



The effect of platinum in a Nafion membrane on the durability of the membrane under fuel cell conditions

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ABSTRACT

The effect of platinum on free radical generation and membrane degradation in proton exchange membrane (PEM) fuel cells is investigated using three typical cell configurations. Examinations of the fluoride emission rates (FERs) under different testing conditions indicate that platinum deposited in the membrane plays an important role as a catalytic center for the formation of H₂O₂ and HO• free radicals, leading to PEM degradation. The chemical durability of the membranes is tested in accelerated Fenton tests. It confirms the formation of free radicals in the presence of platinum in the decomposition of H₂O₂ by colorimetric method with dimethyl sulfoxide (DMSO) as the trapping agent. In addition, structural and morphological changes of the membranes are characterized using FT-IR spectroscopy and scanning electron microscopy (SEM).

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1. Introduction

While significant progress has been made in the developments of proton exchange membrane (PEM) fuel cells, many critical challenges still remain [1]. The stability and durability of PEMs have attracted much attention because of their impact on the durability and lifetime of PEM fuel cells.

Degradation of proton exchange membranes may originate from chemical, electrochemical, mechanical, and thermal causes [2]. Among them, the chemical/electrochemical degradation is directly related to the structural stability of the polymer molecules under different fuel cell operation conditions. In a chemical/electrochemical degradation, the formation of hydrogen peroxide and its decomposition to HO• and HO₂• are considered as an important factor. It is known that hydrogen peroxide and HO• radicals produced during fuel cell operation may degrade PEMs by attacking the backbone and the side chain of the polymers. The formation of H₂O₂ is resulted mainly from a 2-electron ORR process on the cathode side of the cell [3] and/or on the anode with the oxygen crossover from the cathode [4,5]. The two possible pathways for

the formation of HO• radical or other oxidized species (like HO₂•) include (i) decomposition of H₂O₂ [6,7] and (ii) reactions between hydrogen and oxygen without H₂O₂ formation on the surface of the catalyst in an anode/cathode [8]. In the past decade, the effects of radical species on the degradation of fuel cell membrane have been well studied [9–11].

It is recently reported that Pt and its ions (Pt²⁺, Pt⁴⁺) [12] are present within PEMs under various testing conditions, including open circuit condition [13] and potential cycling [14]. The dissolution, migration, and deposition of Pt within PEMs could reduce the activity of the electrode catalyst and the ion exchange capacity (IEC). However, the effect of platinum catalyst on free radical generation and membrane degradation is still under debate. In 2006, Watanabe et al. [15,16] reported that Pt particles in the electrolyte were found to suppress the PFSA ionomer decomposition by scavenging H₂O₂ and/or HO• radicals under both the anodic (H₂-rich) and cathodic (O₂-rich) conditions. They claimed that Pt dispersion in the membrane improved membrane durability and, accordingly, proposed the concept of self-humidifying membranes with Pt/SiO₂ (or Pt/TiO₂, Pt/ZrO₂) [17]. In contrast, Kim et al. [18] and Endoh et al. [19] identified the existence of oxygen radicals through indirect measurement of carbon radicals by electron spin resonance (ESR). It was believed that the dissolved/deposited Pt could generate oxygen radicals with the crossover hydrogen and oxygen, which could attack the backbone and side chain of the polymer. They also found that the membrane degradation was not limited to the area of the

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membrane near the catalyst and the fluoride emission rate (FER) increased with the amount of Pt in the membrane. They concluded that platinum charged species acted as centers for the generation of free radicals that chemically degraded the membrane.

Here we report our findings on the effect of Pt deposited within a PEM on the degradation of the PEM. We will present evidence on the formation of free radicals in the presence of Pt in the decomposition of H_2O_2 by colorimetric method with dimethyl sulfoxide (DMSO) as the trapping agent. Moreover, we have also evaluated the impact of platinum on the membrane durability under open cell conditions, including structural and morphological changes of the membranes.

2. Experimental

2.1. Preparations of Pt/NRE 212 composite membrane

NRE 212 membrane (Du Pont) was used in all experiments. The Pt/NRE 212 membrane was prepared as described elsewhere [20]. The NRE 212 membrane in the H^+ form was dried and weighed before impregnated. Then the H^+ form membrane was exchanged to the Na^+ form and equilibrated at 60°C with 100 ml of 2.0 mM H_2PtCl_6 solution a co-solvent of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (3/1, v/v) was used in this impregnation step. Following this step, the NRE 212 membrane was immersed in 100 ml of 0.1 M NaBH_4 solution at 50°C for 2 h. Then, the Pt/NRE 212 membrane was exchanged to H^+ form with 0.5 M H_2SO_4 prior to drying for weighing. The content of platinum in the membrane was 4 wt.%.

2.2. Characterization of PEM structure and morphology

The infrared spectra of the membrane samples were recorded using an FT-IR spectrometer (JASCO FT/IR-4100) with a resolution of 4 cm^{-1} . The Pt distributions and the morphologies of fractured cross-sections of the sample membranes were examined using a scanning electron microscope (Hitachi S-800 FE SEM).

2.3. Detection of the free radical generation

The generation of hydroxyl radicals (HO^\bullet) was detected using a UV-vis spectrophotometer (HP 8453) [21], as did in other PEM degradation studies [22].

1 mg sample (Pt/C, XC-72) was added into 9 ml of a mixed solution consisting of 200 mM DMSO and 10 mM HCl (in Fenton test, 25 mM FeSO_4 was added). Then 1 ml 80 mM H_2O_2 was added. The 1 ml of the mixed solution was transferred into another test tube and 2 ml 1.5 mM Fast Blue BB Salt (Alfa Aesar, fresh prepared and kept in the dark) was added. Ten minutes were allowed for product development at room temperature in the dark. 4 ml ethyl acetate was then added and mixed for extraction. After the extraction for 5 min, the upper phase with diazosulfones was transferred into a cuvette and the absorbance is determined at 410–420 nm against a blank without samples carried through the same procedure.

2.4. Fluorine ion determination

Fluoride emission rate was detected using an ion selective electrode (ISE) [23]. It is well known that the measurement may be interfered by sample pH values. Hydroxide ions may interfere with the electrode response to fluoride when $\text{pH} > 7$, whereas protons may complex with some fluoride ions in solution by forming the un-dissociated acid HF and HF^{2-} ions when $\text{pH} < 5$. To avoid these interferences, we used TISAB buffer solution to keep the pH within the desired range of 5–7 and to maintain good ion strength. The concentration of the fluoride was measured using standard addition method [24–26].

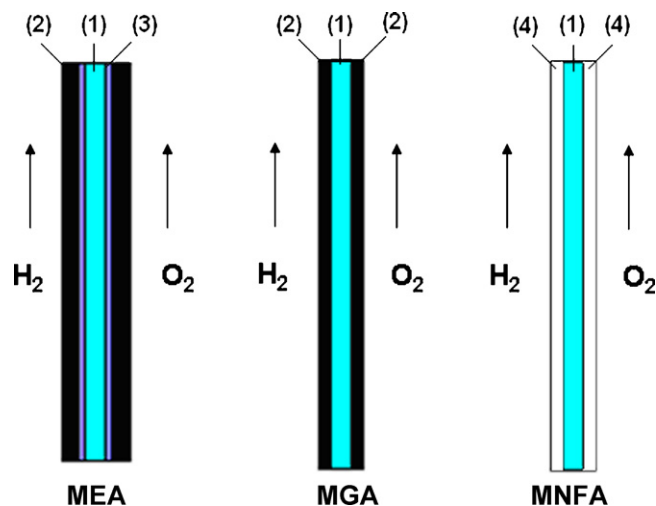


Fig. 1. Schematics of the cell configurations tested at 80°C , 50% RH with H_2 and O_2 as the reactant gases. (1) Sample membrane; (2) gas diffusion layer; (3) electrode layer; (4) non-woven fabric layer.

2.5. Hydrogen peroxide decomposition—oxygen generation evaluation

The catalytic activities of Pt/C and XC-72 for hydrogen peroxide decomposition were examined via the oxygen generation test. Gas volumetric method was used to measure the oxygen generated in an appropriate reaction chamber with thermostatic bath to keep the temperature constant within an accuracy of $\pm 0.2^\circ\text{C}$. The chamber sealed was equipped with temperature sensor. The oxygen generation was measured at 80°C in 3 wt.% H_2O_2 solution.

2.6. Membrane durability studies

Membrane durability was evaluated using both *ex situ* and *in situ* accelerated tests. The *ex situ* durability was tested in a Fenton solution (3 wt.% H_2O_2 , 20 ppm Fe^{2+}) with the H^+ formed membranes. Fresh sample membranes were dried and weighed, then immersed into 15 ml Fenton solution at 80°C for 20–30 h. The fluoride concentration measurements were carried out by removal of 1 ml aliquots from the reaction flask. The reaction media (Fenton solution) was discarded and refreshed, the degraded samples were converted back to H^+ form by immersing in 0.5 M H_2SO_4 and dried for weighing before the next round of the degradation test.

In the *in situ* accelerated test, three typical cell configurations, as schematically shown in Fig. 1, were used for the perfluorosulfonic ionomer degradation studies in PEMFC. They were denoted as MEA (Membrane Electrode Assembly), MGA (Membrane Gas Diffusion Assembly) and MNFA (Membrane Non-woven Fabric Assembly). Vulcan XC-72 (Cabot Corp.), carbon paper (SGL Carbon Group) and PTFE suspension were used for the gas diffusion layer preparation. Electrodes were fabricated using a screen-printing technique. Pt/C catalyst (46.6 wt.% Pt/CB; TKK Corp.), Nafion® solution (5%, Du Pont) were used for the electrode preparation. The Pt/C catalyst loading in the anode and cathode were 0.3 and 0.5 mg Pt cm^{-2} , respectively. Nafion loading was 0.4 mg cm^{-2} in both electrodes. Non-woven fabric made of polyester (provided by Tianbang National Engineering Research Center of Membrane Technology Co., Ltd. (TBM)) was used to prepare MNFA. The MEA, MGA, and MNFA were prepared by hot pressing and the effective area of the electrodes was $\sim 4\text{ cm}^2$.

All the cells were tested at 80°C and 50% RH with H_2 and O_2 as the reactant gases. The flow rates of inlet gases were controlled at a fixed rate (H_2 40 ml min^{-1} , O_2 60 ml min^{-1}). The accelerated

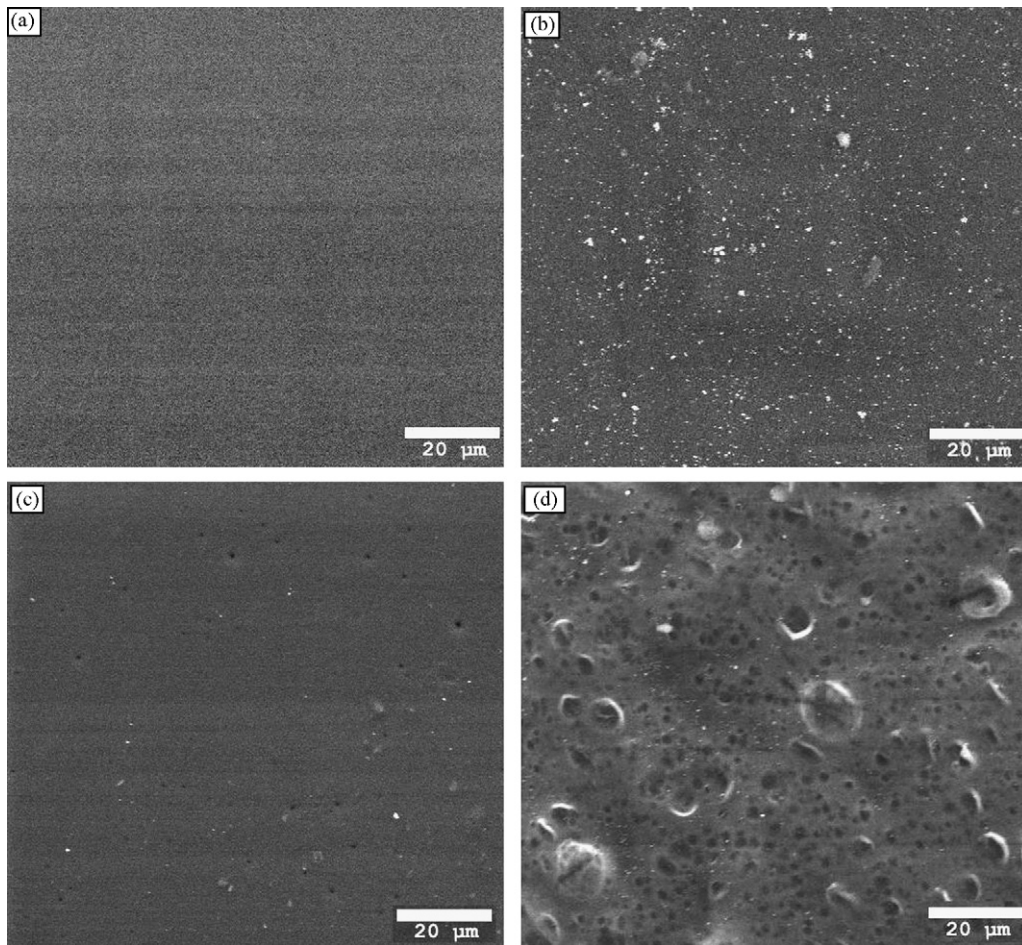


Fig. 2. Scanning electron micrographs of NRE 212 and Pt/NRE 212 membrane: (a) fresh NRE 212 membrane; (b) fresh Pt/NRE 212 membrane; (c) degraded NRE 212 membrane; (d) degraded Pt/NRE 212 membrane.

durability test lasted for 24 h. Water from the H₂ side and the O₂ side effluents was collected in cold traps for the fluoride analysis.

3. Results and discussion

3.1. Microstructures of Pt/NRE 212 composite membranes

Shown in Fig. 2 are some typical images of the surface of a NRE 212 and a Pt/NRE 212 membrane sample, before and after accelerated degradation procedure, showing that the degree of damage was increased by the presence of Pt in the NRE 212 membrane. Large defects, such as bubbles, tears and bumps, were found on the Pt/NRE 212 membrane surface.

3.2. Effect of Pt particles on the FER in an *ex situ* Fenton test

Both Fenton tests [27–29] and H₂O₂ flow cell tests [30] have been used for *ex situ* characterization of PEM degradation. Though there is still a debate on how well these *ex situ* accelerating tests correlate to the PEMs degradation under conditions for real fuel cells operation [31], the exposure to liquid-phase (Fenton's tests) and gas-phase (H₂O₂ flow cell tests) oxidizing species (e.g. H₂O₂ and HO• free radicals) could be used to evaluate the chemical durability of the electrolyte materials.

As shown in Fig. 3, the trends of the FER and weight loss curves indicated that the degradation rate of the samples decreased with the exposure time, consistent with previous *ex situ* Fenton studies by others [23,29]. Compared to the FER and weight loss results of

a NRE 212 membrane, the deposition of Pt particles in the Pt/NRE 212 membrane accelerated the production of F⁻ ions.

Shown in Fig. 4 are some typical FT-IR spectra of the NRE 212 and Pt/NRE 212 membranes before and after the Fenton solution treatment, suggesting (i) a change in the state of the hydrogen-bonded water and; (ii) the oxidative degradation of –SO₃H and the formation of cross-linked R–SO₂–O–SO₂–R group (as shown in Scheme 1).

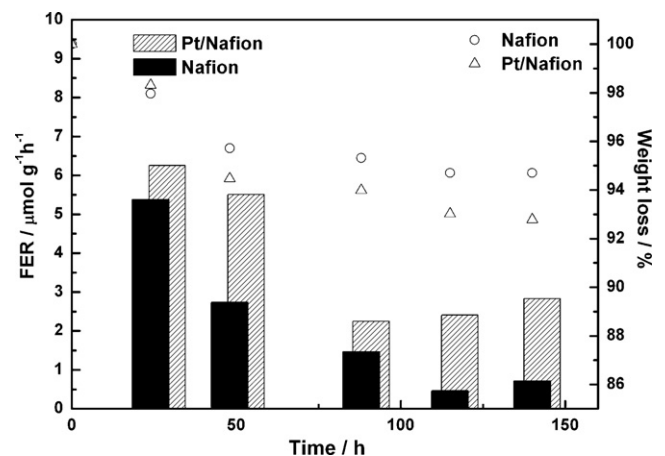


Fig. 3. Degradation rate (fluoride emission rate (FER) and weight loss) of NRE 212 and Pt/NRE 212 membranes.

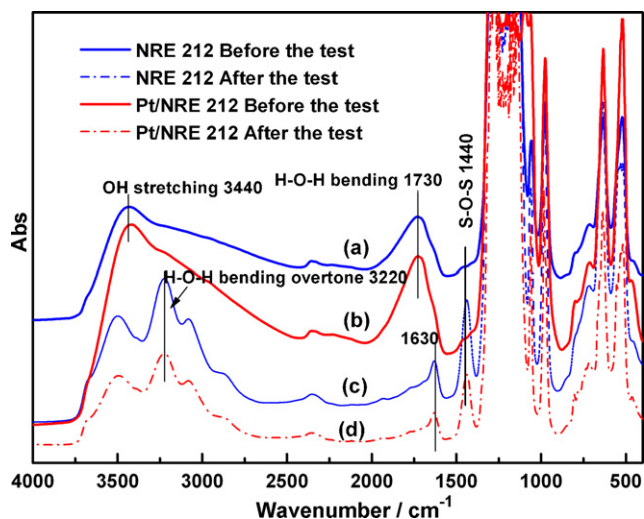


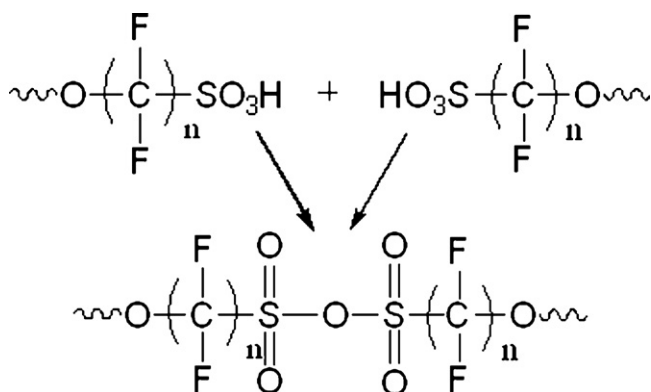
Fig. 4. The FT-IR spectra of the Nafion membrane: (a) fresh membrane, (c) degraded membrane; and Pt/Nafion membrane: (b) fresh membrane, (d) degraded membrane.

A broad band at 3440 cm^{-1} (ν_3 OH water stretch) and a strong absorption at 1730 cm^{-1} (bands of protonated water H_3O^+ molecules) [32] are present in the fresh sample. With the Fenton solution treatment, two peaks in the range of $3000\text{--}3500\text{ cm}^{-1}$ (the bending overtone of H–O–H) were observed. And the H–O–H bending peak shifted from 1730 cm^{-1} to 1630 cm^{-1} , similar to those reported by Qiao et al. [33] and Rieke and Vanderborgh [34]. The spectral changes implied that the hydrogen-bonded water in the membrane was broken with the treatment of Fenton solution. A narrow, intense peak at 1440 cm^{-1} was easily identified in the IR spectra of the degraded membrane samples. This peak accompanied with the loss of water peak (1630 cm^{-1}) and the appearance of the 3220 cm^{-1} peak (H–O–H bending overtone). This band represented to the antisymmetric SO_2 vibration, which was attributed to the cross-linking of $-\text{SO}_3\text{H}$ groups [33,35,36].

Moreover, the FT-IR spectra indicated that the NRE 212 and the Pt/NRE 212 membrane underwent the same chemical degradation process during the Fenton solution treatment. However, the presence of the Pt particles greatly accelerated the degradation rate of the polymer, due most likely to enhanced production of HO^\bullet free radicals by Pt particles.

3.3. Detection of free radicals in the decomposition of H_2O_2

It was reported that free radical species formed in the H_2O_2 decomposition on heterogeneous catalysts [8,37]. To verify whether H_2O_2 decomposition on Pt catalyst could generate the pos-



Scheme 1. Formation of the cross-linking R– SO_2 –O– SO_2 –R group.

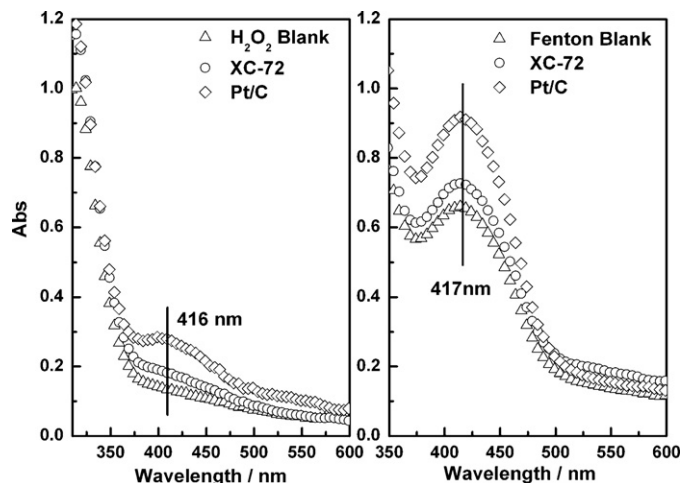


Fig. 5. Effect of Pt/C and CB XC-72 on hydroxyl radical generation in the H_2O_2 solution (a) and Fenton reaction (b).

sible accelerated degradation species (HO^\bullet free radicals), a simple colorimetric method was used as described elsewhere [21,22].

Considering that Pt came mainly from the Pt/C catalyst in a real fuel cell under operating conditions, we used the commercial Pt/C and carbon black (CB) XC-72 in our study. As shown in Fig. 5(a), the HO^\bullet free radicals could not be detected in the blank H_2O_2 solution. When the same amount (1 mg) of Pt/C and XC-72 was added into the reaction media separately, the characteristic absorption peak appeared at 417 nm, confirming the presence of free radicals (HO^\bullet). The intensity of the absorption peak of Pt/C (0.2744) is higher than that of XC-72 (0.1794), indicating that the catalytic activity of Pt/C is much higher than that of active carbon XC-72. Fig. 6 also demonstrated that the decomposition rate of H_2O_2 in the presence of Pt/C is about 7 times greater than that with XC-72. The results suggested that (i) both Pt/C and XC-72 could catalytically decompose H_2O_2 with the generation of HO^\bullet , and (ii) the activity to produce HO^\bullet with Pt is higher than that of XC-72. As Mittal and Motupally reported [38], the adsorbed peroxide decomposed with the formation of HO^\bullet radicals at any potential if peroxide molecule bonds with one Pt site. Furthermore, the Pt is oxidized to Pt^{2+} . The divalent platinum could also facilitate the production of HO^\bullet , which had been confirmed by the identification of HO-DMPO spin adducts using ESR spectroscopy [39]. The possible mechanism is shown in Scheme 2.

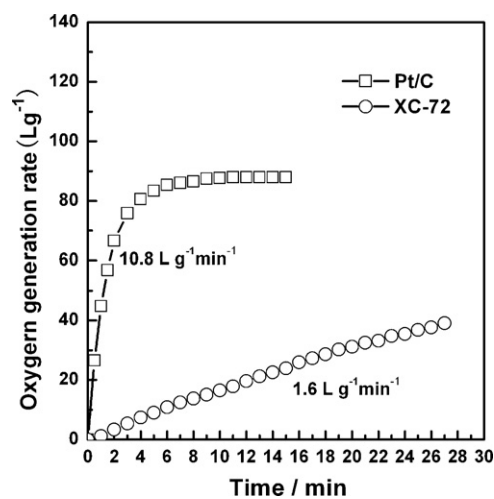
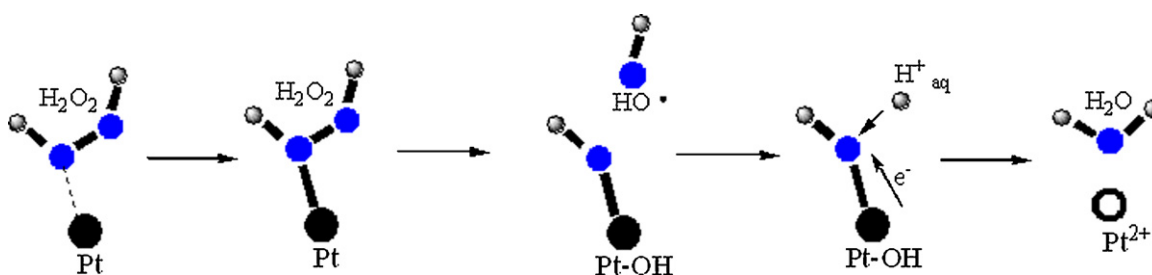


Fig. 6. Comparisons of H_2O_2 decomposition rate with Pt/C and XC-72 at 80°C in 3 wt.% H_2O_2 solution.



Scheme 2. Free radical formation on the surface of Pt during the decomposition of H_2O_2 .

Similar mechanism may occur on the surface of active carbon. Oliveira et al. [40] studied the H_2O_2 decomposition and oxidation of organics in an aqueous medium in the presence of activated carbon. They concluded that the reducing sites in the carbon can activate H_2O_2 to generate HO^\bullet radicals which can lead to two competitive reactions, i.e. the hydrogen peroxide decomposition to oxygen or the oxidation of organics in water.

Moreover, the same conclusions could be obtained in the Fenton system shown in Fig. 5(b). It also showed that the Fe (II) ion enhanced the activity to produce HO^\bullet in the presence of Pt/C or XC-72. These results strongly suggested that Pt could accelerate the membrane degradation in H_2O_2 solution and Fenton environment as well.

3.4. *In situ* OCV accelerated test with three different cell configurations

The *in situ* durability tests were performed in three typical cell configurations under open cell conditions, which represent the most severe conditions for degradation of PEMs [41–44], especially at low humidity with relatively high partial pressures of the reactant gases.

It is noted that the F^- released was not only from the degradation of the membrane but also from the perfluorosulfonic ionomer used in the electrode. Two cell configurations (Fig. 1(a) and (b)), were designed for comparison. Fig. 7 shows the total FER from the MEA mode cells with Nafion and Pt/Nafion membranes at 80°C and 50% RH exposed to H_2 and O_2 at OCV. Obviously, Pt dispersed in the membrane aggravated the degradation of the MEA. It was well known that the fuel cell operating condition was similar to the Fenton-like system with possible contamination (Fe^{3+} , Ni^{2+} , Cu^{2+}) from the end plates. H_2O_2 could generate on the cathode side in

the ORR process on the surface of Pt/C catalyst ($\text{O}_2 + 2\text{H}^+ = \text{H}_2\text{O}_2$; $E_0 = 0.695\text{ V}$) [45], and on the anode side with the reaction of crossover oxygen from the cathode side and the H_{ads} atom adsorbed on Pt site [46]. H_2O_2 was detected electrochemically with the membrane using Pt microelectrodes by Liu and Zuckerbrod [5]. The complementary mathematical model was established by Chen and Fuller [47] to understand the mechanisms of H_2O_2 formation, transport and reaction in PEMFCs. Previous experimental evidence [48] supports the membrane degradation mechanism involving H_2O_2 formation and subsequent radical attack.

As discussed in the previous section, the H_2O_2 formed in the anode and cathode side could decompose to form HO^\bullet radicals if it bonds with an active Pt site [38,49]. Because of the short lifetime of the oxygen radicals such as HO^\bullet and HO_2^\bullet , Kim et al. [18] provided evidence of indirect radical (carbon radicals) formation on Pt deposited in the membrane using electron spin resonance (ESR). Cai et al. [50] reported similar results in the studies of fuel cell catalysts degradation.

Shown in Scheme 3 is a possible reaction sequence for formation of hydrogen peroxide and HO^\bullet radical at a Pt active site and the dissolution of Pt [38,41,45,51,52]. The Pt dispersed in the membrane could also catalyze the reaction of hydrogen and oxygen crossed from the anode and cathode sides. Furthermore, the Pt ion (Pt^{2+} , Pt^{4+}) could be the center of free radicals formation [12]. Thus H_2O_2 and the intermediate HO^\bullet generated during this process. That was the reason that Pt in the membrane could aggravate the degradation of the MEA.

We recognized that it is possible for radical species to form through other pathways, like the reaction of hydrogen and oxygen at an active site of Pt with the formation of free radicals directly. This has been confirmed using *in situ* characterization under fuel cell operation conditions [10,11].

On the other hand, it could be seen in Fig. 7 that the membrane degradation was still visible in the absence of electrode, and the FER of MGA cell was reduced by one order of magnitude compared to that of the MEA cell. This can be explained as follows: first, in the absence of Pt/C catalyst in the GDL, the OCV value of the MGA cell (at round 0 V vs anode side as the reference electrode) is much lower than that of the MEA cell (between 0.9 V and 1.0 V vs anode side as the reference electrode). And the process shown in Scheme 3 did not occur under the MGA cell condition. Second, the catalytic activity of XC-72 is much lower than that of Pt/C for the formation of H_2O_2 (the ORR process) and decomposition of H_2O_2 as shown in Fig. 6 [50]. Third, in the MGA cell, the whole F^- ions released from the degradation of the membrane without the F^- from perfluorosulfonic ionomer in the electrode layer. The result from Fig. 7 provided another evidence that Pt played a very important role in accelerating the membrane degradation.

In order to eliminate the effects of Pt/C and active carbon XC-72, we designed the MNFA cell (in Fig. 1(c)). Under this condition, it clearly showed that the FER of the Pt/NRE 212 membrane is higher than that of the NRE 212 membrane (Fig. 8), implying that Pt may accelerate membrane degradation. However, Fig. 8 indicates that

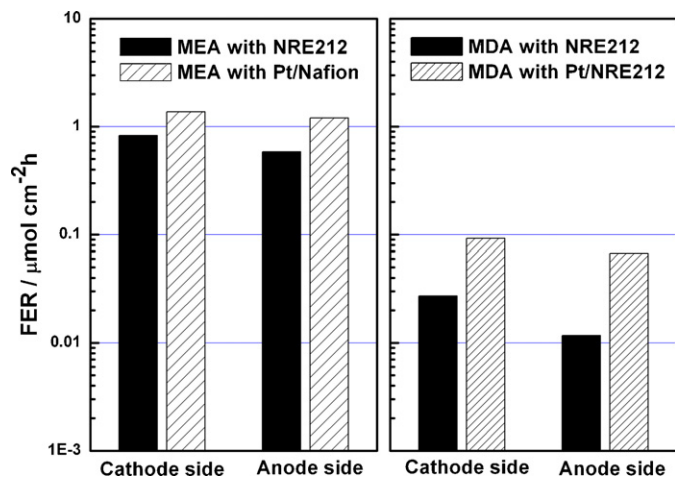
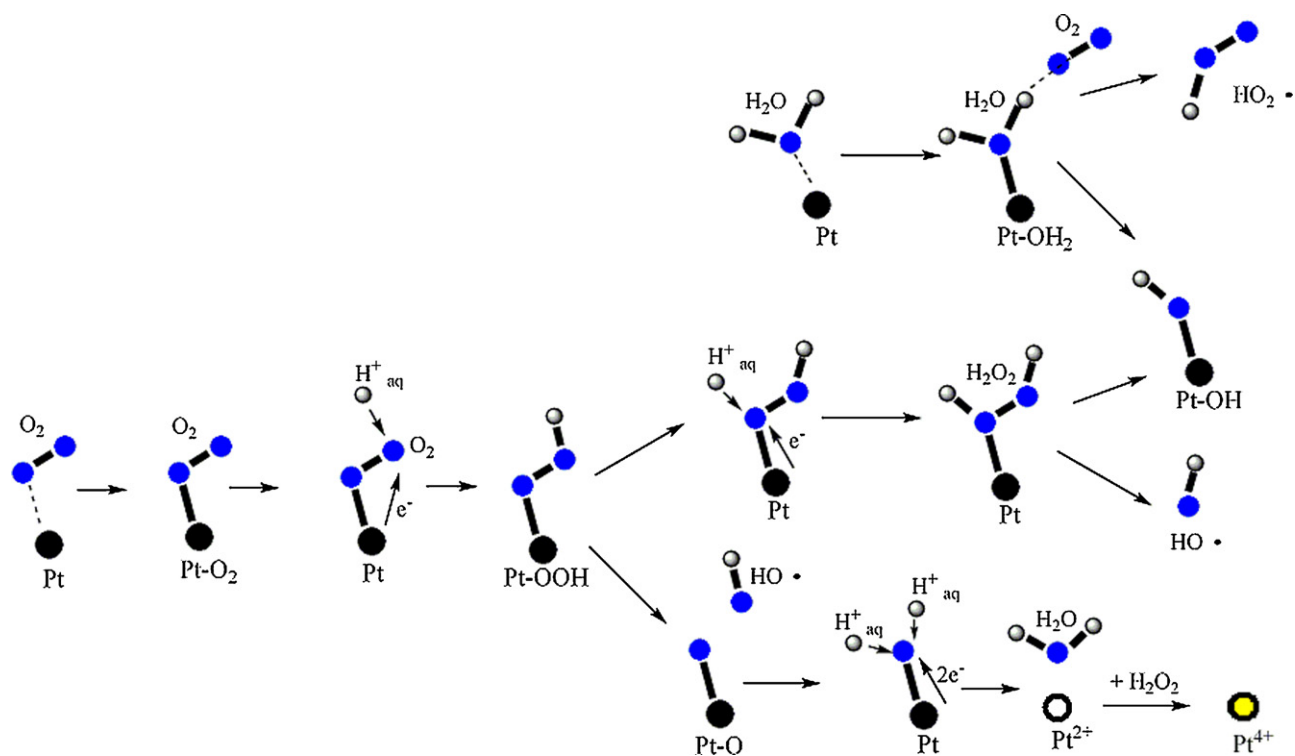
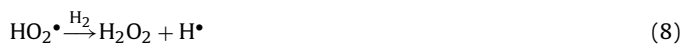
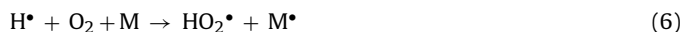


Fig. 7. Fluoride emission rate (FER) of Nafion and Pt/Nafion membrane in the MEA and MGA cell modes ($T_{\text{cell}} = 80^\circ\text{C}$, RH = 50%).



Scheme 3. Free radical formation on one Pt active site and the dissolution of Pt in fuel cell environment.

the membrane degradation is still observable because low pressure explosive reaction of hydrogen and oxygen was a typical branched-chain reaction (Eq. (1)–(8)), leading to the formation of H_2O_2 and HO^\bullet :



4. Conclusions

The effect of platinum on a Nafion membrane degradation in PEMFCs was investigated. *Ex situ* accelerated Fenton tests indicated that Pt deposited into the membrane may accelerate the degradation, consistent with an increase in the FER and observed changes in morphology. The generation of hydroxyl radicals (HO^\bullet) was characterized by UV–vis spectrophotometer using dimethyl sulfoxide (DMSO) as the trapping agent. It was confirmed that Pt catalyst could aggravate the production of HO^\bullet free radicals in the decomposition of H_2O_2 . In the *in situ* test, three typical cell configurations were used. In all the three configurations, the FERs of the Pt/NRE 212 membrane were higher than those of the NRE 212 membrane. The Pt deposited in the membrane functioned as a catalytic center for H_2O_2 and HO^\bullet free radicals formation that led to PEM degradation. Moreover, the degree of degradation in the three cell configurations follows the order of MEA > MGA > MNFA, suggesting that Pt in the catalyst layer still could accelerate the degradation of the PEM and the active carbon also had some activity in aggravating this process. However, the detailed degradation mechanism is yet to be determined, especially the effect of morphological character of the platinum deposited within the membrane.

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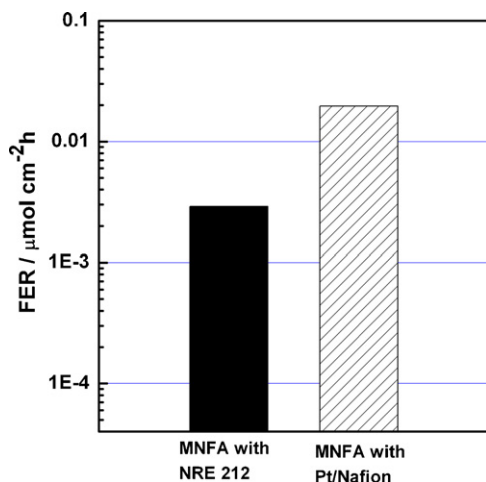


Fig. 8. Fluoride emission rate (FER) of NRE 212 and Pt/NRE 212 membrane in the MNFA cell mode ($T_{\text{cell}} = 80^\circ\text{C}$, $\text{RH} = 50\%$).

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