation of the electrolyte membrane is done by an ex-situ fluoride emission rate-test using a potentiometric with an ion-selective electrode. The concentration of fluoride ions is easily affected by several external factors, such as total ionic strength, pH, temperature, and stirring speed, which causes many errors while reporting the fluoride concentration. Furthermore, the micromorphology of recast Nafion membranes before and after FER rest was thoroughly examined by scanning electron microscope (SEM) and X-ray photoelectric spectroscopy. Here, we report the influence of several external parameters over total fluoride concentration during the estimation of fluoride concentration for the proper correlation of the rate of chemical degradation in polymer electrolytes. This systematic study is beneficial for removing errors while measuring fluoride concentration and removing the discrepancy present in FER results reported in the literature.

Keywords: Fuel Cell, Nafion, Durability, Chemical Degradation

INTRODUCTION

Polymer-electrolyte membrane fuel cells (PEMFCs) are capable of being clean power sources for transportation and electricity [1-5]. Though, the extensive application of this clean-energy tool is still vulnerable to the durability problems of fuel cell electrolyte membrane [6]. As such, membrane durability, to some extent, governs the durability of PEMFCs. The sulfonic and carboxylic functional groups (Scheme 1) present on the perfluoro backbone act as proton-conducting paths and are found to be a starting point for the chemical degradation of membranes [5,6].

Chemical degradation of PFSA membranes involves radical-induced decomposition of the polymer structure. The degradation of polymer electrolytes leads to a reduction in cell performance and lifetime. The chemical degradation finally results in pin-hole formation of PEMs resulting in fuel cross-over decreasing cell efficiency. Additionally, this tearing of the membrane leads to the gradual reduction of ionic conductivity, an increase in the total cell resistance, and the reduction of voltage and loss of output power [9-11]. The process of chemical degradation is not yet fully understood. Currently, the extent of degradation is evaluated by the emission of fluoride ions, which are readily quantified with the help of fluoride ion-selective electrodes [12-15]. The fluoride electrode consists of a sensing element in contact with a solution containing fluoride ions, and an electrode potential develops across the sensing element. The measured potential corresponding to the level of fluoride ion in a solution is described by the Nernst equation [16]:



Scheme 1. Scheme showing the radical attack resulting in degradation of Nafion membrane.

$$E=E_o+S\times\log(a) \quad (1)$$

where E and E_o are the measured electrode potential and a reference potential, S and (a) are the slope of electrode and activity of fluoride ion activity in aqueous solution, respectively. The activity or effective concentration of free fluoride ion in solution is related to the free fluoride ion concentration C_{F^-}, by the activity coefficient γ_{F^-}:

$$a=\gamma_{F^-}\bullet C_{F^-} \quad (2)$$

Ionic activity coefficients are variable and largely depend on total ionic strength, pH, temperature, and Fe^{2+} concentration in the Fenton solution. To understand the rate and extent of membrane deg-

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radation, it is important to precisely control the above-mentioned parameters to correctly measure the total fluoride emission concentration.

Hence, the purpose of this study was to systematically investigate the effect of several external parameters, such as pH, stirring speed, size of the membrane, membrane thickness, concentration of Fenton solution, and annealing temperature over the chemical degradation. These factors are vital for fluoride concentration measurement and should be properly fixed while reporting fluoride ion concentration. Generally, these thermodynamic factors were never controlled and monitored closely in previous Ex-situ FER measurements, which affects the reliability and reproducibility of the reported studies. Consequently, a series of variable results were reported for Nafion through a separate research study. This systematic study is beneficial for removing errors while measuring fluoride concentration. Due to the discrepancies present, it is very difficult to compare the Nafion-based membrane durability of one study with another in the area of PEMFC.

EXPERIMENTAL

1. Experimental Materials

Nafion ionomer (1100 EW, 20 wt%) was purchased from Alfa Aesar Company. 30% of H_2O_2 aqueous solution was purchased from Dae-Jung chemicals, and $FeSO_4 \cdot 7H_2O$ was purchased from Sigma Aldrich.

2. Nafion Membrane Preparation

The Nafion membrane was synthesized using the solution casting technique. The Nafion perfluorinated resin solution (20 w/w % in water and 1-propanol, >1.00 meq/g exchange capacity) was used. 10 g of Nafion solution was directly cast on Teflon film using a doctor blade (Model number- Imoto 1117/200MM). The resulting cast solution was dried in a stepwise manner. First, the temperature was slowly raised to 60 °C where it was held for two hours, then at 80 °C for two hours to bring out homogeneous and uniform drying of the polymer membrane. Finally, thermal annealing was performed at 100 °C and 160 °C for 30 minutes each. The digital micrometer was utilized to measure the thickness of the membrane and the thickness of all membranes was ~25±1 μm. The membrane obtained was used for further studies.

3. Fluoride Emission Test

All the potential measurements were at room temperature using a digital pH/mV meter (Metrohm AG). A combination electrode was used for pH measurements. The potential measurements with the membrane electrode were carried out using saturated calomel as the reference electrode. The fluoride meter was calibrated each time before measurement using two standard fluoride concentrations, and the slope of the calibrated curve lies in the range of ~−54 to −60 mV per decade. The ex-situ durability test was performed for 24 hours using 10 ppm Fenton solution (10 wt% H_2O_2 solution and 10 ppm Fe^{2+}) at room temperature. The amount of fluoride released into Fenton's solution was determined with a fluoride ion meter. Total ionic strength adjustment buffer (TISAB-III) was added to all collected solutions to provide a constant ionic strength (~1 M). The fluoride release of the membranes (mg g^{-1}) was expressed by the following equation:

$$\text{Fluoride release} = \frac{[F^-] \times V_{solution}}{m_{dry}} \tag{3}$$

where $[F^-]$ is the measured fluoride concentration (ppm), $V_{solution}$ is the volume of the Fenton's solution (ml), and m_{dry} is the initial dry weight of the membrane (mg).

4. Parameters for Fluoride Emission Test (FER) Measurement

Nafion perfluorinated resin solution (20 w/w % in water and 1-propanol, >1.00 meq/g exchange capacity) was used for preparing membranes for the present study. The pH of the solution was adjusted to 5 using ammonium hydroxide. The membrane weight taken for performing the FER reaction was 200 mg and the Fenton solution volume taken was 200 ml (30% H_2O_2 solution and 10 ppm Fe^{2+}) in a 250 ml glass beaker. The Fenton solution concentration selected was 10 ppm. The reaction temperature was 80 °C for performing the FER study. The stirring speed while measuring fluoride solution was 50 rpm. For measuring fluoride concentration 50 ml of solution was taken out from the main reaction solution and a total ionic strength adjustment buffer (TISAB-III) of 5 ml was added. The sample was annealed at 160 °C for 30 minutes before FER measurement. The thickness of all the membranes was ~25± 1 μm.

RESULTS AND DISCUSSION

The cumulative fluoride emission rate for the Nafion membrane was studied by varying several parameters, such as the effect of pH, stirring speed, size of the membrane, the concentration of the Fenton solution, and annealing temperature.

The pH of the fluoride-containing solution is an important factor that can affect the quantitative estimation of fluoride concentration. The ionic form of fluoride ions is sensitive to the pH of the solution. To precisely detect the emission of fluoride ions, a concentration of fluoride ions was studied by varying the pH range from 2 to 5 at 25 °C and 80 °C. The FER experiment was performed for 24 hours and after the completion of the reaction, the pH was changed in the range of 2-5 while keeping other parameters constant. The pH adjustment of the solution was done by using dilute

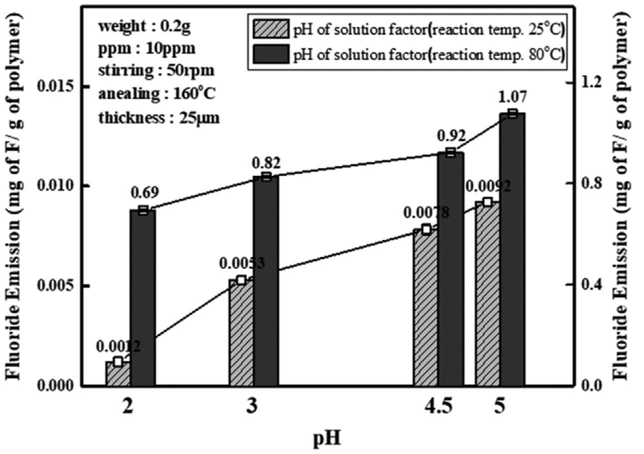

Fig. 1. Effect of pH on fluoride emission rate measurement at 25 °C and 80 °C.

ammonium hydroxide and hydrochloride solution. Fig. 1 shows the effect of pH on the fluoride concentration emission. It was found that with an increase in pH from 2 to 5 the value of the fluoride concentration also changed from 0.0012 mg/g to 0.0092 mg/g for 25 °C and from 0.69 mg/g to 1.07 mg/g for 80 °C reaction condition. This variation in fluoride concentration by changing pH indicates that the transition in the ionic form of the fluoride ion may be taking place in acidic conditions to HF, H_2F_2 and HF_2^- [12]. The change of fluoride ion in other complexions in acidic condition results in deviation in actual fluoride concentration and it cannot be detected by fluoride selective electrode. Additionally, when the pH level is below 3 the concentration of fluoride detected is much lower than the actual value. This sharp drop in fluoride concentration detection may also result from a decrease in radical species at this pH, which limits the effective radical attack on the membrane. At a pH level below 3, the radical generation reaction could be slowed down because hydrogen peroxide can probably be stable by acquiring a proton to form an oxonium ion such as $H_3O_2^+$ in Eq. (4):

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \tag{4}$$

Thus, conversion of hydrogen peroxide to its electrophilic oxonium ion substantially reduces the reactivity, and $H_3O_2^+$ reacts very slowly with ferrous ion. Consequently, the radical generated is much lower than expected, which may affect the FER study and a deviation will be observed in the actual fluoride ions concentration.

It was found that the pH of the solution should be fixed in the range of pH 5 to detect the precise concentration of the fluoride ions, as at this pH there is no chance for fluoride complex compound forms such as HF, H_2F_2, and HF_2^-. An adequate amount of radical species will be generated for effective radical attacks during the FER test.

To study the effect of an increase in the size of the film on fluoride emission concentration, experiments were conducted employing Nafion membrane doses ranging from 0.2 to 1.0 g. The results are presented in the Fig. 2(a), where the concentration of fluoride ion emitted is lower for the higher weight of Nafion film. The decrease in fluoride ion concentration with an increase in the weight of membrane may occur because the C-F bond available may not be effectively utilized or participate in Fenton reaction for 10 ppm Fenton solution at the higher weight of membrane in comparison to lower membrane weight. Therefore, it might be possible that the evolution of fluoride ions decreases as membrane weight increases. Although the amount of the C-F bond increases, the amount of radical remains constant. Consequently, effective radical attack decreases with an increase in membrane amount, resulting in lesser fluoride emission. Thus, from our measurement, we obtained the membrane amount to 0.2 g to get a reliable scavenging interaction for 10 ppm of Fenton solution. Four different membranes having the major difference between each membrane being thickness was evaluated towards FER test. The membrane thickness and its initial fluoride emission are plotted in Fig. 2(b). The fluoride ion release rate was measured using an ion-specific electrode to indicate the chemical degradation rate of the membrane. In Fig. 2(b), the membrane having a thickness of 70 μm has a higher FER value, ranging from 1.37 and 0.012 mg/g than membrane having thickness 50, 25, and 10 μm at 80 and 25 °C. The FER value for membrane having thicknesses 50, 25, and 10 μm are 1.065 and 0.0092, 1.04 and 0.0055 and 0.86 and 0.0069 mg/g. The obvious distinction of the FER is between four different membranes having different membrane thickness, which may lead to different hydrogen permeability during fuel cell operation condition. Thus, it can be correlated that the production of fluoride ions after interaction with hydroxyl radicals and hydroperoxyl radicals increases with an increase in membrane thickness.

The effect of Fenton solution concentration on the degradation of the Nafion membrane was evaluated by varying the Fenton solution concentration from 10 to 50 ppm using the 10% hydrogen peroxide solution as shown in Fig. 3. The concentration of fluoride emission was found to increase with increasing Fenton solution concentration up to 50 ppm, suggesting the formation of more radical ions at higher Fenton concentration, resulting in more membrane degradation. The degradation of the Nafion membrane usually takes place by hydroxyl and hydroperoxyl radicals generated by the reaction of Fe^{2+} or Fe^{3+} with hydrogen peroxide [19] in Eqs. (5) and (6):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + HO^- \tag{5}$$

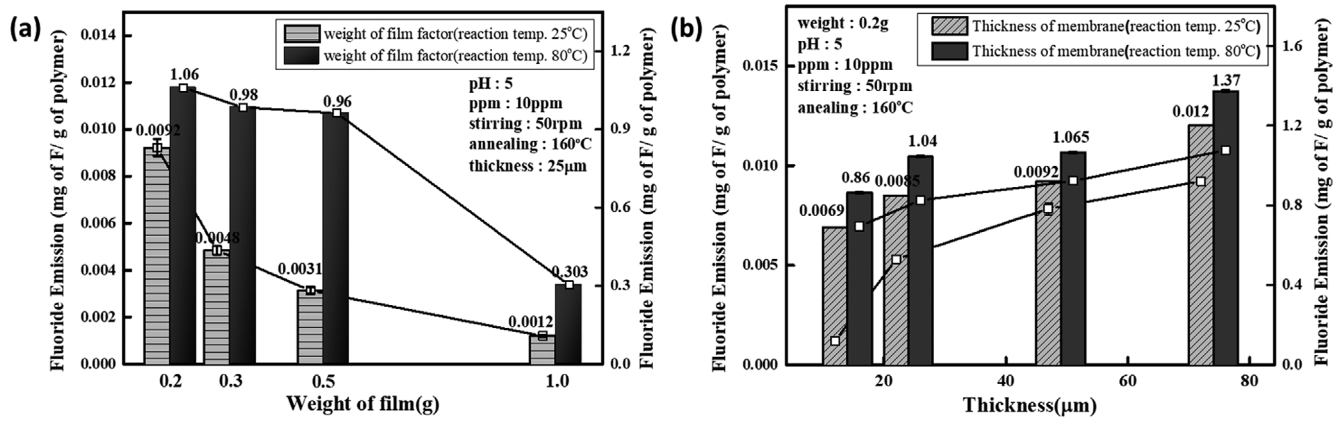

Fig. 2. (a) Effect of weight of Nafion membrane on fluoride emission rate measurement and (b) effect of Nafion membrane thickness on fluoride emission rate measurement.

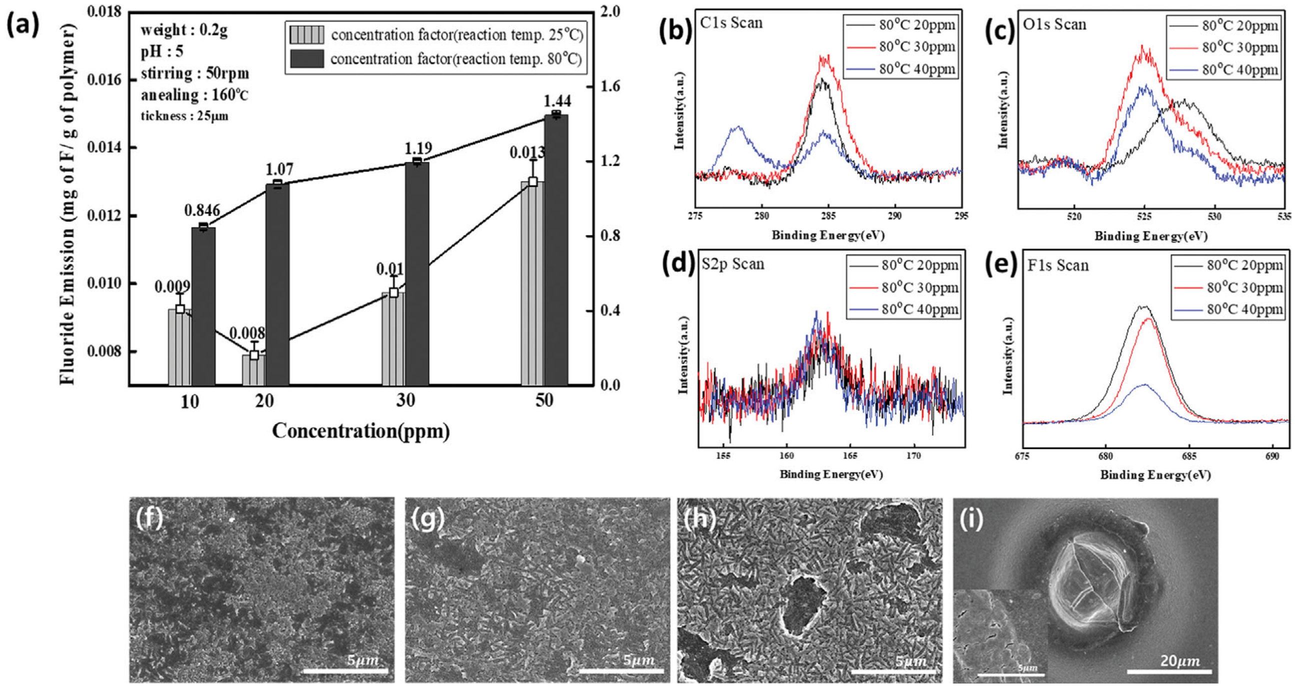

Fig. 3. (a) Effect of fenton concentration on fluoride emission rate measurement 25 °C and 80 °C, (b)-(e) XPS C1s, O1s, F1s and S 2s spectra of different concentration of fenton solution (20, 30 and 40 ppm) at 80 °C and (f)-(i) FESEM image nafion membrane after FER with different concentration of fenton solution (10, 20, 30 and 40 ppm) study at 80 °C.

$$Fe^{3+}+H_2O_2\rightarrow Fe^{2+}+HOO^{\bullet}+H^{+} \tag{6}$$

According to the obtained results, 10 ppm was selected as the concentration value and it was used in the rest of the study because the maximum concentration of radicals generated in fuel cell operating conditions cannot exceed the radical concentration generated from 10 ppm solution. When the FER experiment is performed in high Fenton solution concentration, there is more chance of experimental error due to the existence of Fe^{3+} in Fenton’s reagent [20]. The impact of Fenton solution concentration (10, 20, 30, and 50 ppm) on the morphological damage of Nafion membrane was analyzed using FESEM at 80 °C (Fig. 3(f)-(i)). The monitoring of membrane damage by the pinhole and crack formation is a very crucial step for monitoring gas leakage problems leading to catastrophic cell failure. Fig. 3(f)-(i) present the FESEM image of Nafion membrane after FER experiment at different Fenton concentration. Some cracks are observed in the Nafion after the reaction and the number of cracks increases with an increase in Fenton solution concentration. The crack is very small in the case of a 10 ppm solution; however, the crack is around 20 μm in a 50 ppm solution. This behavior can be related to extent of oxidation reactions with the amount of reactive oxygen with changing Fenton solution concentration. Furthermore, XPS analysis was performed to analyze the impact of the concentration of Fenton solution on the C-F bond and structure of the Nafion membrane. Fig. 3(b) shows the C 1s core-level spectra of Nafion membrane at different Fenton concentrations. The peaks at around binding energy value ~284.2 eV and 278.2 eV are the characteristic peaks of carbon present in CF$_2$ and C-CF or C-C configuration. It was seen that with increasing the concentration of Fenton solution the intensity of the peak at 284.2 eV decreased, subsequently suggesting the oxidation of fluorocarbon (-CF$_2$n) backbone. On the contrary, the intensity of the peak at 278.2 eV increased, indicating that the relative concentrations of C-C or C-CF configurations increased with increasing Fenton solution concentration. This data suggest that fluorine atoms are depleted from the Nafion backbone with increasing Fenton solution concentration. Fig. 3(c) shows the O1s core-level spectra for the Nafion membrane at different concentrations. With increasing Fenton solution concentration, it was observed that the binding energy peak shifted to lower values. This shift in peak position may arise from two factors: the formation of the oxo-bonded iron complex along with the loss of -SO$_3$H groups from the membrane on the membrane surface. Fig. 3(d) shows the S$_{2p}$ element scan of different membranes at around 163 eV, and the intensity of this peak shows very minute variation with peak position remaining unchanged with increasing Fenton solution concentration. This pattern suggests loss of sulfur due to oxidation via radical at higher Fenton concentration. The core-level spectra of F$_{1s}$ for different membrane is shown in Fig. 3(e), showing a peak at binding energy value of 684 eV. It can be seen that peak intensity substantially decreases with an increase in Fenton solution concentration, suggesting a decrease in fluorine atomic content on Nafion background with the increase in Fenton solution concentration. Thus, from the above data, it can be concluded that at higher Fenton solution concentration environment, the radicals generated may attack fewer active bonds such as C-O and other side groups in the polymer. So, to remove this interfering side reaction the Fenton solution, concentrations must also be kept rather low so that the degradation mechanisms (or pathways) can be considered as representative of those occurring during fuel cell operation. A Fenton solution

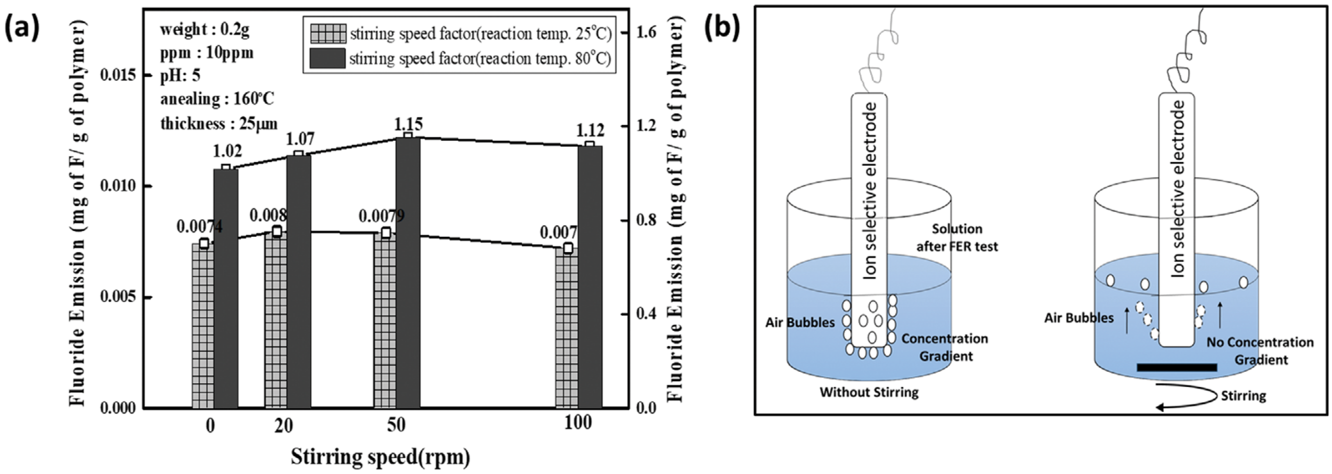

Fig. 4. (a) Effect of stirring speed on fluoride emission rate measurement at 25 °C and 80 °C and (b) schematic representation of a gas bubble attached to fluoride selective electrode at stationary state and stirring state.

concentration of 10 ppm should be applied for obtaining the most effective and reliable result for defining the durability of electrolyte membrane using the ex-situ FER approach because in 10 ppm of solution the amount of Fe^{2+} is appropriate to efficiently catalyze the decomposition reaction of H_2O_2 in free radicals and ensure significant membrane degradation without producing other interfering reactions.

Furthermore, a stationary condition for emitted fluoride concentration measurement is the most unfavorable condition for FER measurement because air bubble formation takes place around the measuring electrode, which causes significant deviation in concentration measurements. The results are shown in Fig. 4(a). The figure shows the impact of stirring speed while performing FER at 25 °C and 80 °C. It was observed that stirring has a very small impact on the FER result and this impact can bring around 0.04% and 4.9% error at 25 °C and 80 °C in the results. Such moderate speed gives a good homogeneity for the mixture suspension, while high speeds may lead to a swirling flow with surface vortex formation and poor F^- ions distribution. Thus, for obtaining a reliable and reproducible FER result the stirring speed should be maintained above 50 rpm. The results discussed above and the possible reasons behind them have been elaborated on in Fig. 4(b). When the fluoride ion-selective electrode was dipped into a fluoride-containing Fenton solution, air bubbles were formed at the interface of the fluoride selective electrode, resulting in the formation of the concentration gradient. These are bubbles of gases that form a partially negatively charged cloud around the electrode. Due to this partial negative cloud, electrostatic interactions occur between the negatively charged electrode and negatively charged F^- ions in the solution. As a result of this interaction, a concentration gradient is created that limits the kinetics of fluoride interaction with electrodes, which overall leads to a deviation from the actual fluoride ion concentration detection as shown in Fig. 4(b). Hence, to overcome this issue, fluoride concentration is measured while stirring. As a result of stirring while measuring, forced convection is created at the electrode-solution interface, which will remove the phenomenon of air bubble formation. Consequently, no concentration gradient is developed and the fluoride concentration detected is reliable and reproducible in every sense. Hence, we have maintained a stirring speed above 50 rpm as the selected stirring speed for all measurements.

It has been already reported that membrane annealing at high temperature has a significant impact on water channel free volume, backbone mobility, crystallinity, and proton conductivity. From point of view of the high quantity of water uptake, mechanical property, and proton conductivity, high-temperature annealing of Nafion membranes is helpful for their application in the industrial PEMFCs. However, no report suggests the impact of membrane annealing on chemical durability [21]. Fig. 5(a) shows the relationship between fluoride emission rates with varying annealing temperatures of the membrane from 100 to 160 °C at 25 °C and 80 °C. Nafion membrane annealed at 100 °C has a lower fluoride emission rate in comparison to 150 °C annealed Nafion film, and a similar trend is obtained when the reaction is performed at 25 °C and 80 °C. This result suggests that the fluoride emission rate is dependent on annealing temperature and it increases with an increase in temperature. It was further found that the fluoride emission rates had a very small decrease or almost no change as the temperature was increased from 150 °C to 160 °C. Thus, we fixed 160 °C as the annealing temperature for FER measurement. The results discussed above and the possible reasons behind them have been elaborated on in Fig. 5(b). Being thermally annealed above this transition temperature, Nafion molecular chains retain sufficient mobility to rearrange and pack themselves to form crystallites. The crystallites acting as physical cross-links always reduce the mobility of Nafion molecular chains, thereby suppressing the swelling and water uptake of overall Nafion membranes. During the water adsorption process, water molecules may prefer to bind to the sulfonic acid groups ($-SO_3H$) via hydrogen bonds to form the hydronium ions ($-SO_3^-(H_3O)^+$). In the present study, results suggest that FER increases with an increase in annealing temperature, which may be attributed to the low quantity of water inside the water channel or it can be said that the degree of dryness is much higher around the sulfonic acid group. Thus, radical ions can easily approach the polar

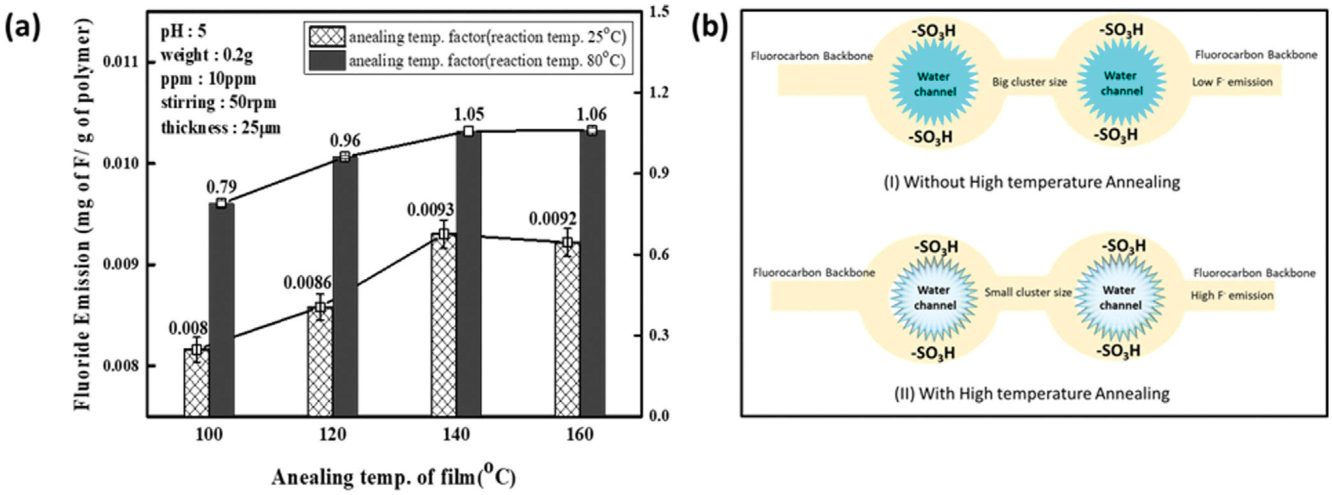

Fig. 5. **(a) Effect of annealing temperature on fluoride emission rate measurement and (b) schematic representation of water channel unannealed and annealed nafion membrane.**

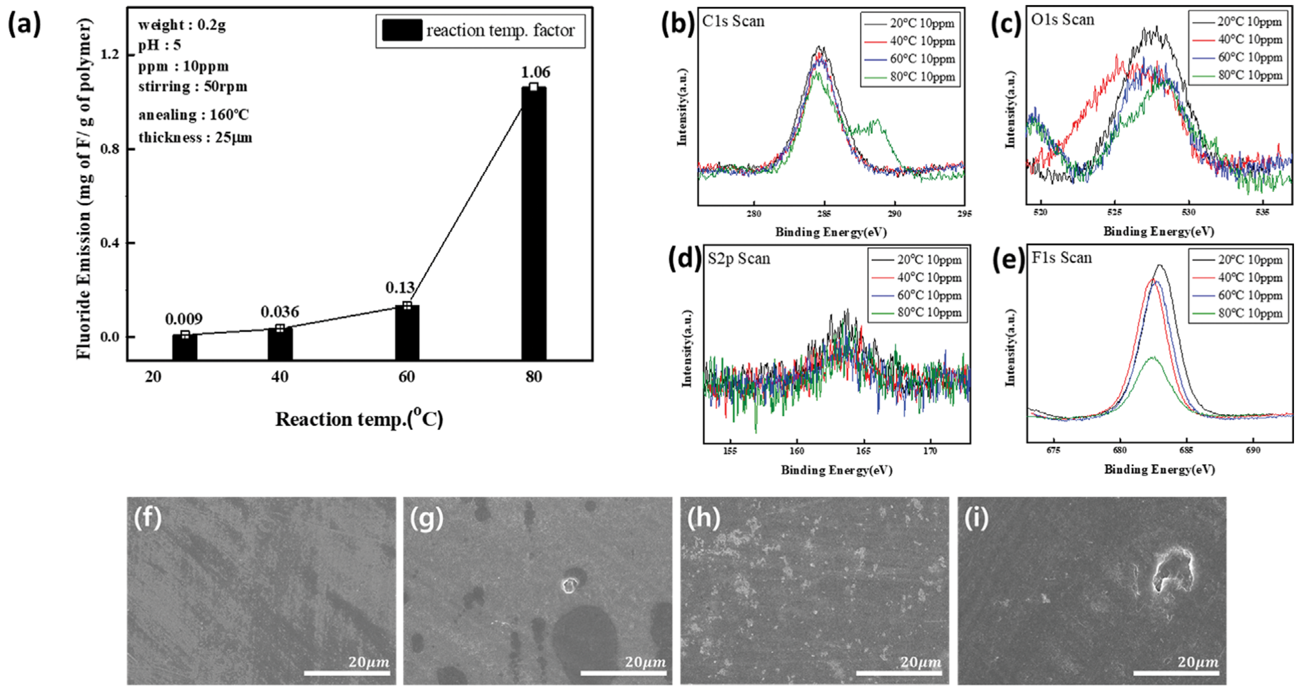

Fig. 6. **(a) Effect of reaction temperature on fluoride emission rate measurement (b)-(e) XPS C1s, O1s, F1s and S 2s spectra of different reaction temperature (25 °C, 40 °C, 60 °C and 80 °C) for 10 ppm fenton solution and (f)-(i) FESEM image nafion membrane after FER with of different reaction temperature (25 °C, 40 °C, 60 °C and 80 °C) for 10 ppm fenton solution.**

group and the rate of chemical degradation is much higher as compared to the film annealed at low temperatures [22]. Whereas in low temperature annealed sample the water content inside the channel is high and the polar group is covered with a higher number of water molecules. As a result, the radical ions cannot easily approach the sulfonic group, resulting in a decrease in fluorine emission. This annealing temperature, however, helps to increase the polymer crystallinity, which improves the mechanical strength and conductivity significantly, as it brings the membrane to a stable equilibrium state [23].

The effect of reaction temperature on the fluoride emission rate study of the Nafion membrane was studied at 25 °C, 40 °C, 60 °C, and 80 °C with 10 ppm Fenton solution at pH=5.0. The results are demonstrated in Fig. 6. It was found that temperature exerts an intense effect and the rate of fluoride emission was accelerated drastically with a temperature rise. The concentration of fluoride emitted rose from 0.009 mg/g to 1.06 mg/g as a result of increasing temperature from 25 °C to 80 °C after 24 hours. Typical XPS studies of Nafion membrane after performing FER study with changing temperature were performed at 25 °C to 80 °C. The C1s core level XPS spectra (Fig. 6(b)) for the 25 °C samples showed less modification compared to the XPS spectrum at 80 °C, suggesting a lower degree of degradation. However, C1s core level XPS spectra of 80 °C showed a reduction in the intensity of carbon bands, suggesting enhancement in polymer degradation with increasing temperature. Fig. 6(c) shows the O1s core-level spectra for the Nafion membrane at the different reaction temperatures. With increasing reaction temperature, the binding energy peak shifted to lower values. This shift in peak position suggests the loss of $-SO_3H$ groups from the membrane on the membrane surface. Fig. 6(d) shows the S_{2p} element scan of the different membrane at around 163 eV, and the intensity of this peak showed very minute variation with peak position remaining unchanged with increasing reaction temperature. This pattern suggests loss of sulfur due to oxidation via radical at the higher reaction temperature. The core-level spectra of F_{1s} for different membrane is shown in Fig. 6(e), showing a peak at binding energy value of 688 eV. It can be seen that peak intensity decreases drastically with an increase in reaction temperature, suggesting enhancement in Nafion background degradation with an increase in reaction temperature. Fig. 6(f)-(i) presents the FESEM image of the Nafion membrane after the FER experiment at the different reaction temperatures. Morphology evolution differs considerably with increasing temperature in comparison to unreacted Nafion membrane. The size and appearance of cracks increase with an increase in reaction temperature. This significant enhancement of fluoride emission, which is directly proportional to Nafion membrane degradation, is mainly arising because higher temperatures increase the rate of reaction for the Fenton reaction. By increasing the temperature of the Fenton solution, hydrogen peroxide reacts more rigorously with ferrous ions, increasing the generation of oxidizing species such as $HO^{\cdot}$ and $HOO^{\cdot}$ radical.

CONCLUSION

This study revealed that the detection of fluoride concentration is highly sensitive to the solution's total ionic strength. The ionic strength is dependent on several parameters, such as pH, stirring speed, size of the membrane, the concentration of Fenton solution, and the annealing temperature. To obtain a reliable and reproducible fluoride emission rate result, it is important to fix these parameters in the area of PEMFC to examine the durability of the electrolyte membrane. The used measurement conditions for the fluoride emission experiment were: the solution pH should be fixed at 5 to 5.5, the weight of membrane 0.2 g, Fenton solution concentration 10 ppm, stirring speed 50 rpm, 80 °C for reaction conditions, and annealing temperature of 160 °C. It is essential to have the above-provided parameters to be seriously considered to evaluate the lifetime of the Nafion-based electrolyte membrane, and this study will help to decrease the discrepancy present in the FER result reported in the literature in the area of PEMFC.

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