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Study on hydrocarbon based electrolyte membrane by using positron annihilation spectroscopy

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High proton conductivity is one of the desirable features for electrolyte membrane of fuel cell. In general, this depends not only on spatial structure but also electronic state relating to functional group. Positron annihilation technique seems is a powerful method to analyze such properties, since the size of open space can be measured by lifetime of positron/positronium and the electronic states can be estimated by Doppler broadening of annihilation gamma-rays which is characterized by line shape parameter, S. We have measured the electrolyte membranes composed of hydrocarbon in backbone with sulfonic group in side chain by positron annihilation technique and found that the lifetime and S were influenced by the density of sulfonic group.
Key words: positron, positroniu, PEEK, s-PEEK, PEMFC

1. INTRODUCTION

The fuel cell is attracting a lot of attention as one of the new energy source which has little effect on the environment. It converts hydrogen and oxygen into electrical energy without emitting carbon dioxide. Polymer electrolyte membrane fuel cell (PEMFC) is expected to be used as energy sources for a mobile phone and cars. The desired characteristics of polymers used for Polymer Electrolyte Membrane in Fuel Cell (PEMFC) are high proton conductivity, good chemical stability, gas barrier function and mechanical stability [1].

Nafion™, which is developed by DuPont consisting of the backbone with fluorocarbon and the side chain with sulfonic group, has several excellent properties as PEMFC, since it has high chemical and mechanical stability and high proton conductivity. However, it has still some remaining problems such as lack of water uptake and durability over 100℃. To improve these properties, different types of hydrocarbon PEM with more durability at high temperature have been synthesized [2, 3].

Poly (ether-ether-ketone) (PEEK) used in this study has also excellent chemical, thermal and frictional durability, and sulfonated-PEEK(s-PEEK) is studied with a view to utilities it on a polymer electrolyte membrane (scheme. 1). In recent studies, formation of complex with metals and evaluation of chemical and physical properties were performed [4-6].

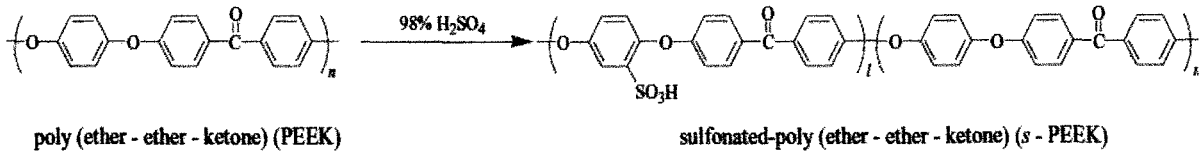
Having a potential to detect less occupied spaces and electronic states with high sensitivity, positron annihilation spectroscopy (PAS) would be very powerful method to evaluate PEMFC. At present, correlation between the number of fluorine in the polymers and S-parameter that evaluates the shape of a photopeak of annihilation gamma-ray was reported by D.Bamford et al [7], and correlation between lifetime of o-Ps and volume phase transition point of polymer gel was reported by K. Ito et al.[8].

In this study, the positron annihilation lifetime and the Doppler broadening of annihilation gamma-ray in s-PEEK were measured in order to elucidate the relation between the proton conductivity, nanoscopic structure and electronic state of hydrocarbon PEM.

2.Experimental

Preparation of s-PEEK

PEEK was obtained from VICTREX. Sulfonation of



Scheme. 1 Chemical structures of PEEK and its sulfonated polymer.

PEEK was carried out using the method of Christian Bailly et al. [9]. PEEK was dried in a vacuum oven at 100℃ overnight. Four gram of polymer was dissolved in 100 ml of concentrated (95 - 98%) sulfuric acid (H_2SO_4) and vigorously stirred at room temperature for the desired time range. Then the polymer solution was gradually precipitated into a large excess of ice-cold water under continuous mechanical agitation. The agitation was continued 1 h further and then the polymer suspension was left to settle overnight.

The polymer precipitate was filtered and washed several times with distilled water until the pH becomes neutral. The polymer was then dried under vacuum for 8–10 h at 25-100℃. The final product is sulfonated PEEK (*s*-PEEK). The dried *s*-PEEK was dissolved in *N,N*-dimethylacetamide (DMF) and cast onto a glass plate for PALS measurement. The samples were dried in a vacuum oven at 80℃ for a few days. FT-IR spectroscopy was used for the confirmation of the chemical structure of formed s-PEEK [10].

The degree of sulfonation (DS) of *s*-PEEK membranes were determined by titration. Membrane samples (0.5 g) in acid form were immersed in 1M NaCl solution for at least 24 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). Then the H^+ ions were titrated with 0.1M NaOH solution using phenolphthalein as indicator [11].

Measurement of proton conductivity

The proton conductivity was measured in accordance with the four-terminal method in which the measuring frequency was 500 to 1280 Hz and the applied voltage was 10mV by using an impedance analyzer produced by HIOKI.

Measurement of positron annihilation spectroscopy

^{22}Na (46 kBq) covered with Kapton film was used as positron source. Positron annihilation lifetime (PAL) was measured with two BaF_2 scintillation counters coupled to photomultipliers (Hamamatsu Photonics), and Doppler broadening of annihilation gamma-ray was measured with one SSD. The positron source was sandwiched by two samples. In the conventional positron lifetime spectroscopy, the γ -ray of 1.275 MeV, accompanied by β^+ decay, is used as a start signal and one of the annihilation γ -rays is used as a stop signal. Three million counts were accumulated to obtain each lifetime spectrum and photopeak of annihilation gamma-ray. Time resolution was around 245ps. The measurements were performed at 293±1K and 50±5% relative humidity. PATFIT program were used to analyze the lifetime spectra.

3. Result and discussion

Proton conductivity of s-PEEK

Sulfonation of PEEK using 95 to98 wt.% H_2SO_4 is the well established process in which a small amount of the water avoids the cross-linking reaction between sulfo groups.

Fig. 1 shows FT-IR spectra of PEEK and s-PEEK measured using ATR method. Compared with PEEK, *s*-PEEK has a characteristic peak around 1100 cm^{-1}

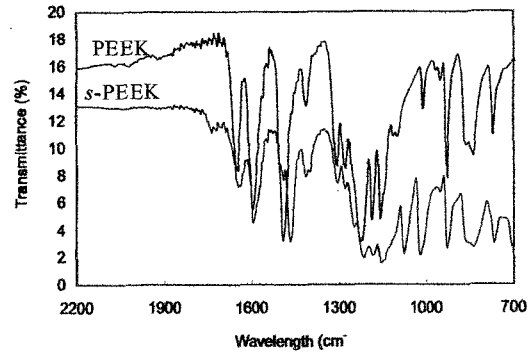


Fig. 1 FT-IR spectra of PEEK and *s*-PEEK

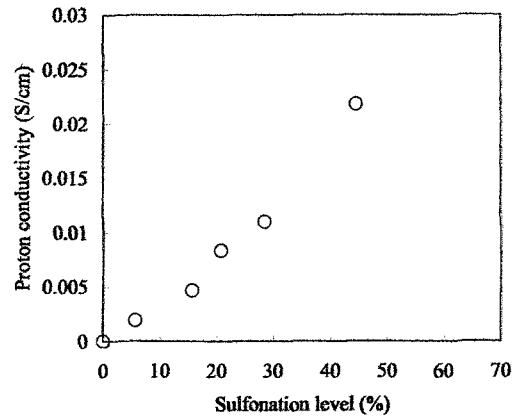


Fig. 2 Relation between proton conductivity and degree of sulfonation.

which corresponds to stretching vibration of O=S=O bond, and it indicates the formation of s-PEEK. The result of DS measurement showed that the introduction rate of the sulfo groups to PEEK increased with increase in reaction time. The degree of sulfonation also increased with increase in reaction temperature.

Fig. 2 shows the proton conductivity as a function of degree of sulfonation. It indicates that proton conductivity increases with increase in degree of sulfonation.

Measurement of positron annihilation lifetime and Doppler broadening

From the results of positron annihilation lifetime spectroscopy, the lifetimes τ_1, τ_2 and τ_3, and the relative intensities I_1, I_2 and I_3 had no relation to proton conductivity.

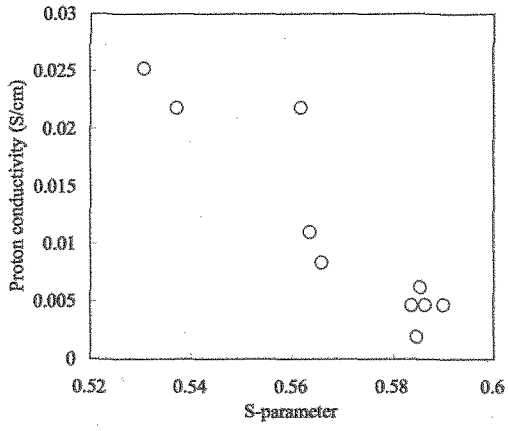


Fig. 3 Relation between S-parameter and proton conductivity

On the other hand, S-parameter and proton conductivity had strong negative correlation as shown in Fig. 3.

This is because the momentum of electron annihilated with positron or positronium changed by degree of sulfonation.

Study on Molecular orbital method

The results above mentioned indicates that there was no significant correlation between the proton conductivity and lifetime of o-Ps (τ_3), whereas that S-parameter and DS have strong negative correlation.

In order to examine the electronic state of s-PEEK,, the molecular orbital was calculated using the Permanent Method 3 of WinMOPAC.

As shown in Fig.4, S-PEEK has a highest occupied molecular orbital (HOMO) extending to the part of benzene-ether-benzene.

From the results of positron annihilation lifetime and Doppler-broadening in hydrocarbon PEM, following two possibilities are considered;

① Free annihilation of positron tends to occur around sulfonic groups which is the reason why S-parameter and DS had strong negative correlation.

② The yield of *o*-Ps in *s*-PEEK is low, and it annihilates in the vicinity of benzene-ring in PEEK. Therefore, the correlation was not seen between the density of sulfonic group and τ_3.

Conclusion

In order to understand the relation among the proton conductivity, nanoscopic spatial structure and electronic state of *s*-PEEK, positron annihilation lifetime and Doppler broadening in s-PEEK with different degrees of sulfonation were measured, and the results were verified by molecular orbital calculation.

A strong negative correlation between S-parameter and the proton conductivity was seen even in the polymer in which HOMO does not include around the functional group.

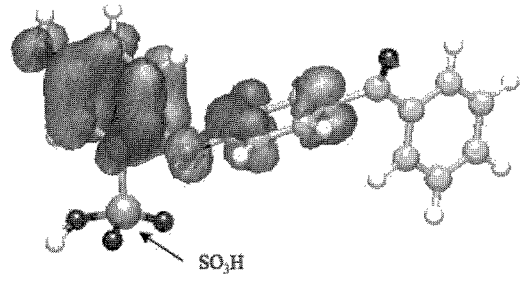


Fig. 4 Fig. 4 Highest Occupied Molecular Orbital (HOMO) of s-PEEK.

From these results, it was shown that the Doppler-broadening measurement (S-parameter) by positron annihilation technique can be used as a highly sensitive probe to investigate the electronic state of functional group for all kinds of PEM with sulfonic group as an ion exchange sites.

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