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Dielectric behaviour of UV-crosslinked sulfonated poly (ether ether ketone) with methyl cellulose (SPEEK-MC) as proton exchange membrane

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ABSTRACT

Proton exchange membrane materials based on sulfonated poly ether ether ketone (SPEEK) with Methyl Cellulose (MC) are developed by solution cast technique and exposed to UV radiation with Bezoin Ethyl Ether (BEE) as photoinitiator. The addition of MC into SPEEK polymer enhances the conductivity up to 8.7×10^{-3} Scm^{-1} at 30 °C temperature and 80% relative humidity. This new crosslinked hybrid membrane shows good prospect for the use as proton exchange membrane in fuel cell.

Introduction

Proton exchange membrane is the most vital part of a fuel cell as it separates the fuel from oxidant and conducts electrons to external load. Among the sulfonated aromatic polymers (SAP), Sulfonated poly ether ether ketone (SPEEK) is the most promising proton exchange membrane (PEM) for fuel cell application [1,2]. PEEK is a thermoplastic with outstanding chemical, mechanical and thermal resistance properties. Sulfonation of PEEK introduces hydrophilic properties to this PEM. However SPEEK is too dependent on its degree of sulfonation, DS. Too high DS could lead to membrane dissolution, while PEM with too low DS results in low conductivity [3,4]. To

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rectify this issue, the UV-crosslinking technique is introduced. This simple but powerful method can be used to improve the dimensional stability of PEM [4–6]. However this technique consumes $-SO_3H$ groups that lead to lower proton conductivity compared with the non-crosslinked PEMs. Thus photoinitiator Benzoin Ethyl Ether (BEE) is introduced in the polymer to initiate crosslink by the formation of a C–C bond instead of $-SO_3H$ [7]. UV-crosslinking SPEEK polymer with biodegradable polymer modifies the hybrid membrane by restricting the mobility of polymer chains hence forming more compact network [6,8,9]. To improve our result from the previous study [3], Cellulose Acetate (CA) is replaced with Methyl Cellulose (MC) as CA could not withstand temperature above 50 °C. Methyl Cellulose is a biodegradable, non-expensive and non-toxic polymer. It is a modified type of cellulose with a tendency to form crosslinked three-dimensional network hydrogels that tend to swell in water or biological fluids [10]. This paper investigates the influence of the MC compositions on the PEM electrical. In this approach, both frequency and temperature are varied for dielectric spectroscopy, so that a wide range of molecular mobility can be examined. Electrochemical Impedance Spectroscopy (EIS) is used to study the conductivity and dielectric properties of PEM to provide information on both of the membranes structure and electrical properties.

Experimental

PEEK polymer is dissolved in concentrated H_2SO_4 (95%–98%) at room temperature with constant stirring for 65 h. The ratio of PEEK polymer to the H_2SO_4 is 10 g:25 mL. After the sulfonation process is completed the resulted Sulfonated PEEK (SPEEK) is washed several times to remove the excess acid until the pH is neutral and is dried in an oven at 50 °C for 8–10 h [6,11]. Then the DS of the SPEEK membrane is determined by 1HNMR [6]. For this study SPEEK with DS of 68% used is obtained from previous study [3]. The next stage is the synthesis of Sulfonated Poly Ether Ether Ketone–Methyl Cellulose (SPEEK-MC) hybrid membrane with composition ratio of $SPEEK_{(1-X)}MC_{(X)}$ (X = 2,4,6,8,10) and the weight of the total membrane is 1.7 g. Prior of mixing both the polymer together, each of SPEEK and MC is dissolved in DMSO separately. After mixing, the homogenous solution is exposed with UV-irradiation for 15 and 30 min. The Benzoin Ethyl Ether (BEE) is used as photoinitiator and lastly the solution is left to dry in an oven at the temperature of 50 °C for 48 h [12,13]. To check the performance of the membrane, electrochemical impendence spectroscopy (EIS) is used for conductivity study [14]. The conductivity (σ) was calculated with the following equation;

$$\sigma = \frac{L}{RS} \tag{1}$$

which σ = Proton conductivity
L = Sample thickness
R = Resistivity obtain from EIS
S = Surface area

Results and discussion

Conductivity studies of SPEEK-MC membrane

Conductivity is the most crucial parameter for PEMs and is obtained from semicircle shape from complex impedance spectra and this shape is very dependent on the humidity of the environment. For this part, all membranes are tested in a closed system at 80% relative humidity (RH) and room temperature. Fig. 1 shows part of the semicircle of the Nyquist plot for (94%)SPEEK(6%)MC and its circuit diagram. The rest of the samples bulk resistivity (z′) results are tabulated in Table 1. The part of the semicircle at high frequency represents the PEM impedance and is modeled by the resistor R and constant phase element (CPE). Both R and CPE are the actual ohmic resistance and capacitive behavior of the PEM respectively. While at the low frequency, the tail represents the impedance between the membrane and electrode interfaces and is modeled by CPE_{int}. The bulk resistance decreases with increasing amount of MC and low bulk resistance indicates high conductivity. Every sample undergoes conductivity test in the hydrous condition. The conductivity values are obtained by using Equation (1). The conductivity of the hybrid membrane as a function of methyl cellulose (MC) composition at room temperature is plotted in Fig. 2. The conductivity increases with increasing MC composition and reaches its maximum value of 4.78 × 10^{-3} Scm^{-1} at (94%)SPEEK(6%)MC. The MC polymer in the membrane enhances the proton transfer through the membrane by retaining water within the membrane. The OH ends of the cellulose chain allow for hydrogen bonding with the water molecules. While conducting proton they created water mediated pathways thus improving the water retention property of SPEEK membranes. Fig. 3 shows water uptake (wu) continues to increase with increasing amount of MC. Thus, leads to membrane dissolution in water. Past studies have shown high water uptake can gives high conductivity and low dimensional stability properties to a PEM [3,15]. However, contrary to non-crosslinked membrane the water uptake for crosslinked membrane is

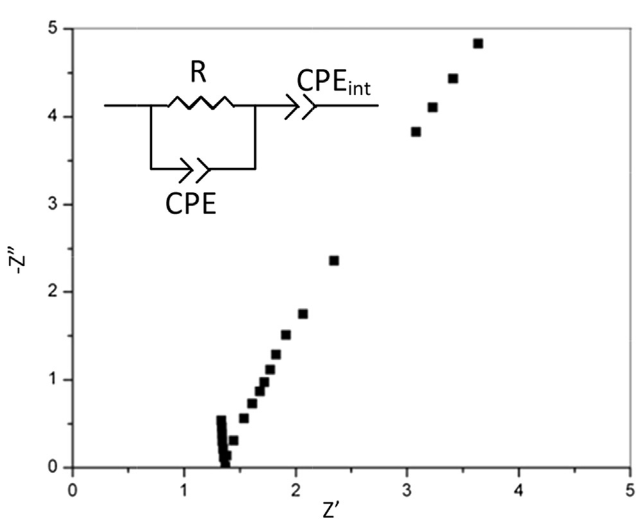

Fig. 1 – Nyquist plot of a (94%)SPEEK(6%)MC.

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