Preparation and Characterisation of Composite Sulfonated Polyether Ether Ketone for Direct Methanol Fuel Cells

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Abstract. Direct Methanol Fuel Cell (DMFC), uses a proton exchange polymer electrolyte which one of the key components developed to realize the commercialization of fuel cells in transportation and portable equipment. Poly Ether Ether Ketone (PEEK) is a thermoplastic material that has a combination of physico-chemical and good mechanical properties. The introduction of cesium tungstophosphoric acid (Cs-PWA) into the polymer matrix is an easy strategy to improve the properties of sulfonated PEEK. This research aims to study the effect of amount Cs-PWA loading in the fabrication of sulfonated PEEK on the membrane characteristics such as FTIR and XRD analysis, water uptake, methanol permeability, and proton conductivity. The results indicated that sPEEK/Cs-PWA membranes were potential candidate as proton conductive membrane for application of DMFC due to enhancement of proton conductivity and methanol permeability performance.

Key words – DMFC, fuel cells, sPEEK, composite membrane

1. Introduction

Fuel cell acquires a serious attention as an alternative energy source, replacing conventional energy system (fossil), due to its high efficiency, low negative impact to environment, and flexibility in various applications of electricity needs. The technology of Direct Methanol Fuel Cell (DMFC) is similar to the Proton Exchange Membrane Fuel Cell (PEMFC), where methanol substitutes hydrogen to be fed directly into a fuel cell. The DMFC has been realised for many years as the best candidate to open the market for portable fuel cell technology caused by easy liquid fuel storage and handling.

Electrolyte membrane is the key component in developing DMFC. Today membrane from ionomer of perfluoronated like Nafion® (DuPont) is used commercially due to its high conductivity. In DMFC application, one of the arising problems is crossover of methanol from anode to cathode causing low cell potential. Other frailty, the perfluoronated membrane is not appropriate if applied at temperatures beyond 100°C. As well, its high cost is another challenge to solve.

Hydrocarbon polymers containing polar groups have high water absorption over a wide range of temperatures. Some examples of developed hydrocarbon polymers are polyethersulfon (PESF) [1,2], poly(arylen ether), polyester and polyimide [3]. The sulfonation process of commercial polymer is one of strategies developed to obtain modified polymer acting as a proton exchange membrane [4]. The degrees of hydrophilic, conductivity and mechanical properties of sulfonated membrane depend on the
degree of sulfonation (DS) [5]. In addition, previous researchers [6] reported that to reduce the permeability of methanol from anode to cathode, non-fluoronated membranes such as polybenzimidazol (PBI), sulfonated poly(ether ether ketone) (sPEEK), and 2-akrilamindo-2-metil propane sulfonat (AMPS) were developed by adding inorganic components. This approach has been successful in reducing the permeability without decreasing the proton conductivity.

The hydrocarbon polymer material which is potential to develop as a proton exchange membrane is sulfonated polyether ether ketone (sPEEK). The presence of group of sulfonat acid causes sPEEK more hydrophilic because it increases the polymer acidity [7]. The DS is controlled by the temperature and reaction time of sulfonation. The use of various types of inorganic fillers is to enhance and maintain a suitable hydration and to improve mechanical properties. Heteropoly acids are one of the promising acids to be incorporated into the polymer matrix. Cesium salt of tungstophosphoric acid (Cs-PWA, Cs$_2$H$_3$$_{3}$PW$_{12}$O$_{40}$) modified with Nafion membranes has been reported demonstrating low H$_2$ crossover [8] and high conductivity membranes at low RH [9]. This work presents the synthesis and characterization of Cs-PWA incorporated into sPEEK membranes. Physico-chemical characterizations including FTIR, XRD, water uptake, ion exchange capacity (IEC), methanol permeability and proton conductivity were conducted by varying Cs-PWA loading.

2. Experimental

The materials used in the experimental works include: PEEK from Victrex kindly provided by the Goodfellow Cambridge Limited, sulfuric acid 95-97 wt.%, methanol, and dimethyl acetamide from Merck. Tungstophosphoric acid and cesium carbonate were received from Aldrich.

2.1. Sulfonation of Poly Ether Ether Ketone

Pellets of PEEK were dried in an oven at 80°C in a vacuum for 12 hours. These PEEK were then dissolved and reacted with sulfuric acid in the ratio of 1:20 (w/v). To get the perfect reaction, PEEK with sulfuric acid was stirred vigorously. Sulfonation reaction can be stopped by the precipitation process by inserting the polymer solution into ice water (in order to return to forms dense polymer sPEEK). Excess acid in the sPEEK precipitate can be washed with water repeatedly until pH neutral (6-7). sPEEK dried in an oven at room temperature for 12 hours, and at 60°C for 12 hours.

2.2. Filler Preparation

Cs-PWA was prepared by dripping a solution of cesium carbonate (0.1 M) into a flask containing a solution of tungstophosphoric acid (0.1 M) at a constant temperature and stirring speed. Mixture then left overnight at room temperature. The deposition was separated by using a rotary evaporator at a temperature of 60°C and a pressure vacuum.

2.3. Membrane Preparation

The sPEEK were dissolved in dimethyl acetamide (DMAc) aided by stirring for 2 hours. Cs-PWA and sPEEK composite membrane were prepared by casting on petridish from polymer solutions containing the amounts of Cs-PWA. Membranes were dried at 50°C for 48 hours. The membrane is taken slowly and washed with HCl and distilled water then heated 1 hours at 80-90°C in vacuum. The thicknesses of prepared membranes were about 100 μm.

2.4. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy was used to identify the sulfonat group in the polymeric membrane. In this study, FTIR spectra were given by the spectrometer IR Prestige 21 Shimadzu. The spectra were measured at a wave number range of 400 – 4000 cm$^{-1}$. 
2.5. X-Ray Diffraction

X-Ray diffraction (XRD) was used to analyse the crystallites structure of membrane. The XRD data were recorded with a Bruker D8 Diffractometer using Cu Kα radiation (λ = 1.54 nm). Radiation was generated at 60 KV and 60 mA. The 20 angular regions between 10° and 70° were explored at a nominal step size of 0.033° 20 and time per step of 100 seconds. The scan was carried out in continuous mode.

2.6. Water Uptake

The membrane water uptake was measured in water at room temperature. It was calculated from the difference in weight between wet and dry samples. The wet weight was determined after immersion of the samples in the water at room temperature for 48 hours. Subsequently, the membrane surfaces were wiped with a tissue paper and weighed immediately. To obtain the dry weight, the samples were heated in an oven at 120°C for 2 hours.

\[
WUT = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100\%
\]

where WUT, \(m_{\text{wet}}\), and \(m_{\text{dry}}\) represent water uptake (wt.%), wet and dry membranes weight, respectively.

2.7. Methanol Permeability

Methanol permeability was measured with a two-compartment glass cell. One compartment was filled with 100 dm³ of 3 mol dm⁻³ ethanol solution and the other was filled with 100 dm³ of deionised water. The membrane was clamped between two compartments. Solutions in each compartment were stirred continuously during measurement. Ethanol concentration in the receiving compartment was measured as a function of time by measuring the refractive index of a 0.5 dm³ sample from each compartment. The observed refractive index was compared to the corresponding value of the calibration curve. The time dependence of methanol concentration in the receiving compartment followed Fick’s first law, assuming \(C_B \ll C_A\); hence \(C_A\) was considered constant.

\[
V_B \frac{dC_B(t)}{dt} = \frac{A}{L} DK C_A
\]

where \(C_A\) and \(C_B\) are ethanol concentrations in compartment A and B; \(A\) and \(L\) are the cross section of membrane area and membrane thickness, respectively; and \(D\) and \(K\) are the ethanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. \(D\) was assumed constant throughout the membrane and \(K\) was independent of concentration. The product \(DK\) is membrane permeability calculated from the slope of \(C_B\) with respect to time, \(C_B(t)/t\), was as follows:

\[
P = \frac{C_B(t) V_B L}{t C_A A}
\]

2.8. Proton Conductivity

Proton conductivity was measured using conductivity cell connected to LCR meter, HIOKI 3522-50 LCR HiTESTER. Measurement was carried out in fully humidity condition.

3. Result and Discussion

3.1. FTIR Analysis

The infra-red absorption spectra for the PEEK, sPEEK and sPEEK/Cs-PWA are shown in Fig 1. The following IR absorption bands show the present of sulphuric acid groups: 1080 cm⁻¹ absorption band arising from symmetric O=S=O stretch, band at 1024 cm⁻¹ is attributed to S=O bending, and band at 709 cm⁻¹ is ascribed to S-O stretching. Similar result was reported by Oh et al. [10]. There is a
The stretching band at around 985 cm\(^{-1}\) indicating the presence of cesium salt. On the other hand, Basheer and Anitha [11] showed that characteristic peaks of keggin structured tungstophosphoric acid identified at 1081 cm\(^{-1}\) (P-O stretching in the central tetrahedron PO\(_4\)), 796 and 893 cm\(^{-1}\) (bands for W-O\(_c\)-W and W-O\(_b\)-W corner and bridge respectively), 985 cm\(^{-1}\) (band W=O interacting to Cesium).

Fig. 1 FTIR spectra of sPEEK/Cs-PWA

3.2. XRD Analysis

Figure 2 shows the XRD pattern of the composite sPEEK/Cs-PWA membrane corresponding to unmodified sPEEK and Cs-PWA powder. The peak appeared in this figure confirmed the presence of crystalline structure of Cs-PWA salt. The crystalline structure of sPEEK are found at 2\(\theta\) of 20\(^{\circ}\), 22\(^{\circ}\) and 15\(^{\circ}\) which is belonged to PEEK crystalline plane [12] signifying low sulfonated PEEK [7]. The broad peak centered at about 2\(\theta\) of 20\(^{\circ}\) is indicated amorphous structure of sPEEK. It can be seen that the location of XRD peak of Cs-PWA in sPEEK/Cs-PWA is very similar to that of the Cs salt powder. However, the XRD peak intensities of the Cs-PWA are reduced significantly.

Fig. 2 XRD of sPEEK/Cs-PWA membranes
3.3. Water Uptake
Analysis of water uptake is carried out in order to investigate the performance of membrane related to the proton conductivity and mechanical strength. The proton transfer is facilitated with the presence of water in the membrane, and also it is able to increase the ionic conductivity of the membrane. However, the membrane will lose mechanical strength if it is able to absorb lots of water.

Figure 3 shows the effect of the addition of Cs-PWA composition to the water uptake properties of the membrane at room temperature. The increase of Cs-PWA loading, the water uptake values of membrane increase from around 20% to 80% water uptake with Cs-PWA loading from 1% to 15%. Similar result was shown by Doğan et al. [13] in another study on composite membrane sPEEK with Cs-TPA, although their result exhibited that with 15% Cs-TPA loading the water uptake was only about 35% for pristine sPEEK. They also reported that degree of sulfonation membrane affected the water uptake value due to the content of the protonated site (‒SO\(_3\)H) in membrane. Therefore, the water uptake of sPEEK/Cs-PWA is associated with two factors including sulfonic group in the sPEEK and hygroscopic nature of Cs-PWA.

![Fig. 3. The relationship between the composition of Cs-PWA and Water Uptake](image)

3.4. Methanol Permeability

![Figure 4. Methanol Permeability and Swelling Degree sPEEK/Cs-PWA membranes as a function of Cs-PWA amount loading](image)
Methanol permeability analysis performed using special preparatus which uses the principle of H-Cell. Figure 4 shows the effect of Cs-PWA composition to methanol permeability. It can be seen that methanol permeability decreases with increasing Cs-PWA loading and then increases after 9% Cs salt loading. The lowest methanol permeability at the value of $1.13 \times 10^{-8}$ cm$^2$/s is assigned at the composition of Cs-PWA 9% in membrane. This is lower than that of Nafion® 117 $5.66 \times 10^{-5}$ cm$^2$/s [12]. In another study on composite membrane sPEEK with Cs-TPA showed value of methanol permeability $4.7 \times 10^{-7}$ cm$^2$/s [13].

It seems that degree of sulfonation affects the characteristic of methanol permeability. An increase in the permeability of methanol with the loading Cs-PWA more than 9% might be caused by more water content in the membrane. Therefore, mechanical strength declines affected by too much primary water molecules deposited by sulfonate groups thus opening the axes of the membrane [8].

3.5. Proton Conductivity

![Fig. 5 Proton conductivity of sPEEK/Cs-PWA vs % Cs-PWA loading](image)

The proton conductivity of sPEEK/Cs-PWA membranes varying Cs-PWA loading with 100% RH is presented in Figure 5. The incorporation of inorganic Cs-PWA particles into the polymeric matrix improves the ionic conductivity of the membranes, but then dramatically decreases at the loading of Cs salt 12-15%. The highest ionic conductivity is shown by sPEEK/Cs-PWA 9% at around 0.02 S cm$^{-1}$. Similar trend was found with published result that higher loading of Cs salt than 10% caused decreased ionic conductivity [13]. The incorporated Cs-PWA particles provide water retention capability and acidity of the composite membrane. The enhanced acidity by introduction of Cs-PWA which is the well known as strong solid acid [11]. The proton conductivity of sPEEK/Cs-PWA is much higher than that of Nafion 117 ($0.0032$ S cm$^{-1}$) [14].

The overall result recommends that Cs-PWA combined into sPEEK membranes are potential membranes as proton exchange membrane for DMFC application. The further tests in the single cell of DMFC should be performed to investigate the overall appropriateness for commercial application.

4. Conclusions

Sulfonated polyether ether ketone incorporated with cesium tungstophosphoric acid have been synthesized and characterized with FTIR, XRD, water uptake, methanol permeability and proton conductivity measurements. The incorporation of cesium salt into polymeric matrix of sPEEEK increased the proton conductivity up to 0.02 S cm$^{-1}$ which was much higher than Nafion 117
conductivity. The methanol permeability of the composite membrane was greatly lower than that of commercial Nafion 117. However, the amount of Cs salt loading determined the performance of membranes.

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