Stability of SPEEK/Cloisite®/TAP nanocomposite membrane under Fenton reagent condition for direct methanol fuel cell application


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1. Introduction

Polymer electrolyte membrane (PEM) is one of the core components in the direct methanol fuel cell (DMFC). It serves as the heart of DMFC operation, where it connects the anode and cathode half-cell by allowing protons to flow from the anode to cathode but blocks the electrons current, while simultaneously preventing crossover of the reactant and fuel, thus keep the anode and cathode electrode separated [1]. High proton conductivity and low methanol permeability are essential characteristics for PEM in DMFC operation in order to develop a high energy and high efficiency DMFC system [2]. The most widely use PEM in the DMFC system is the perfluor sulfonic acid (PFSA) membrane as it shows excellent performance and stability in the PEMFC operation [3]. However, due to electro-osmotic drag phenomenon, the methanol fuel has high tendencies to permeate through the PFSA membrane, thus reduce the efficiency of the DMFC system up to 35% [4]. In addition, the high production cost of PFSA membrane affects the overall production cost of DMFC system, thus makes the DMFC technology unappealing for mass production [5]. To solve this problem, the non-fluorinated, hydrocarbon-based polymeric membranes have been extensively developed and modified as an alternative to replace the PFSA membrane due to their superior chemical and thermal stability, and low cost [6,7]. A nanocomposite membrane developed by Juhana et al. [8] using SPEEK hydrocarbon-based polymer incorporated with Cloisite® 15A particles (a modified montmorillonite (MMT) organoclay) and 2,4,6-triaminopyrimidine (TAP) compatibilizer was able to outperform the commercial Nafion® 112 PFSA membrane in terms of proton conductivity and methanol permeability, and produce higher power output in the DMFC performance test. Hence, the SP/CL/TAP nanocomposite...
membrane holds a good potential to be developed as PEM for the DMFC system. Although the SP/CL/TAP nanocomposite membrane shows a better performance than Nafion® membrane in the DMFC application, so far, there is no extensive study has been done to evaluate the membrane’s durability and stability against the harsh DMFC system environment. It is crucial for the PEM to withstand severe conditions during the DMFC operation in order to achieve 5000 h operational lifespan as outlined in the United States Hydrogen Energy Program reports [9–11]. Various studies have been performed on the DMFC lifespan, which showed that the DMFC can operate up to 2000 h before its performance started to decline [6,12–16]. However, conducting the DMFC lifetime test is not practical due to lengthy testing time which consumes large resources [17]. Therefore, the accelerated stress test (AST) can become an alternative test to shorten the fuel cell lifetime test by accelerating the DMFC system and its components degradation for a short period of time [18–20].

Chemical degradation is one of the major contributors to the PEM faulting during DMFC operation. In DMFC system, partial reduction of oxygen gas (O₂) at the cathode side will form hydrogen peroxide (H₂O₂). Due to a highly acidic condition during DMFC operation, the iron back plate has high tendencies to corrode, thus formed the iron ion (Fe²⁺) at the anode side. The Fe²⁺ ion then will migrate along the water channel in the membrane to the cathode side and react with the H₂O₂ to form free radical [17]. A similar formation of the free radical also occurs in Fenton reagent solution, where the Fe²⁺ ion from iron salt will react with the hydrogen peroxide solution to form free radical [21]. For that reason, there is no doubt to employ the Fenton reagent test to replicate the free radical attack. The ultimate study is the correlation between the Fenton reagent test and DMFC lifetime test to predict the DMFC lifespan when SP/CL/TAP nanocomposite membrane is applied as its electrolyte.

2. Methodology

2.1. Materials

Poly ether ether ketone (PEEK) in powder form was obtained from Vitrex Inc., USA. Cloisite® 15A powder was obtained from Southern Clay Products, Inc. The PEEK and Cloisite® 15A were pre-heated in the ventilation oven at 80 °C for 24 h to remove the possible entrapped moisture. Ferrous sulphate (FeSO₄) salt was purchased from Dalian Jinshi Chemical Industry Ltd., China. Concentrated sulfuric acid (H₂SO₄) (95–97%) was purchased from QRex. 30% hydrogen peroxide (H₂O₂) solution was purchased from Merck. Dimethylsulfoxide (DMSO), 2,4,6-Triaminopyrimidine (TAP) in powder form, and Nafion® 117 membrane was purchased from Sigma-Aldrich, and used as received.

2.2. Preparation of SPEEK polymer

Sulfonation reaction was conducted using the concentrated H₂SO₄. 50 g of PEEK powder was used to prepare a 1000 mL sulfonated PEEK (SPEEK) solution. The 50 g of PEEK was poured bit by bit in stages into 1000 mL concentrated H₂SO₄ under stirring process at room temperature for 1 h to avoid agglomeration of SPEEK in the solution. The solution was then continuously stirred at 55 °C for 3 h to obtain SPEEK with 60–65% of the degree of sulfonation (DS). The SPEEK polymer was recovered by precipitating the acid polymer solution into a large excess of ice water. The resulted SPEEK polymer was filtrated and washed thoroughly with deionized water until the pH became 6–7. Finally, the SPEEK polymer was dried in the drying oven at 80 °C for 24 h.

2.2.1. Preparation of S/SPEEK membrane

For pristine SPEEK membrane preparation, 10 g of SPEEK polymer was added to 90 mL DMSO and stirred at 60 °C for 24 h. Then, the solution was cast on a glass plate with a casting knife to form a thin film. The resulting film was first dried in the open air for 6 h to settle down the solution into the half-solidified membrane. The membrane was then dried in ventilation oven for 24 h at 80 °C followed by another 6 h at 100 °C to remove any residual solvent completely. After that, the film was detached from the casting glass by immersing into the water. Then, the membrane was dried for another 3 days at 80 °C in the drying oven.

2.2.2. Preparation of SP/CL/TAP nanocomposite membrane

To produce SPEEK nanocomposite membrane, 10 g of SPEEK polymer, 0.25 g of Cloisite® powder, and 0.5 g of TAP powder were added into three different Schott bottles containing 60 mL, 15 mL and 15 mL of DMSO respectively. The solution was stirred separately for 24 h at 60 °C to ensure its homogeneity before mixing together to produce a single SPEEK/Cloisite®/TAP solution. The final 90 mL solution was vigorously stirred for 24 h at 60 °C to produce a homogeneous solution. The solution was cast on a glass plate with a casting knife to form a thin film. The resulting film was first dried in the open air for 6 h to settle down the solution into the half-solidified membrane. The membrane was then dried in the ventilation oven for 24 h at 80 °C, followed by another 6 h at 100 °C to remove any residual solvent completely. After that, the film was detached from the casting glass by immersing into the water. Then, the membrane was dried for another 3 days at 80 °C in the drying oven.

2.3. Fenton reagent: chemical degradation test

Before testing, the pristine SPEEK, SP/CL/TAP nanocomposite, and Nafion® membranes were treated in 1 M H₂SO₄ solution for 1 day at room temperature and subsequently rinsed with excessive water to remove any remaining acid on the film until the pH reach 6–7. The membranes were then dried for 24 h at 60 °C to remove the remaining moisture.

5 wt% of H₂O₂ and various loading of FeSO₄ salt were mixed together to prepare the Fenton Reagent solution. Four Fenton reagent solutions were prepared with different FeSO₄ concentrations: 0.8 ppm, 3.0 ppm, 12.0 ppm and 50.0 ppm. The Fenton reagent test was conducted at room temperature. The mass of all membranes was identified before immersing in the Fenton Reagent solution for 6 h. After 6 h, the membranes were taken out from the solution and rinsed with excessive water to stop the degradation process. The degraded membranes were then dried for 24 h at 60 °C and weighed prior the characterization. The residual weight of the
membranes was calculated using Equation (1).

\[
\text{Residual weight (\%) = \frac{\text{Weight after the Fenton test (g)}}{\text{Weight before the Fenton test (g)}} \times 100%}
\]

(1)

The test was repeated for 12, 24, 48, and 96 h using new Fenton reagent solution. The un-degraded pristine SPEEK, SP/CL/TAP nanocomposite, and Nafion® membranes were used as comparison. Table 1 summarizes the procedure of the Fenton reagent testing.

2.4. Characterizations of SP/CL/TAP nanocomposite membrane after Fenton reagent test

The morphology behaviour of pristine SPEEK and SP/CL/TAP nanocomposite membrane was investigated using a field emission scanning electron microscope (FESEM) (JSM-7600F, JEOL USA, Inc.). The membrane specimen was vacuum sputtered with a thin layer of gold before FESEM examination. The images of the specimen surface were taken at the magnification between 500 \times 10,000 \times .

Tensile strength test was conducted using 2.5 kN universal test machine (LRXPLUS-E, Lloyd Instruments Ltd.). Five samples with each 2.5 cm length and 0.5 cm width were prepared for the test. The samples were placed between the grips of the testing machine and stretched at 1 mm/min rate. The tensile strength of the samples was calculated using Equation (2).

\[
\text{Tensile strength, } \sigma \text{(MPa)} = \frac{\text{Load (N)}}{\text{Gauge width (mm)} \times \text{Membrane thickness (mm)}}
\]

(2)

The water contact angle was conducted using the VCA Optima Surface Analysis System (AST Products Inc.). Samples with a dimension of 5.0 cm \times 1.5 cm were prepared for this test. The sample was placed on the clip specially designed for flat sheet membrane and slightly stretched to form evenly flat membrane surface. A drop of distilled water was dropped onto the membrane surface using a micro syringe (Hamilton Company). Three measurements were taken from different spots on the sample and the average values were calculated and presented.

Fourier transform infrared spectroscopy (FT-IR) was conducted using Nicolet Magna 560 IR Spectrometer. The degraded SPEEK nanocomposite membrane was cut into small pieces to form powder-like specimen for FT-IR analysis. The specimen was examined in the transmittance mode with wave number range of 4000 to 700 cm\(^{-1}\).

Water uptake was used to determine the membrane’s capacity to retain water in its matrices. Prior to the test, the membrane was dried in an oven at 60 °C for 48 h to remove the remaining moisture. The membrane was weighed before being immersed in the water container overnight at room temperature. After that, the membrane was weighed to determine its weight in the wet condition. The moisture on the surface of the membrane was blotted dry using absorbent paper before the weight measurement. The water uptake (WU) of the membrane was calculated using Equation (3) as shown below:

\[
\text{WU (\%)} = \frac{\text{Wet weight, } W_w (g) - \text{Dry weight, } W_d (g)}{\text{Dry weight, } W_d (g)} \times 100\%
\]

(3)

The transverse proton conductivity of the membrane sample was measured by Solatron 1260 Impedance instrument over a frequency range of 1 Hz–10^7 Hz with 50 mV–500 mV oscillating voltage. The hydrated membrane was sandwiched between two stainless steel block electrodes. The conductivity, \(\sigma\), of the sample in the transverse direction was calculated from the impedance data, using the relationship as follows:

\[
\sigma \text{(S/cm)} = \frac{d \text{(cm)}}{R(U) \times S \text{(cm}^2\text{)}}
\]

(4)

where \(d\) and \(S\) are the thickness and surface area of the membrane sample respectively, and \(R\) was derived from the low intersection of the high frequency semi-circle on a complex impedance plane with the \(Re(Z)\) axis. The resistance of each membrane sample was obtained by using an interpolation method in the Frequency Response Analyser (FRA) software.

Methanol permeability was used to determine the barrier properties of membranes towards methanol migration. A diaphragm diffusion cell was used in this test, where two compartments with one contain methanol solution and another one

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The Fenton reagent concentration and testing time.</th>
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<tbody>
<tr>
<td>Membrane</td>
<td>(\text{H}_2\text{O}_2) concentration (wt. %)</td>
</tr>
<tr>
<td>Pristine SPEEK</td>
<td>5</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>SP/CL/TAP Nanocomposite</td>
<td>5</td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Nafion® 117</td>
<td>5</td>
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<td></td>
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</table>
contains water was separated with the tested membrane. The compartment A (VA = 50 cm³) of the permeation cell was filled with aqueous methanol solution with a concentration of 1 mol/L while compartment B (V_B = 50 cm³) was filled with water. The nanocomposite membrane was first immersed in the water for 24 h to hydrate it. After 24 h, the hydrated membrane was measured several times to get an average membrane thickness. The membrane (A = 7.07 cm²) was then clamped between the two compartments. The methanol molecules were let to diffuse along the concentration gradient through the membrane into the opposite compartment of the permeation cell. Both compartments were continuously stirred throughout the test. 1 mL sample from the compartment B was taken for every 30 min to determine the methanol concentration using the Pelkin Almer Flexar Liquid Chromatograph. The test was run for 3 h at room temperature. The methanol permeability, P was calculated using the formulation as shown below:

$$P\left(\text{cm}^2/\text{s}\right) = \alpha(\text{mol/L-s}) \times \frac{V_B(\text{cm}^3)}{A(\text{cm}^2)} \times \frac{L(\text{cm})}{C_A(\text{mol/L})}$$  \hspace{1cm} (5)

From Equation (5), $\alpha$ is the slope of linear interpolation of methanol concentration in the compartment B at time t, $V_B$ is the volume of water in the compartment A, $A$ is the membrane cross-sectional area (effective area), $L$ is the membrane thickness, and $C_A$ is the concentration of methanol in the feed compartment (compartment A) at time t, $t_0$ is the time lag that related to diffusivity.

Membrane selectivity was chosen to evaluate the overall performance of the degraded membrane. Selectivity for the DMFC application can be calculated as the ratio of proton conductivity over methanol permeability as describe in Equation (6).

$$\text{Selectivity } \left(\text{S}/\text{s}/\text{cm}^3\right) = \frac{\text{Proton conductivity, } \sigma(\text{S/cm})}{\text{Methanol permeability, } P(\text{cm}^2/\text{s})}$$  \hspace{1cm} (6)

2.5. SP/CL/TAP nanocomposite membrane lifespan correlation

A correlation between the Fenton reagent test and DMFC lifetime test was developed to predict SP/CL/TAP nanocomposite membrane lifespan in DMFC operation. The concentration of the free radical exposed to membranes by the Fenton reagent test and DMFC lifetime test was calculated to correlate both tests. Based on the theoretical study done by Zhao et al. [22] and Ishimoto and Koyama [23], the OH⁺ radical is the most reactive and also is the main reason that causes the degradation of PEM during DMFC operation. Therefore, the concentration of the OH⁺ radical was used as a basis to correlate the Fenton reagent test and DMFC lifetime test.

The concentration of OH⁺ radical for Fenton reagent test was calculated using Equation (7), where $c_{OH^+}$ is the concentration of OH⁺ radical, $r_{OH^+}$ is the OH⁺ radical formation rate, and $t_{Fenton}$ is duration of Fenton reagent test conducted in seconds. The formation rate of OH⁺ radical is the product of reaction rate coefficient, $k$ multiply by the concentration of H₂O₂ and Fe²⁺ in mol/L (Equation (8)). Based on literature [24–27], the value of $k$ for the reaction between H₂O₂ and Fe²⁺ to form OH⁺ radical is 70 M⁻¹ s⁻¹.

$$c_{OH^+}(M) = r_{OH^+}(M/s) \times t_{Fenton}(s)$$  \hspace{1cm} (7)

$$r_{OH^+}(M/s) = k(M^{-1}s^{-1}) \times c_{H_2O_2}(M) \times c_{Fe^{2+}}(M)$$  \hspace{1cm} (8)

Due to the short lifetime of OH⁺ radical and its reactivity with fluorescent dye, direct detection of the OH⁺ radical during DMFC operation is not possible [28–30]. Therefore, theoretical OH⁺ radical formation rate from Shah et al. [31] modelling study was used in this study. Since there are no researches conducted to study the changes of OH⁺ radical formation rate during DMFC operation, it is assumed that the OH⁺ radical is increasing linearly with the DMFC operation time. Other than that, the DMFC lifetime test correlation curve developed in this study only considers the OH⁺ radical attack impact towards the DMFC degradation performance as there is no correlation coefficient developed for other DMFC degradation mechanism with DMFC operation time. Hence, based on those assumptions, the concentration of OH⁺ radical during DMFC operation was calculated using Equation (9).

$$c_{OH^+} = \frac{50\mu M}{s} \times t_{DMFC}(s) \hspace{1cm} (9)$$

3. Results and discussions

3.1. SP/CL/TAP nanocomposite membrane stability study

When the polymeric organic membrane is exposed to Fenton reagent solution, free radicals, which are formed from the iron ion and hydrogen peroxide reaction will attack the weak organic bonding within the polymeric chemical structure and cause the membrane to deteriorate and break apart [21]. The degraded part of the organic membrane will detach from the polymer chain, thus reduce the molecular weight of the polymer and the membrane’s weight. Therefore, weight residual of the membrane can be used as an early indicator to determine the stability of the polymer electrolyte membrane against the radical attack.

Fig. 1 shows the residual weight of pristine SPEEK, SP/CL/TAP nanocomposite, and Nafion® 117 membranes after exposing to the Fenton reagent solution for 96 h. In general, it can be clearly seen that the weight reduction trends for each membrane are consistent across all the Fenton reagent solutions, but reach higher magnitude as the concentration of the Fenton reagent concentration is increasing. Based on the results from Fig. 1, it can be summarized that the Nafion® 117 membrane shows lowest weight loss among the tested membranes, followed by the SP/CL/TAP nanocomposite membrane and lastly the pristine SPEEK membrane. The Nafion® 117 membrane can retain more than 90% of its weight after being degraded under 0.8 ppm Fenton reagent test for 96 h (92.7%). The Nafion® 117 membrane also can retain its final weight higher than other two membranes when the Fenton reagent concentration is increasing with 85.4%, 70.7%, and 41.4% of 3.0, 12.0, and 50.0 ppm Fenton reagents respectively. In theory, PFSA membrane is more robust as compared to the hydrocarbon-based membrane as it requires a higher energy to break the C–F bonding (−485 kJ/mol) as compared to C–H bonding (350–435 kJ/mol) [15]. Due to this factor, the Nafion® 117 membrane possesses higher resistance towards the radical attack and can retain its weight better than the SPEEK-based membrane under the Fenton reagent test.

In contrast, the pristine SPEEK hydrocarbon membrane shows the highest weight loss among the tested membranes. The pristine SPEEK membrane can only remain intact up to 48 h, 24 h, and 12 h in 0.8 ppm, 3.0 ppm, and 12.0 ppm Fenton reagent solutions respectively. At 50.0 ppm concentration, the pristine SPEEK fails to withstand the radical attack even up to 6 h of continuous testing. However, after adding Cloisite® inorganic particles into the SPEEK matrix, the resulting SP/CL/TAP nanocomposite membrane shows a better resistance towards the radical attack. The SP/CL/TAP
nanocomposite membrane can maintain its weight comparable to Nafton® 117 membrane up to 48 h for all the Fenton reagent concentration. After that, a distinct declination of residual weight can be observed from 48 to 96 h of testing. The residual weights of SP/CL/TAP nanocomposite membrane at 48 h were 96.4%, 93.6%, 88.1%, and 81.9% while the Nafton® 117 membrane residual weights were 96.2%, 92.4%, 84.9%, and 69.7%, at 0.8 ppm, 3.0 ppm, 12.0 ppm and 50.0 ppm concentration respectively.

Cloisite® is an inorganic material. Since the free radical only can degrade an organic compound, so Cloisite® particles are not affected by the radical attack [32]. The presence of inorganic particles in SP/CL/TAP nanocomposite membrane have increased its resistance towards the radical attack, thus the membrane can retain its weight better than the pristine SPEEK membrane in the Fenton reagent test. Similar observation was also reported by Park et al. [33], where presence of the cerium inorganic particles in SPEEK/Ce composite can improve the composite membrane’s stability in the Fenton reagent test up to 48 h as compared to the pristine SPEEK which can only remain stable up to 12 h before being degraded completely. Another study conducted by Rowshanzamir et al. [34] also found out that SPEEK nanocomposite membrane incorporated with Pt–Cs2.5H0.5PW12O40 particles can retain 65% of its weight after being immersed for 1 h in the Fenton reagent, which is better than the pristine SPEEK membrane which only retains 46% of its weight after the test. Based on the findings obtained from previous studies, it can be concluded that addition of Cloisite® inorganic particles can improve the durability of the SP/CL/TAP nanocomposite membrane against the radical attack.

3.2. FT-IR spectra analysis

FT-IR characterization was carried out to determine changes of pristine SPEEK and SPEEK nanocomposite membranes’ functional groups after exposing to the Fenton reagent solution. Fig. 2 shows the IR spectrum of the pristine SPEEK membrane and Table 2 summarizes the functional group of each corresponding band. From Fig. 2, it can be clearly seen that a broad peak is observed at 3396 cm⁻¹ band due to O–H stretching of bound water molecules in the membrane lattice. The peak at 1644 cm⁻¹ band was corresponding to C=O stretching of the carbonyl group. The C–C aromatic ring vibration was detected at 1470 and 1490 cm⁻¹ bands, which represent the two benzene rings in the SPEEK chemical structure. The ether linkage between two aromatic rings in the SPEEK backbone was detected at 1217 cm⁻¹ band. The presence of sulfonate acid functional group was detected at 1080 and 1024 cm⁻¹ bands, which was corresponding to asymmetric and symmetric stretching of –SO₃H group.

The IR spectrum of the pristine SPEEK membrane after exposing to the Fenton reagent solution shows similar peaks with original pristine SPEEK membrane before undergoes the Fenton reagent test. From Fig. 2, it can be clearly observed that there is no distinct new peak is emerged after the pristine SPEEK polymer undergoing the Fenton reagent test, which indicates that no new functional group is formed after the oxidation reaction between the pristine SPEEK membrane and free radical. The intensity of the pristine SPEEK membrane’s IR spectrum before and after Fenton reagent test was calculated using the OMNIC software and its results are tabulated in Table 3. Based on the results obtained in Table 3, the peak’s intensity of the pristine SPEEK membrane’s functional groups was reduced after prolong exposing to the Fenton reagent solution except for O–H stretching band. Based on DFT study done by Zhao et al. [22], the bonding between ether linkage (C–O–C) and sulfonate acid group (–SO₃H) is vulnerable towards OH⁺ radical attack. The bonding breaks up by the radical attack causes these functional groups to detach from the SPEEK polymer backbone and dissolve into the Fenton reagent solution. Another DFT study by Panchenko [35] and Perrot et al. [36] also showed that the phenylene ring is susceptible to OH⁺ radical attack, which may lead to the opening of the carbon ring. Based on the DFT studies, oxidation reaction between the OH⁺radical with sulfonate acid, ether linkage and phenylene ring groups will form new –OH functional group. The IR spectrum also shows that the peak intensity of the –OH group is increasing with the testing time. These results show that degradation of the pristine SPEEK membrane is due to the OH⁺radical attack that causes the sulfonic acid and ether linkage groups to detach from the membrane structure, and leads to the opening of
the phenylene ring.

Table 4 lists the corresponding functional groups for each peak in SPEEK nanocomposite membrane IR spectrum (Fig. 3). The IR spectrum of the SP/CL/TAP nanocomposite membrane has similar characteristic peaks with the pristine SPEEK polymer [37]. It can be clearly seen that there are no apparent peaks of functional groups for Cloisite® surfactant and TAP compatibilizer. In addition, based on Table 5, all significant peaks of SPEEK polymer show a lower intensity as compared to pristine SPEEK membrane. The absence of peaks for both Cloisite® surfactant and TAP compatibilizer functional groups and the intensity reduction of the SPEEK polymer peaks suggests that bonding formation is occur between SPEEK parent polymer with both modifiers due to electron withdrawing between ketone and methyl group, and dipole-dipole interaction between amine, sulfonate acid, and ether linkage group [3].

Table 2
<table>
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<tr>
<th>Peak assignment</th>
<th>Wavenumber (cm⁻¹)</th>
<th>0 h</th>
<th>6 h</th>
<th>12 h</th>
<th>24 h</th>
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<tr>
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<td>3396</td>
<td>3396</td>
<td>3396</td>
<td>3383</td>
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<td>C–O stretching</td>
<td>1644</td>
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<td>C–O–C stretching</td>
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<td>–SO₃H asymmetric stretching</td>
<td>1080</td>
<td>1080</td>
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<tr>
<td>–SO₃H symmetric stretching</td>
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Table 3
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<td>C–O–C stretching</td>
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<td>–SO₃H asymmetric stretching</td>
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<tr>
<td>–SO₃H symmetric stretching</td>
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Fig. 2. FT-IR spectrum of the pristine SPEEK membrane between 1000 and 1700 cm⁻¹ bands.
solution. All peaks corresponding to the SPEEK polymer functional groups show a reduction in intensity after exposing to the Fenton reagent test. The reduction of peaks intensity of SPEEK polymer functional group suggests that the SPEEK nanocomposite membrane has a similar degradation mechanism with pristine SPEEK membrane. Two new peaks were observed in the IR spectrum of degraded SPEEK nanocomposite membrane at 2923 and 2852 cm⁻¹ bands. These peaks are corresponding to C–H asymmetric and symmetric vibration of dimethyl group in Cloisite® quaternary ammonium salt modifier structure. The presence of peaks for the methyl group in Cloisite® modifier suggests that the bonding between methyl and ketone group might have broken due to loss of ketone functional group from the SPEEK polymer structure. The bonding formation between SPEEK and TAP also is broken due to loss of sulfonic acid and ether linkage groups from the SPEEK polymer structure. However, no peaks for TAP compatibilizer functional groups was detected in the degraded SPEEK nanocomposite membrane IR spectrum. This indicates that the TAP compatibilizer has dissolved into the Fenton reagent solution after the bonding with SPEEK polymer was broken.

3.3. Morphological analysis

Fig. 4 shows the FESEM images of pristine SPEEK and SP/CL/TAP nanocomposite membranes' surface before and after the Fenton reagent test. All images were taken at 1000 × magnification. The pristine SPEEK and SP/CL/TAP nanocomposite membranes in Fig. 4 (a) and (e) show a smooth membrane surface. No agglomeration can be detected on the surface of SP/CL/TAP nanocomposite membrane. Similar observation also was reported by Jaafar et al. [8], where the TAP compatibilizer provide an additional interaction site between SPEEK and Cloisite®, thus allowing Cloisite® particles to disperse homogeneously in the SPEEK nanocomposite membrane structure.

After undergoing the Fenton reagent test, the surface of both pristine SPEEK and SP/CL/TAP nanocomposite membranes were starting to deform, and the formation of defects are increased when the immersion time is increased as shown in Fig. 4 (b), (c), and (d); and in Fig. 5 (b), (c), (d), (e), and (f). Oxidation reaction between the free radical and organic polymer will produce carbon dioxide (CO₂) as the by-product [21]. The CO₂ gas by-product will form a gas bubble and has the high tendency to burst when the membrane structure cannot withstand the pressure from the gas bubble, thus causing the membrane structure to deform. FESEM images in Fig. 4 also show that the deformation of pristine SPEEK and SP/CL/TAP nanocomposite membranes is not only occurred on the membrane surface, but also inside the membrane structure. Deformation occurs inside the pristine SPEEK and SP/CL/TAP nanocomposite membranes are most likely due to the radical attack through the water channel inside the membrane structure. Membrane deformation is also observed in previous study did by F. Wang et al. [38], Y. Zhu et al. [39,40], H. Tang et al. [41] and Z. Wang et al. [42].

Other than that, the appearance of small particles is spotted on the SP/CL/TAP nanocomposite membrane surface after exposing to the Fenton reagent test. Energy-dispersive x-ray spectroscopy (EDX) was used to identify the elements of the particles on the degraded SP/CL/TAP nanocomposite membrane surface. Fig. 5 shows the EDX analysis of the degraded SPEEK nanocomposite membrane surface. Based on the EDX analysis, particles on the SPEEK nanocomposite membrane surface have been confirmed to consist of silicon and aluminium, which are the main elements of Cloisite® particles structure. The appearance of Cloisite® particles on the SP/CL/TAP nanocomposite membrane surface after the Fenton reagent test suggests that the interaction between SPEEK polymer, Cloisite® particles and TAP compatibilizer have been compromised by the radical attack. From this observation, it can be concluded that the bonding formations between SPEEK polymer, Cloisite® particles and TAP compatibilizer are vulnerable towards the radical attack. Similar finding was reported by Zhao et al. [42] where CeO₂ particles are spotted after the Nafion/CeO₂ composite membrane was immersed in the Fenton reagent for 24 h.

3.4. Tensile strength analysis

Tensile strength test was conducted to study the impact of the radical attack towards the mechanical stability of pristine SPEEK and SPEEK nanocomposite membranes. A PEM with good mechanical strength is needed to develop flexible yet durable membrane that is suitable for DMFC application. Fig. 6 shows the tensile strength for both membranes after being exposed to the Fenton reagent solution. The SP/CL/TAP nanocomposite membrane shows higher mechanical strength (51 MPa) as compared to the pristine SPEEK membrane (47 MPa). The presence of TAP compatibilizer in SP/CL/TAP nanocomposite membrane structure helps to improve the compatibility between the SPEEK polymer and Cloisite® particles. Thus, Cloisite® particles can disperse uniformly inside the SP/CL/TAP nanocomposite membrane structure and consequently improve the intermolecular contact and its structure compactness [43]. Thus, the SP/CL/TAP nanocomposite membrane shows improvement in mechanical strength as compared to the pristine SPEEK membrane. Mechanical strength improvement were also reported by Kim et al. [43] and Villaluenga et al. [44] after incorporating of modified MMT particles in their nanocomposite membranes.

From the results obtained in Fig. 6, both pristine SPEEK and SP/CL/TAP nanocomposite membranes show the reduction in the mechanical strength after being degraded by the Fenton reagent solution. The tensile strength of the pristine SPEEK membrane has dropped 100% after being immersed in the Fenton reagent solution for 24 h. Based on the morphological analysis, prolong exposure to the free radical has caused the membrane structure to deform. Structural deformation can affect the structural integrity of the membrane, thus reducing the mechanical strength of the membrane. Similar observation was also reported by Wang et al. [38], where the mechanical strength of the Nafion® membrane has dropped after 48 h being exposed to the Fenton reagent test due to the deformation of the membrane structure. As compared to the pristine SPEEK membrane, the SP/CL/TAP nanocomposite membrane shows a lower mechanical strength reduction after the Fenton reagent test. The tensile strength of the SP/CL/TAP nanocomposite membrane dropped 62% from 51 MPa to 31.4 MPa after 96 h exposing to the Fenton reagent test. Incorporation of Cloisite® particles has increased the membrane structure compactness and provide an additional mechanical support to the membrane [43].
Fig. 3. FT-IR spectrum of the SPEEK nanocomposite membrane between (a) 2800-3800 cm\(^{-1}\) bands and (b) 1000-1700 cm\(^{-1}\) bands.
Therefore, the SP/CL/TAP nanocomposite membrane can retain its mechanical strength better than the pristine SPEEK membrane after being exposed to the radical attack.

3.5. Contact angle analysis

Contact angle measurement was used to determine the changes of pristine SPEEK and SPEEK nanocomposite membranes hydrophilicity after exposing to the Fenton reagent test. Hydrophilicity measures the affinity of PEM to absorb water molecules. Since water is needed in the proton transportation, hydrophilic PEM is essential to developed the high-performance PEM for DMFC application.

Fig. 7 shows the contact angle measurement of pristine SPEEK and SP/CL/TAP nanocomposite membranes after exposing to the Fenton reagent solution. The contact angle value of pristine SPEEK and SP/CL/TAP nanocomposite membranes before the Fenton reagent test was 74° and 67° respectively. Both membranes show contact angle value below 90°, indicate that both membranes were hydrophilic in nature due to the presence of the sulfonic acid functional group in the SPEEK polymer chain [37]. The contact angle of both membranes was increased after prolong exposing to the Fenton reagent test. The contact angle of pristine SPEEK and SP/CL/TAP nanocomposite membrane increase from 74° to 96° and from 67° to 99° respectively. From DFT study done by Zhao et al. [22], Panchenko [35], and Perrot et al. [36], the radical has tendencies to break the bonding between the sulfonic acid functional group and phenylene ring and causes the sulfonic acid group to detach from the SPEEK polymer backbone. Loss of sulfonate acid group reduces the membranes affinity with water and changes the hydrophilicity of the membranes to slightly hydrophobic based on contact angle values obtained.

3.6. Water uptake analysis

Water uptake measures the membrane ability to absorb water. Water absorption capability is important for PEM since water is needed to transport proton from the anode to cathode [11]. Thus, changes in the water uptake of PEM might alter its ability to conduct proton, which affect the performance of the DMFC.

Fig. 8 shows the water uptake of SP/CL/TAP nanocomposite and Nafion® 117 membranes after exposing to the Fenton reagent solution.
solution for 96 h. The initial water uptake value for SP/CL/TAP nanocomposite and Na\textsuperscript{117} membranes were 28\% and 18\% respectively. Due to the high separation between sulfonic acid group in SPEEK polymer structure, the water channel formation inside the membrane was narrower and more branched as compared to Na\textsuperscript{117} membrane \cite{45}. Narrow and high dead-end, branched water channel have caused the SPEEK polymer-based membrane to have low proton conductivity as compared to Na\textsuperscript{117} membrane. Therefore, higher concentration of sulfonic acid groups were needed in order for SPEEK polymer-based membrane to have a similar conductivity properties with Na\textsuperscript{117} membrane. Higher concentration of sulfonic acid group increases the membrane affinity with water. Thus, the SP/CL/TAP nanocomposite membrane can absorb more water than Na\textsuperscript{117} membrane.

Both SP/CL/TAP nanocomposite and Na\textsuperscript{117} membranes show a reduction in water uptake after exposing to the Fenton reagent test for 96 h. Based on Table 6, the Na\textsuperscript{117} membrane shows a lower water uptake reduction (18\textendash 44\%) as compared to SP/CL/TAP nanocomposite membrane (27\textendash 67\%) across all concentration of the Fenton reagent solution. DFT study conducted by Ye et al. \cite{47} reported that the radical attack on sulfonic acid group in Na\textsuperscript{117} structure requires \textasciitilde 92.626 kJ/mol energy, which is much higher as compared to SPEEEK nanocomposite membrane (\textasciitilde 152.46 kJ/mol) \cite{22}. Therefore, the bonding between \textendash CF\textsubscript{2}\textendash SO\textsubscript{3}H in the Na\textsuperscript{117} structure is more durable than \textendash C\textsubscript{6}H\textsubscript{4}\textendash SO\textsubscript{3}H bonding in the SP/CL/TAP nanocomposite membrane structure. Thus, the Na\textsuperscript{117} membrane lost fewer sulfonic acid group from its structure after the radical attack and could retain higher hydration than SP/CL/TAP nanocomposite membrane after Fenton reagent test.

3.7. Proton conductivity analysis

High proton conductivity is a crucial trait that must be possessed by PEM for fuel cell applications. This is because higher proton movement between the anode and cathode side in fuel cell will increase the reaction rate in DMFC operation, thus prompt higher production of free electron to generate electricity and produce higher energy output \cite{7}. Therefore, proton conductivity was studied to evaluate the PEM performance in DMFC operation. Fig. 9 shows the proton conductivity of SP/CL/TAP nanocomposite and Na\textsuperscript{117} 117 membranes in the Fenton reagent test. From the data obtained, the initial conductivity of the SP/CL/TAP nanocomposite membrane was 1.75 \times 10\textsuperscript{2} S/cm, which is slightly lower than the commercial Na\textsuperscript{117} 117 membrane (1.87 \times 10\textsuperscript{2} S/cm). Due to high hydrophobicity of perflourinated polymer
backbone and high hydrophilicity of sulfonic acid group, the hydrophobic and hydrophilic regions in the Naﬁon® membrane is clearly separated [45]. High separation of hydrophobic and hydrophilic regions reduces gaps between sulfonic acid group in Naﬁon® structure. Therefore, the water channel formed in Naﬁon® structure was wider and well connected as compared to SP/CL/TAP nanocomposite membrane, which can allow more proton to be transport inside Naﬁon® membrane structure [48].

The proton conductivity for both SP/CL/TAP nanocomposite and Naﬁon® 117 membranes was reduced after being immersed in the Fenton reagent solution for 96 h. Proton conductivity measurement for SP/CL/TAP nanocomposite membrane at 50 ppm (48 and 96 h) and 12 ppm (96 h) Fenton reagent concentration could not be conducted as the membrane become too brittle and crumble during

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**Fig. 6.** Changes in the tensile strength of pristine SPEEK and SP/CL/TAP nanocomposite membranes after exposing to the Fenton reagent solution.

**Fig. 7.** Contact angle of pristine SPEEK and SP/CL/TAP nanocomposite membranes after exposing to the Fenton reagent solution.
the testing. Therefore, proton conductivity for SP/CL/TAP nanocomposite membrane at 12 and 50 ppm Fenton reagent test was compared to Naion® sample with similar testing time. Based on Table 6, the SP/CL/TAP nanocomposite membrane shows a higher proton conductivity reduction (58–95%) as compared to Naion® membrane (48–69%) for all Fenton reagent concentration. Based on water uptake analysis, the sulfonic acid group bonding in SP/CL/TAP nanocomposite membrane has higher tendencies to dissociate from SPEEK polymer chain due to the radical attack compared to Naion® membrane [22,47]. Loss of the sulfonic acid group will reduce the membrane ability to absorb water. Since water act as a proton carrier for proton transportation via vehicular diffusion and Grotthuss proton hopping mechanism [49], higher hydrophilicity reduction of SP/CL/TAP nanocomposite membrane due to loss of sulfonic acid group causes the membrane to lose its ability to conduct proton higher than the Naion® membrane.

### 3.8. Methanol permeability analysis

Another important characteristic of a good electrolyte for electrochemical application is its ability to keep the anode and cathode side separated. An electrolyte must be able to prevent reactants’ crossover from the anode to cathode or vice-versa [1]. The direct reaction between the reactants due to crossover problem will reduce the electron generation, thus reduced the current and voltage generated from the electrochemical device [50]. For DMFC operation, since methanol is highly soluble in water, methanol molecules tend to crossover along with water molecules due to electro-osmotic drag phenomenon [51]. Thus, a good PEM for DMFC application must be able to block and hinder methanol from crossover to the cathode side. Methanol permeability was used to measure the ability of PEM to resist the methanol migration through the membrane structure.

Fig. 10 shows methanol permeability of degraded SP/CL/TAP nanocomposite and Naion® 117 membranes after going through 96 h of Fenton reagent test. The initial methanol permeability of SP/CL/TAP nanocomposite membrane (1.69 × 10^{-2} cm²/s) was lower than Naion® 117 membrane (2.31 × 10^{-6} cm²/s). Due to the large separation between sulfonic acid groups in SPEEK polymer structure, the SP/CL/TAP nanocomposite membrane has a narrower and more branched water channel as compared to the Naion® membrane, which limits the methanol permeation through the

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Fenton reagent concentration</th>
<th>WU (%)</th>
<th>Reduction (%)</th>
<th>Reduction (S/cm²) × 10^{-2}</th>
<th>Reduction (%)</th>
<th>P (cm²/s) × 10^{-7}</th>
<th>Increment (%)</th>
<th>Selectivity (S·cm²)</th>
<th>Selectivity (S·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 ppm</td>
<td>28 h</td>
<td>20</td>
<td>27</td>
<td>1.75 0.735</td>
<td>58</td>
<td>1.69 2.72 61</td>
<td>103,779</td>
<td>27,037</td>
<td></td>
</tr>
<tr>
<td>3 ppm</td>
<td>28 h</td>
<td>16</td>
<td>41</td>
<td>1.75 0.067</td>
<td>90</td>
<td>1.69 2.99 77</td>
<td>103,779</td>
<td>5599</td>
<td></td>
</tr>
<tr>
<td>12 ppm</td>
<td>28 h</td>
<td>14</td>
<td>49</td>
<td>1.75 0.181</td>
<td>91</td>
<td>1.69 3.19 89</td>
<td>103,779</td>
<td>5685</td>
<td></td>
</tr>
<tr>
<td>50 ppm</td>
<td>28 h</td>
<td>9</td>
<td>67</td>
<td>1.75 0.0820</td>
<td>95</td>
<td>1.69 3.20 89</td>
<td>103,779</td>
<td>690</td>
<td></td>
</tr>
<tr>
<td>Naion® 117</td>
<td>0.8 ppm</td>
<td>18</td>
<td>15</td>
<td>1.87 0.972</td>
<td>48</td>
<td>23.1 29.5 28</td>
<td>8089</td>
<td>3292</td>
<td></td>
</tr>
<tr>
<td>3 ppm</td>
<td>18 h</td>
<td>14</td>
<td>23</td>
<td>1.87 0.775</td>
<td>59</td>
<td>23.1 32.5 40</td>
<td>8089</td>
<td>2386</td>
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<td>18 h</td>
<td>12</td>
<td>32</td>
<td>1.87 0.480</td>
<td>64</td>
<td>23.1 35.9 49</td>
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<tr>
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<td>69</td>
<td>23.1 39.2 63</td>
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<td>159</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. Water uptake of SP/CL/TAP nanocomposite and Naion® 117 membranes after exposing to the Fenton reagent solution for 96 h.
membrane [45,52]. In addition, due to high width to length ratio of Cloisite® particles, the exfoliated Cloisite® particles can create the tortuous pathways for methanol crossover, thus improve methanol barrier properties of SP/CL/TAP nanocomposite membrane [3,8].

Based on Table 6, it can be clearly seen that methanol permeability of both SP/CL/TAP nanocomposite and Naﬁon® 117 membranes increase when the Fenton reagent concentration and testing time increase. Like the proton conductivity analysis, the methanol permeability for SP/CL/TAP nanocomposite membrane can only be measured up to 48 and 24 h at 12 and 50 ppm Fenton reagent concentration respectively due to the membrane condition. From Table 1, the SP/CL/TAP nanocomposite membrane shows a higher methanol permeability increment (61–89%) than Naﬁon® membrane (28–63%) across all the Fenton reagent concentration. Since lower energy is needed to break C–H bonding in SP/CL/TAP nanocomposite membrane than C–F bonding in Naﬁon® membrane [15], the SP/CL/TAP nanocomposite membrane is more vulnerable towards the radical attack, which causes more pinholes and cracks to form. Pinholes and cracks formation will create a pathway for methanol to pass through, thus reduce methanol barrier properties of SP/CL/TAP nanocomposite membrane. In addition, the detachment of Cloisite® particles from SP/CL/TAP nanocomposite structure due to bonding scission between Cloisite® particles and SPEEK polymer has reduced the SP/CL/TAP nanocomposite membrane ability to create the tortuous pathways for methanol permeation, thus allowed more methanol to permeate. All these reasons have contributed to the higher methanol permeability reduction of SP/CL/TAP nanocomposite membrane as compared to Naﬁon® membrane.

Even though SP/CL/TAP nanocomposite membrane shows a higher methanol permeability increment than Naﬁon® membrane, methanol permeability value for SP/CL/TAP nanocomposite membrane remains lower than Naﬁon® membrane. This might due to the presence of wide and well connected water channel in Naﬁon® membrane, which create easier pathways for methanol to permeate. Therefore, the SP/CL/TAP nanocomposite membrane has shown to have better methanol barrier properties than Naﬁon® membrane even after being degraded by the free radical.

3.9. Membrane selectivity

Membrane selectivity was used to evaluate the overall properties of the PEM for DMFC operation. Membrane selectivity measures the PEM ability to conduct proton while at the same time block the permeation of methanol fuel. The membrane with high proton conductivity and low methanol permeability is more favourable for DMFC operation as high proton conductivity will increase the rate of electrochemical reaction and produce higher energy output while low methanol permeability will reduce the fuel loss due to fuel crossover and increase the DMFC efficiency. Therefore, the membrane selectivity can be used evaluate the overall performance of the PEM for DMFC application.

Fig. 11 show the selectivity of SP/CL/TAP nanocomposite and Naﬁon® 117 membranes before and after exposing to the Fenton reagent solution at various concentration for 96 h. The selectivity of original SP/CL/TAP nanocomposite and Naﬁon® 117 membranes were 103,779 S·s/cm² and 8089 S·s/cm² respectively. Even though Naﬁon® 117 membrane shows a better proton conductivity than SP/CL/TAP nanocomposite membrane, however, well defined and large water channel inside Naﬁon® 117 structure allow methanol to permeate through the membrane easily because of electro-osmotic drag, thus reduce methanol barrier properties of Naﬁon® 117, which affect the membrane overall performance. In contrast to Naﬁon® 117 membrane, high methanol barrier properties of SP/CL/TAP nanocomposite membrane because of a narrower water channel formation and presence of Cloisite® particles can compensate for the membrane low proton conductivity ability, thus improve the overall performance of the membrane.

The selectivity for both SP/CL/TAP nanocomposite and Naﬁon® 117 membrane decreased as a function of time for all the Fenton reagent concentration. Based on Table 6, the selectivity of SP/CL/TAP nanocomposite membrane shows higher reduction than
Nafton® membrane selectivity. This is due to the high proton conductivity and methanol permeability reduction of SP/CL/TAP
nanocomposite membrane after being degraded by the free radical. However, due to its high methanol barrier properties, the SP/CL/TAP nanocomposite membrane can retain a higher selectivity value than Nafton® membrane. Therefore, it can be concluded that SPEEEK nanocomposite membrane has good stability against the radical attack and suitable to be used as the PEM for high performance and long lifespan DMFC system.

3.10. Chemical degradation mechanisms of SPEEEK nanocomposite membrane under the Fenton reagent test

Based on the physicochemical changes of the SP/CL/TAP nanocomposite membrane, it can be concluded that the bonding in the SP/CL/TAP nanocomposite membrane was strongly affected by the radical attack. Based on the DFT study done by Zhao et al. [22], chemical bonding between the phenylene ring and sulfonic acid group, and phenylene ring with ether linkage are vulnerable towards the radical attack. The required activation energy used to break C=O–C and −SO3H bonding by OH· radical attack was −59.65 kJ/mol and −152.46 kJ/mol respectively. The negative activation energy indicates that the degradation mechanism on these bonding was barrier-less and instantaneous. The DFT study by Panchenko [35] and Perrot et al. [36] showed that the phenylene ring was also susceptible to the OH· radical attack and will cause the opening of the carbon ring. The FT-IR spectra analysis results show a good agreement with the DFT studies, where the IR peaks intensity for sulfonic acid, ether linkage and phenylene ring groups were reduced after being exposed to the Fenton reagent solution for 96 h. The result indicates that the functional groups were detached from the SPEEEK nanocomposite chemical structure and replaced by the −OH functional group. The morphological and IR spectrum analysis also revealed that the bonding between Cloisite® particles, SPEEEK polymer, and TAP compatibilizer was affected by the radical attack. Therefore, based on the physicochemical observation of degraded SP/CL/TAP nanocomposite membrane and DFT analysis did by Zhao et al., Panchenko and Perrot et al., Fig. 12 was constructed to visualize the suggested degradation mechanism of the SP/CL/TAP nanocomposite membrane by the radical attack.

3.11. Lifespan estimation of the SP/CL/TAP nanocomposite membrane in DMFC application

Fig. 13 shows the correlation curve between the Fenton reagent test and DMFC lifetime test. The straight line in Fig. 13 represents the DMFC operation time while the red and blue markers represent the selectivity of SP/CL/TAP nanocomposite and Nafton® 117 membranes respectively. Membrane selectivity was used as an indicator because it can evaluate overall performance of the PEM for the DMFC application.

Based on Fig. 13 and Table 1, the selectivity of SP/CL/TAP nanocomposite membrane dropped below Nafton® membrane at 24 h under 50 ppm Fenton reagent concentration, which corresponded to 1760 mol/L of OH· radical concentration. Therefore, this point was considered as a limit point for SP/CL/TAP nanocomposite membrane to be able to perform better than Nafton® 117 commercial membrane in the DMFC system. When this point was projected to DMFC lifetime test correlation curve, the SP/CL/TAP nanocomposite membrane was predicted to be able to operate effectively in DMFC system up to approximately 9800 h. The lifespan value from this correlation was much higher as compared to lifespan value produced from the previous DMFC lifetime test [12,53–57] because this correlation only considers the chemical degradation impact on the DMFC lifespan. Despite the shortcoming, the correlation shows that the SP/CL/TAP nanocomposite membrane has comparable lifespan with Nafton® membrane in the DMFC system.

4. Conclusion

In summary, this study was conducted to investigate the durability of SP/CL/TAP nanocomposite membrane against the radical attack and its impact towards the SP/CL/TAP nanocomposite properties for the DMFC application. Based on the physicochemical study and previous DFT studies, the ether linkage and sulfonic acid group bonding with phenylene ring in the SPEEEK polymer structure was most likely to be attack and break-up by the free radical. Bonding scission between the sulfonic acid group and phenylene ring has caused the functional group to detach, thus reduced the hydrophilicity of the SP/CL/TAP nanocomposite membrane and changed it to slightly hydrophobic. Chain scission between ether...
linkage with phenylene ring caused the phenylene ring and ketone group lost support and detached together with ether linkage group. Loss of ether linkage, phenylene ring, and ketone groups have caused the SP/CL/TAP nanocomposite membrane structure to deform. Structural deformation of SP/CL/TAP nanocomposite membrane has deteriorated the mechanical strength of the membrane. Incorporation of Cloisite® particles in SPEEK polymer matrix could provide additional resistance and stability against the radical attack. Based on these results, it is concluded that the ether linkage bonding, sulfonic acid bonding, and hydrogen bonding formed between SPEEK polymer, Cloisite® particles and TAP compatibilizer were affected by the radical attack.

In general, the SP/CL/TAP nanocomposite membrane has shown a higher water uptake, proton conductivity, and methanol permeability changes than the Naﬁon® membrane. The Naﬁon® membrane could retain its membrane properties better than the SP/CL/TAP nanocomposite membrane due to the higher resistivity of C–F bonding against the radical attack as compared to the C–H bonding in SP/CL/TAP nanocomposite membrane structure. However, the membrane selectivity of the SP/CL/TAP nanocomposite membrane was higher than the Naﬁon® membrane because the nanocomposite membrane could retain higher methanol barrier properties after being degraded by the radical attack. Therefore, the selectivity results have shown that the SP/CL/TAP nanocomposite membrane has good stability against the radical attack. The correlation curve has shown that the SP/CL/TAP nanocomposite membrane could operate in the DMFC system up to 9800 h. The lifespan value calculated from the correlation is much higher than lifespan value from DMFC lifetime test because only chemical degradation was considered in developing the correlation curve. However, the correlation has shown that the SP/CL/TAP nanocomposite membrane holds a good potential to be developed as the PEM for high performance and long lifespan DMFC system.

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