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Simple Sulphonation Method of Composite 68% Sulfonated Polyether-Ether Ketone and its Properties as Polyelectrolyte in High Temperature Direct Methanol Fuel Cell

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Abstract: The operation temperature of Direct methanol fuel cell (DMFC) above 100°C is very interesting because at this temperature anode catalyst is not poisoned by CO so the fuel oxidation kinetics will be improved and the cell efficiency will significantly enhance. Current limitation in electrolyte membrane is high methanol crossover permeability at elevated temperatures. In order to solve this problem, we studied the properties of composite based on zeolite and silica dispersed in sulfonated polyether-ether ketone (sPEEK). Experimental methods for studying proton conductivity and methanol permeability of sPEEK composite membrane containing hydrophilic particles (zeolite and silica) over wide range of temperature have been fabricated and characterized. The proton conductivity was investigated using standard bridge impedance spectroscopy at various temperatures (25-140°C). At 140°C, the conductivities of zeolite and silica addition of sPEEK composite membrane (0.072 and 0.076 S/cm) were higher than blank membrane (0.06 S/cm). The activation energy of sPEEK composite membrane (6 and 8 kJ/mol) was lower than blank membrane (14 kJ/mol). The addition of inorganic filler onto sPEEK could reduce the methanol permeability and at higher temperature showed higher mechanical stability than Nafion®117 membrane. Thus sPEEK composite membranes is a promising candidate for high temperature DMFC.

Key words: Sulfonated Polyether-Ether Ketone · Zeolite · Silica · High temperature direct methanol fuel cell.

INTRODUCTION

The direct methanol fuel cell (DMFC) has been receiving great attention as clean and efficient alternative technology for transport application. It can be operated both in low temperature (less than 80°C) and high temperature (more than 100°C). Recently, high temperature DMFC provide faster reaction kinetic in electrodes and reduce Pt-based catalyst poisoning by CO [1]. In the other hand, high temperature will decrease the membrane performance i.e. low proton conductivity due to the humidification and high methanol crossover as methanol vapor is easy to diffuse in membrane. Electrolyte membrane for DMFC's application have to has low methanol diffusion coefficient (less than $5.6.10^{-6}$ cm^2/s at temperature 25°C), high proton conductivity (more than 0.08 S/cm), high chemical and mechanical durability especially at temperature higher than 80°C and low cost [2].

Various efforts have been made to increase proton conductivity such as using composite membrane with inorganic filler to decrease methanol permeability and tto increase thermal stability within polymers structure [3-8]. One of the alternative polymer which has thermal stability is aromatic polymer such as polysulfone [9], polybenzimidazole [10] and polyether-ether ketone [11]. Polyether-ether ketone (PEEK) was selected as based polymer membrane due to good thermal stability and mechanical strength [1]. In order to produce hydrophilicity, polyether-ether ketone must be sulphonated using sulfonic acid to form sulfonated polyether-ether ketone (sPEEK). Various filler as BPO_4, SiO_2, TiO_2 and ZrO_2 were added to improve properties of electrolyte membrane such as sPEEK [12-14].

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In this work we focused on sulfonated PEEK with sulfonation degree 68%. It is known that sulfonation degree less than 68% had lower conductivity but in the other side, higher sulfonation degree with contain higher hydrophilic groups has lower mechanical and thermal stability and make the membrane became more fragile especially at high temperature more than 90°C. Recently, the proton transport properties of sPEEK composite membrane especially for 68% sulfonation degree at elevate temperature have not discussed. In this paper we described the preparation of composite sPEEK membranes with 68% sulfonation degree and the influence of additional particles on the membrane properties such as the proton conductivity and methanol permeability at various temperatures.

Experimental

Modified Membrane Preparation: Polyteher-ether ketone (grade 450-P Victrex Inc.) was sulfonated with concentrated sulfuric acid. Detail procedure sulfonated polyether-ether ketone (sPEEK) was described as previously publications [15]. PEEK powder (5 g) was added into 95-97% sulfuric acid (proanalys, Merck) 100 ml under vigorous stirring for 3 hours at 50°C. Then, the polymer solution was precipitated into a large excess of ice water. To terminate sulfonation reaction the polymer was washed repeatedly with deionized water until the rinse water reached pH around 6-7.

The recovered sPEEK were dried overnight. The sulfonation process at 50°C produced 68% sulfonation degree of membrane. The composite and blank membrane sPEEK was prepared by solvent casting. The sPEEK polymer was firstly dissolved with n-methyl pyrolidone and added with particles (silica were purchased from Trisindo Sejati Corp. Indonesia, H-Yzeolite were purchased from Japan) and stirred for 7 h. Solution were cast onto glass plates and then dried at 60°C for 72 h.

Analysis: Water uptake was measured base on water weight absorbing per dry weight membrane. Weighed films were immersed in deionized water at room temperature for 24 h. The membranes were saturated with water until no further weight gain was observed. The water on the surface of immersed membranes was removed using tissue paper before weighing.

Proton conductivity was measured using standard bridge LCR (Impedance Capacitance Resistance), impedance spectroscopy (HIOKI 3522-50 LCR HiTESTER) with over the frequencies from 3 kHz to 100 kHz and 20 mV oscillating voltage. The conductance of each membrane was measured at 25, 50, 90 and 140°C under fully hydrated condition. A conductivity cell was made up of two gold foils carrying the current and two gold wires sensing the potential drop, which was apart 1 cm as shown in Figure 1.

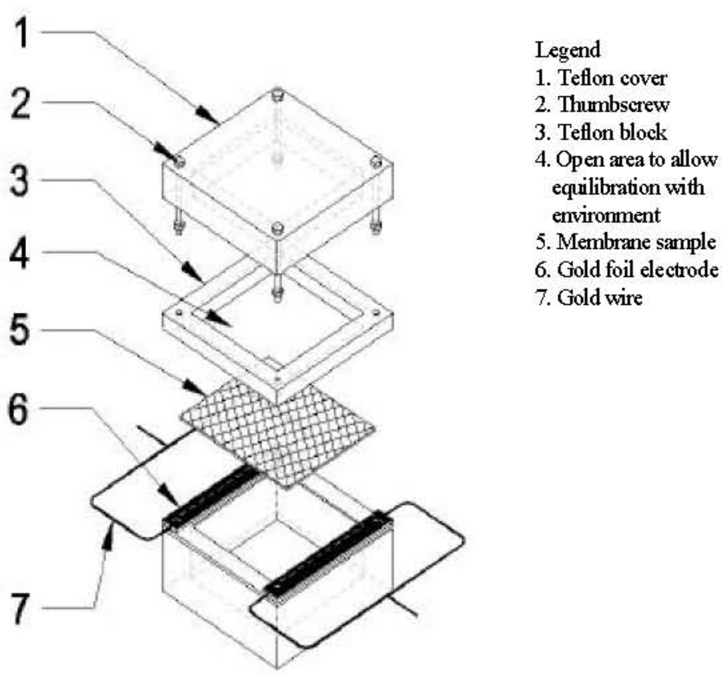

Fig. 1: Conductivity cell

The fully hydrated sPEEK membrane with deionized water during 24 h was cut in 1 cm wide, 4 cm long prior to mounting on the cell. After mounting sample onto two gold foils on the lower compartment, upper compartment was covered and then the upper and lower compartments were clamped as described by authors [8]. The proton conductivity (σ) of the membrane can be calculated using Eq. (1),

$$s = G \times \frac{L}{W.l} \quad (1)$$

where G, L, W and l are conductance (S), the length between the electrode (cm), wide (cm) and thickness of the membrane samples (cm), respectively.

Methanol permeability was determined using a test cell. The membrane was equilibrated in pure water for 5 hour before clamped vertical at the diffusion cell. Magnetic stirrers were used on each compartment to ensure uniformity. A solution containing 2 M methanol in water was placed on cell 1 (C_1) and water was placed on cell B (C_2) [15]. The densities of the initial and final solutions were measured using pycnometer. The duration of measurement was 4 hour. The methanol permeability (DK) was calculated as in Eq. (2) [16],

$$DK = \frac{C_2(t)xV_2xl}{AxC_1(t - t_0)} \quad (2)$$

where C_1 and C_2 are the concentration of methanol in cells 1 and 2, V_2 are the volume of cell 2, A and l are the surface area and thickness of membrane and D and K are the methanol diffusivity and partition coefficient, respectively. The methanol permeability of each membrane was measured at 25, 50, 90 and 140°C.

RESULTS AND DISCUSSION

The Effects of High Temperature on Proton Conductivity of Membranes: Proton conductivity as a function of temperature at 100% relative humidity (RH) of blank, composite sPEEK and Nafion®117 membrane can be seen in Fig. 2. Composite membrane sPEEK showed higher proton conductivity (σ) than blank sPEEK (0.018 S/cm) but lower than Nafion®117 membrane at room temperature. sPEEK and its composite proton conductivity increased as temperature increase up to 140°C

The addition of zeolite and silica on sPEEK membrane caused the increasing of water uptake at room temperature and high temperature as shown in Table 1. It indicates that additive is a hygroscopic particle which could maintain water management at high temperature due to the formation of silanol group in acidy silica [6]. The adsorption of zeolite is caused by water bonding within acidic alumina silicate of it [17]. The membranes that have high absorbance of water would facilitated proton transport, thus proton conductivity could reach up.

Table 1 shows proton conductivity data for Nafion®117, sPEEK and sPEEK composite membrane. Nafion®117 showed higher proton conductivity than sPEEK and composite sPEEK on the temperature up to 90°C, but it was not determined more than 90°C. On the other hand, all sPEEK membranes were more stable at high temperature, up to 140°C. It is clearly that proton conductivity in sPEEK, sPEEK+Z and sPEEK+Si increases with increasing temperature mainly due to higher proton mobility and bigger quantity of adsorbed water.

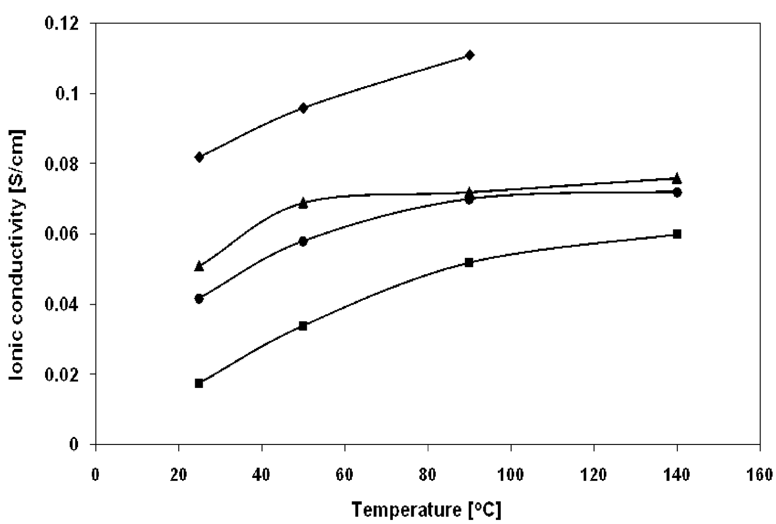

Fig. 2: Influence of temperature in proton conductivity: (♦) Nafion®117; (■) sPEEK; (●) sPEEK+Z; (▲) sPEEK+Si.

Table 1: Properties of proton transport and water uptake of membranes

Type	σ 25°C [S/cm]	σ 90°C [S/cm]	Water uptake, 25°C [wt.%]	Water uptake, 90°C [wt.%]
sPEEK	0.018	0.052	7	15
sPEEK+Z	0.042	0.07	10	20
sPEEK+Si	0.051	0.072	15	34
Nafion®117	0.082	0.111	19	20

Table 2: Activation energy of membrane

	Temperature range [°C]	$E_{a,c}$ (proton migration) [kJ mol^{-1}]	$E_{a,p}$ (methanol permeation) [kJ mol^{-1}]
Nafion®117	25-90	7	12
sPEEK	25-140	14	14
sPEEK+Z	25-140	8	11
sPEEK+Si	25-140	6	10

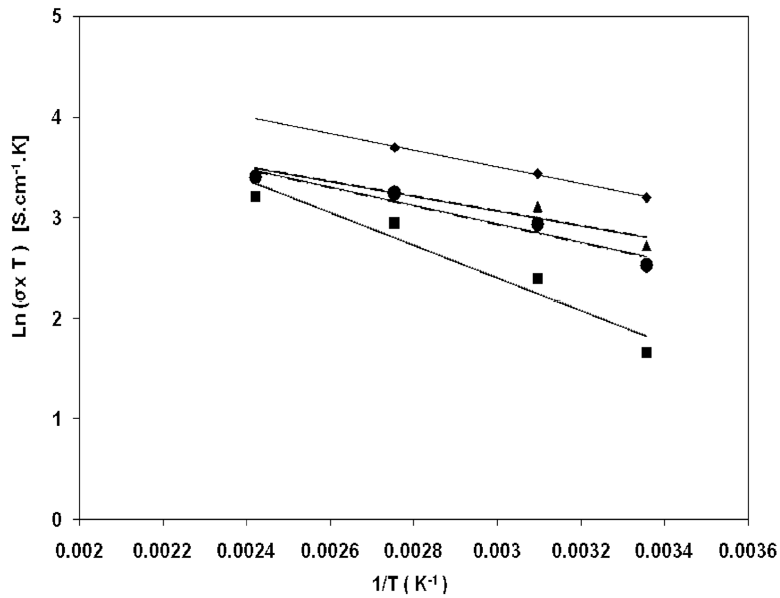

Fig. 3: Arrhenius plot showing dependency of proton conductivity: (♦) Nafion®117; (■) sPEEK; (●) sPEEK+Z; (▲) sPEEK+Si.

Figure 3 show an Arrhenius plot of the proton conductivity (s) as a function of temperature at 100% RH for sPEEK membranes and Nafion®117 membrane. From the Arrhenius Equation (3), the apparent activation energy of membrane can be calculated [18],

$$\ln(\sigma T) = \ln s_o - E_{a,c} / (RT) \quad (3)$$

where R is gas constant, s_o is a constant with respect to T and $E_{a,c}$ is the activation energy of proton conduction. The apparent activation energy of proton migration is reported in Table 2.

The activation energy of Nafion®117 membrane is 7 kJ/mol, which is slightly different, with literature value of 4 kJ/mol [8]. The activation energy of composite membrane sPEEK (silica and zeolite) is close to Nafion®117 membrane. Based on Table, 2 it was found that blank sPEEK membrane has the highest activation energy among all the tested membrane.

It also observed that water uptake membrane affected lowering activation energy.

However, the addition of zeolite and silica make the membrane capable to adsorb more water as a consequence of higher proton conductivity.

The Effect of High Temperature on Methanol Permeability of Membranes: The methanol resistance of membranes at high temperature, is determined by measuring methanol permeability at temperature of 25-140°C. Figure 4 shows the methanol permeability of

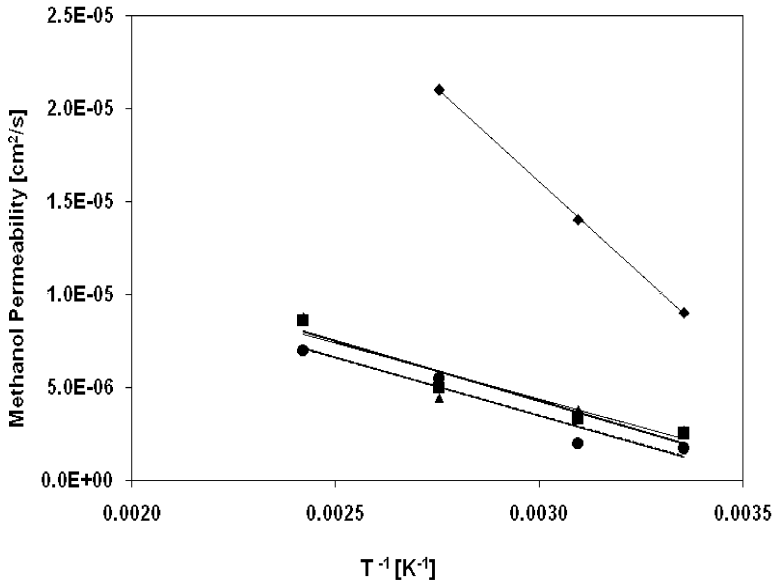

Fig. 4: Arrhenius plot showing the temperature dependency of methanol permeability: (♦) Nafion®117; (■)sPEEK; (●) sPEEK+Z; (▲) sPEEK+Si.

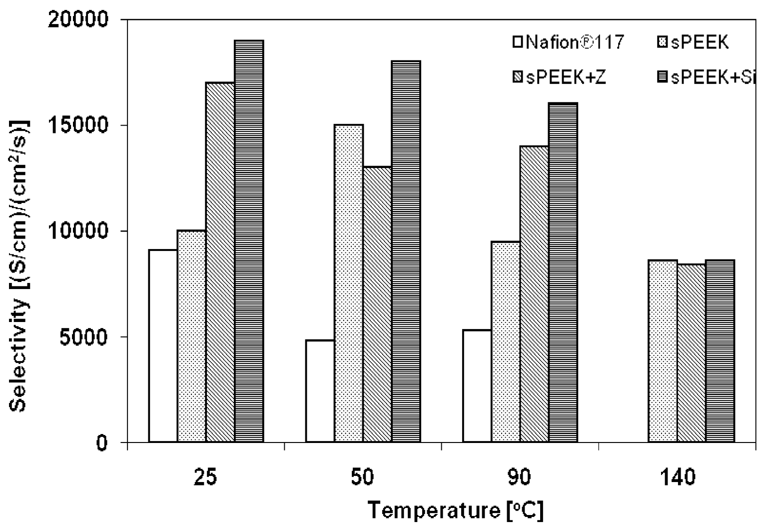

Fig. 5: Selectivity of membrane as a function temperature

membranes as a function of temperature. As shown at Figure 4, the slope of Nafion®117 is 3 times larger than blank sPEEK membrane. In order to observe the methanol permeability in the same condition of sPEEK, Nafion®117 membrane was analyzed up to 90°C. It showed that Nafion®117 had reached 2.3 times than before it degraded at temperature 140°C. Furthermore, the methanol permeability of blank sPEEK membrane was reached 4 times and the sPEEK+Z and sPEEK+Si composite membrane was reached about 3 times than blank sPEEK. Thus the addition of zeolite and silica in sPEEK retained increasing methanol permeability at high temperature.

The dependency of methanol permeability upon temperature is calculated from the Arrhenius type as described in Eq. (4).

$$\ln(DK) = \ln (DK)_o - E_{a,p} / (RT) \quad (4)$$

where DK is the methanol permeability, $(DK)_o$ is the pre-exponential factor, $E_{a,p}$ is the activation energy obtained by correlating diffusivity-temperature data with Arrhenius approach. The apparent activation energies of methanol permeation reported in Table 2.

The activation energy of methanol permeation membrane sPEEK (14 kJ / mol) is higher than the composite sPEEK (10-11 kJ / mol). The higher the activation energy would give a lower permeation of methanol. Activation energy of methanol permeation for all the membranes are around 10-14 kJ/ mol, but for the Nafion-117 only could be observed at 90°C.

The activation energy of composite sPEEK membrane show slightly different with Nafion®117 membrane (12 kJ/mol) with exception of blank sPEEK membrane, for which a considerably higher energy is noted.

Selectivity of Membrane: Selectivity is a ratio between proton conductivity with methanol permeability. Membrane with higher selectivity had better performance in the fuel cell test [11]. In Figure 5 shows selectivity of membranes with the temperature range from 25°C to 140°C. The DMFC which utilized Nafion®117 membrane is also included for comparison. Selectivity at 90°C of composite sPEEK is 3 times higher than Nafion®117. This is very interesting results from the perspective of potential application in high temperature DMFC, because low methanol crossover would be accompanied by proportionate improvement of the fuel cell efficiency and its power density.

CONCLUSIONS

The presence of the additive (silica and zeolite) in sPEEK composite membrane was found to enhance the proton conductivity and at the same time increase the water uptake for a wide range of temperature. The presence of of the additive (silica and zeolite) in sPEEK composite membrane was found to enhance the proton conductivity and at the same time increase the water uptake for a wide range of temperature. The proton conductivity of composite membranes reached to 0.07 S/cm at 140°C and RH 100%. It is clearly seen that all composite sPEEK membranes retained better performance for methanol permeability, activation energy of proton migration and selectivity value than Nafion®117 at elevate temperature. Based on the result, among the investigated experiments reported here, electrolyte membrane based on sPEEK with 68% of sulfonation degree was observed as promising candidate for application in DMFC systems working at temperature up to 140°C.

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Nomenclature

A	=	surface area of membrane	[cm^2]
C_1	=	concentration of methanol in cells 1	[mol/l]
C_2	=	concentration of methanol in cells 2	[mol/l]
D	=	methanol diffusivity	[cm/s]
$E_{a,c}$	=	activation energy of proton conduction	[kJ mol^{-1}]
$E_{a,p}$	=	activation energy of methanol permeation	[kJ mol^{-1}]
G	=	conductance	[S]
K	=	partition coefficient	
L	=	length between the electrode	[cm]
l	=	thickness of membrane	[cm]
R	=	universal gas constant	[J $mol^{-1}K^{-1}$]
T	=	Temperature	[K]
W	=	wide of the membrane	[cm]
o	=	constant of proton conduction with respect to Temperature	[S/cm K^{-1}]
?	=	proton conductivity	[S/cm]

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