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Chemical Degradation of SPEEK/CLOISITE/TAP Membrane Under Fenton Reagent Accelerated Stress Test

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Abstract

The chemical degradation of SP/CL/TAP membrane had been studied using accelerated stress test (AST) to reduce the testing time for membrane degradation. The membrane was prepared using solution intercalation method. The membrane was immersed into Fenton Reagent solution (5% H_2O_2, 50 ppm $FeSO_4$) as a function of time in order to simulate the chemical radical attack on the membrane inside DMFC system. The commercial Nafion® 117 was used as reference membrane. It was found out that the SP/CL/TAP membrane weight reducedby 6% after being immersed in Fenton Reagent for 6 hours. FESEM image of the SP/CL/TAP and Nafion® showed severed development of pinholes on the surface of the membranes after 6 hours of degradation. Both of the membranes showed similar proton conductivity deterioration behaviour; SP/CL/TAP proton conductivity dropped from $5.76x10^{-4}$ S/cm to $3.36x10^{-4}$ S/cm, while Nafion® dropped from $7.46x10^{-4}$ S/cm to $5.20x10^{-4}$ S/cm under 3 hours degradation testingand remained constanttowards the end of the testing. This shows that the performance of the SP/CL/TAP membrane under DMFC severe degradation environment was found comparable to the commercial Nafion® membrane. Thus, it can be concluded that the SP/CL/TAP membrane is a potential proton exchange membrane for long term usage in DMFC system.

Keywords : *SPEEK, composite membrane, degradation, Fenton Reagent, Nafion*

1 INTRODUCTION

Direct methanol fuel cell (DMFC) is a very promising replacement for lithium battery due to ease of refuelling and handling, high energy density, and high efficiency. Furthermore, DMFC itself is a power generation device, thus it eliminates the need to constantly charging from the grid to store energy and improves the mobility of mobile devices.Department of Energy (DOE), United States of America (USA) has put 5,000 hours of operating time as minimal requirement for DMFC before it can be commercialized (Xiao-Zi Yuanet al., 2011). In order to understand the degradation behaviour of DMFC, accelerated stress test (AST) had been introduced. Under AST testing, the DMFC operation will be conducted under severe operating condition, i.e. high electrical loading, extreme relative humidity (RH) changes, high radical environment, etc. Using AST test had been able to shorten the lifetime testing of DMFC and at the same time are able to understand better degradation behaviour of DMFC.

In DMFC operation, partial reduction of O_2 gas at cathode side will form H_2O_2. Due to acidic condition during DMFC operation, the iron back plate have tendencies to be corroded, thus forming Fe^{2+} ion at anode side. The Fe^{2+} ion then will react with H_2O_2 to form radicals which will attack the break up the membrane polymer chain, causing pinholes formation on the membrane which will degraded the DMFC performance. Equation (1), (2) and (3) show the chemical reaction for H_2O_2 and radical formation inside DMFC.

$$O_2 + 4H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH \tag{2}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + OOH \tag{3}$$

Fenton Reagent test is one of the testing under AST use to study the chemical degradation behaviour of membrane electrode assembly (MEA), one of the important component in DMFC. By adding iron salt into H_2O_2 solution, it will prompt the formation of $OH\bullet$ and $OOH\bullet$ radicals, thus mimics the radical formation in DMFC operation.Many research had been conducted to study the chemical degradation behaviour of the membrane using Fenton Reagent test. Haolin Tang et al. (2007) found out that the their Nafion®/PTFE membrane showed lower F- formation compared to Nafion® 111 membrane after immersed in Fenton Reagent for 72 hours. F- is one of the indicator that the radicals are breaking up the PFSA polymer chain, since the PFSA membrane consists of fluorine based polymer. Wang et al. (2008) study the chemical degradation on Nafion® 111 membrane. Based on their findings, the Nafion membrane showed high formation of pinholes after 48 hours of testing. The pinholes formation was the reason for increase in H_2 gas crossover and reduction of membrane mechanical strength.

Juhana Jaafar et al. (2011) developed a new novel SPEEK/Cloisite® 15A/TAP membrane for DMFC system. This new nano-composite membrane showed better proton conductivity and methanol permeability characteristics compared to Nafion® 112 membrane. Thus, this new membrane showed promising opportunities to be a viable replacement for Nafion® in DMFC applications. Since that membrane durability and lifetime is the important requirement for DMFC operation, it is crucial to conduct research to study the chemical degradation behaviour of SP/CL/TAP membrane using Fenton Reagent test.

2 METHODOLOGY

2.1 Materials

Poly (ether ether ketone) (PEEK) in powder form was obtained from Vitrex Inc., USA. Concentrated sulfuric acid (H_2SO_4) (9597%)purchased from QRex. Dimethylsulfoxide(DMSO) was obtained from Sigma-Aldrich as solvent for solution preparation. Cloisite 15A® was obtained from Southern Clay Products, Inc. 2,4,6-Triaminopyrimidine (TAP) in powder form wasobtained from Sigma-Aldrich and was used as a compatibilizer forproducing nanocomposite membranes.

2.2 Membrane preparation

Sulfonation reactions were conducted using H_2SO_4 as thesulfonating agent. A mixture of 50 g PEEK and 1000 mL H_2SO_4 was stirred at room temperature for 1 h. Then thesolution was continuously stirred at $55°C$ for 3 h. The sulfonatedpolymer was recovered by precipitating the acid polymer solutioninto a large excess of ice water. The resulted SPEEK polymer wasfiltrated and washed thoroughly with deionized water until the pH became 67. Finally, the sulfonated PEEK was dried in the dryingoven at $80°C$ for 24 h.

For membrane preparation, a 10 wt% of SPEEK solution was first prepared by dissolving 10 g SPEEKin 60 mL DMSO and stirred at $60°C$ for 24 h. 0.25 g of Cloisite 15A and 0.5 g of TAP was dissolved in 15 mL DMSO in 2 different container to produce 1 wt% solutions. The solutions was stirred for 24 h at $60°C$ to ensure its homogeneity before being added to the SPEEK solution. The final 90 mL mixture of SPEEK, Cloisite and TAP solutions wasvigorously stirred for 24 h at $60°C$ to produce a homogeneous solution.

To produce the SP/CL/TAP membrane, the solution was casted on a glass plate with a casting knife to form a solution film. The result film then dry in a vacuum oven for 24 hours at $80°C$, and another 6 hours at $100°C$ to remove any residual solvent completely. After that, the film is detached from the casting glass by immerse into the water. The film then undergoes another drying process for 3 days at $80°C$ in a vacuum oven. For the final process, the new form film is treated in 1 M sulphuric acid (H_2SO_4) solution for 1 day at room temperature subsequently rinse with water several times to remove any remaining acid on the film and to assure all the sulfonate group is in H form.

2.3 Chemical degradation test

Fenton Reagent test had been used to study the chemical degradation behaviour of SP/CL/TAP membrane. The SP/CL/TAP and Nafion® membrane was dried for 24 hours at $60°C$ to remove remaining moisture. 5% of hydrogen peroxide (H_2O_2) and 50 ppm iron sulphate ($FeSO_4$) was used to prepare the Fenton Reagent solution. Both membrane were weigh before being immersed in Fenton Reagent solution for 6 hours. Each hour, the test will be stopped and the membranes will be taken out from the solutions and rinsed under excessive water to stop the degradation process. The degraded membranes then were dried and be taken to weight measurement and proton conductivity test. After that, the membrane were immersed in new Fenton Reagent solution and the process was repeated until 6 hours of testing ends.

2.4 Morphological study

The morphology of SP/CL/TAP and Nafion® membranes was investigated using a field emission scanning electron microscope (FESEM) (JSM-6701F, JEOL USA, Inc.,). Specimens for the morphological analysis were prepared by freezing the dry membrane samples in liquid nitrogen and breaking them for a cross-section image analyses. Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of gold before FESEM examination.

2.5 Proton conductivity study

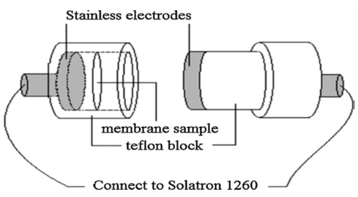

Figure 1: Schematic diagram of proton conductivity cell.

Transverse proton conductivity (PC) of the membrane samples was measured by Solatron 1260 Impedance instrument over a frequency range of 1 Hz to 107 Hz with 50 mV - 500 mV oscillating voltage. The hydrated membrane was sandwiched between two stainless steel block electrodes as shown in Fig. 1. The conductivity, σ, of samples in the transverse direction was calculated from the impedance data, using the relationship:

$$\sigma = \frac{d}{RS} \tag{4}$$

where d and S are the thickness and face area of the membrane sample, respectively, and R is 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 interpolation method in Frequency Response Analyzer (FRA) software.

3 RESULTS AND DISCUSSION

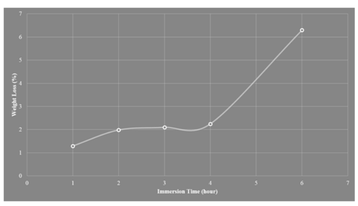

Figure 2: Weight loss of SP/CL/TAP membrane

3.1 Fenton Reagent test

Figure 2 showed the weight loss of SP/CL/TAP membrane after 6 hours Fenton Reagent test.The SP/CL/TAP membrane has lost its weight around 6.5% from its initial condition. The weight reduction can be related to the radicals activity in Fenton Reagent solution. The $OH\bullet$ and $OOH\bullet$ radicals are unstable molecules, thus this radicals will attacked SP/CL/TAP membrane polymer chain to receive the remaining missing valence to formed water. The attacked chain will break up from the membrane, thus reduced the membrane weight after being immersed in Fenton Reagent solution. Same findings also being made by Wang et al. (2008) and Tang et al. (2007), where they observed the formation of F- ion inside the Fenton Reagent solution of the test, which comes from the Nafion® polymer chain after being break up by the radicals.

3.2 Morphological analysis

Figure 3 showed the FESEM image of SP/CL/TAP and Nafion® membrane before and after 6 hours of Fenton Reagent test. Both membranes showed formation of pinholes and deformation of membrane surface after being exposed to Fenton Reagent after 6 hours. Same observation also being reported by Wang et al. (2008) which showed the pinholes formation and severe deformation of Nafion® membrane on its surface. This is because both membranes have undergoes chemical degradation process due to $OH\bullet$ radical attack to the membrane polymer chain. The formation of pinholes and deformation of membrane surface on Nafion® membrane are more severe than SP/CL/TAP membrane. This might happen because of incorporation of Cloisite membrane inside SPEEK polymer chain gives the SP/CL/TAP membrane better resistant towards radical attack, thus gives SP/CL/TAP membrane better chemical degradation resistance than Nafion® membrane.

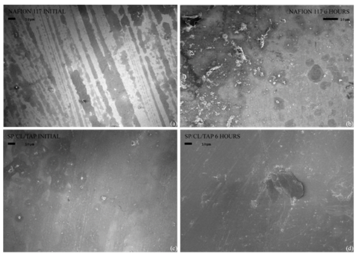

Figure 3: FESEM image for Nafion (a) before and (b) Fenton Reagent test. Image (c) and (d) is the FESEF image of SP/CL/TAP membrane before and after Fenton Reagent test, respectively.

3.3 Proton conductivity analysis

The SP/CL/TAP and Nafion® membrane PC reduction characterisation are shown in Figure 4. It is observed that both SP/CL/TAP and Nafion® membrane showed same degradation behaviour, with SP/CL/TAP membrane PC dropped from $5.76x10^{-4}$ S/cm to $3.36x10^{-4}$ S/cm, while Nafion® membrane PC dropped from $7.46x10^{-4}$ S/cm to $5.20x10^{-4}$ S/cm in 3 hours testing, before being constant towards the end of the 6 hours testing. The degradation behaviour can be related to the detachment of SO_3 acid group and pinholes formation on the membrane, which reduced the conductance side of the membrane. Tang et al. (2007) also added that the pinholes formation on the membrane not only reduce the conductance side of the membrane, but also allowed the reactant to cross over and reduce the mechanical strength of the membrane.

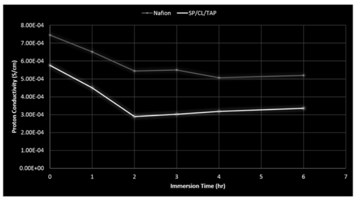

Figure 4: Degradation behaviour of proton conductivity for Nafion and SP/CL/TAP membranes under Fenton Reagent test

4 CONCLUSION

From the findings, it can be shown that the new SP/CL/TAP membrane has good chemical degradation resistance under DMFC conditions. The FESEM image of SP/CL/TAP membrane shown less pinholes formation than Nafion® membrane. The membrane also did not show visible surface deformation as compared to Nafion® observation. For proton conductivity characteristics, the SP/CL/TAP membrane shown similar performance degradation behaviour as Nafion® membrane. Thus, it can be concluded that the SP/CL/TAP membrane is a potential proton exchange membrane for long term usage in DMFC system.

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