IRRADIATION EFFECT OF GAMMA-RAY ON THE PROTON-CONDUCTING POLYMER

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Introduction

In fuel cells, perfluorosulfonic acid membrane, such as Nafion®, Aciplex® and Flemion® are used as electrolyte membrane for fuel cell because of having a high proton conductivity around 373 K [1]. It is hoped the electrolyte is applied at lower temperature and is modified with higher conductivity. So far, it has been proposed that the polymer is modified easily by irradiation [2]. This effect is caused by the cross-linkage and chemical bond breaking, and it is expected that these phenomenon introduce to a change in the proton conduction of the proton-conducting polymer. In the present study, Aciplex® membrane was irradiated by gamma-ray, and the electrical and optical properties were investigated.

Results and discussion

The sample used for the experiments is Aciplex-SF-1004® (10x10x0.117 mm^3). The sample was irradiated at room temperature and atmospheric pressure with 1.17 and 1.33 MeV gamma-ray from a cobalt-60 source in the Takasaki Research Establishment of Japan Atomic Energy Research Institute (JAERI). The absorption doses of the sample by gamma-ray were from 1 to 173 kGy.

The dose dependence and the temperature dependence of the electrical conductivity of the irradiated sample were investigated. The electrical conductivity was obtained using the applied voltage and the measured current and dimension of the sample before and after irradiation. The electrode was Al plate. For dose dependence, the conductivity was measured at 300 K and at humidity of 40 %. For temperature dependence, the conductivity was measured in the temperature range from 300 to 393K in the vacuum under pressure of $3x10^{-5}$ Pa.

In order to understand the change in the conductivity by irradiation, optical absorption measurement were carried out in the wavelength of 190~500 nm using a SHIMADZU UV-2200A.

Conductivity measurement

Fig.1 shows the electrical conductivity at 300K in air after gamma-ray irradiation. The conductivity increased rapidly below 20 kGy and gradually above 20 kGy. The conductivity at 173 kGy was higher by about three orders of magnitude than that of unirradiated one.

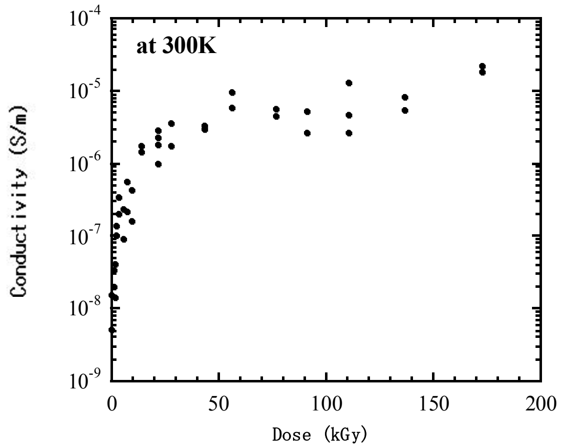

Fig.1. Electrical conductivity at 300 K as a function of absorption dose by gamma-ray irradiation

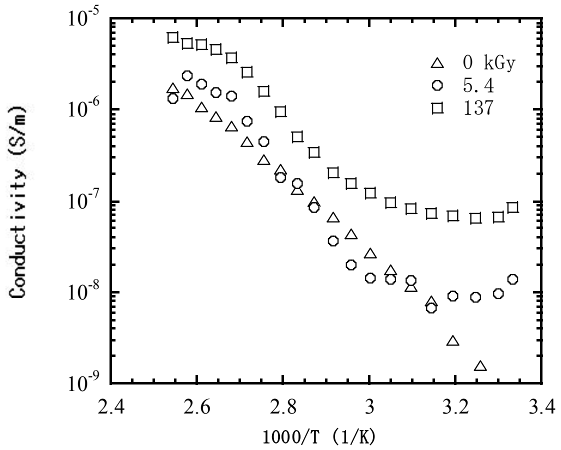

Fig.2. Temperature dependence of electrical conductivity for unirradiated and irradiated samples by gamma-ray at 5.4 and 137 kGy

Fig.2 shows temperature dependence of conductivities for unirradiated and irradiated samples in vacuum. Arrhenius plot for unirradiated sample has one slope. The activation energy, calculated from this slope is about 0.84 eV, associated with proton behavior in sulfonate group. Arrhenius plot for irradiated samples have two slopes. One is similar to unirradiated slope at higher temperature and another has different slope near the room temperature. The activation energy of this slope at lower temperature is about 0.16 eV. The irradiated samples have two kinds of protonic conduction mechanisms, the existing protonic conduction and new protonic conduction produced by irradiation.

UV-Vis optical absorption

The UV-Vis optical absorption spectra in Fig.3 of the unirradiated sample have two absorption peaks at 200 and 275 nm. The intensity absorption of ultraviolet region increased and new absorption band was observed at 215 nm after gamma-ray

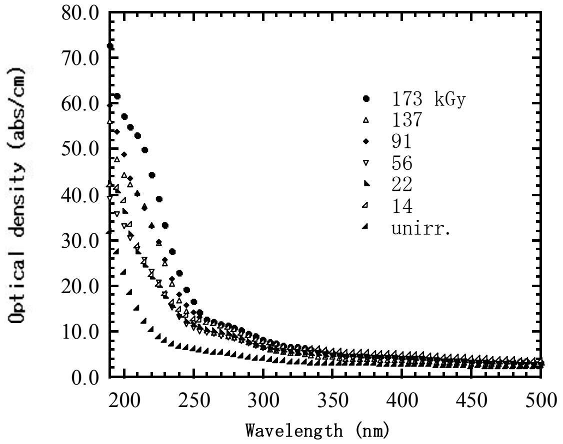

Fig.3. Optical density of the sample before and after irradiation.

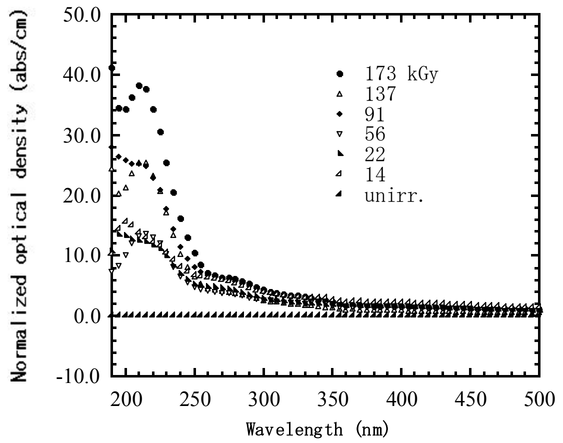

Fig.4. Normalized optical density of the irradiated sample, obtained by subtracting the optical density of unirradiated sample

irradiation, as shown in Fig.4. The optical densities normalized by that of unirradiated sample. Several absorption peaks at 200, 215 and 275 nm were associated with fluorocarbon and peroxy radicals and C=O groups respectively [3]. The cross-linkage and chemical bond breaking of the polymer chain were caused by gamma-ray irradiation.

Fig.5 shows the dose dependence of normalized

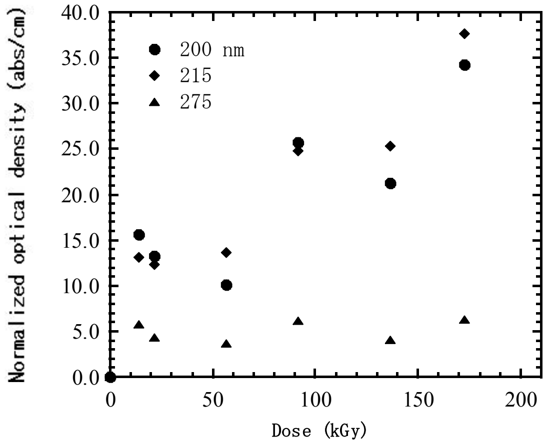

Fig.5. Normalized optical density at the wavelengths of 200, 215 and 275 nm after gamma-ray irradiation

optical density at the wavelength of 200, 215 and 275 nm. The intensities of absorption band around 200 and 215 nm increase with increasing absorption dose, while that around 275 nm is nearly constant. The results may indicate that these radicals and unsaturated bond contribute to the increment of electrical conductivity for the irradiated samples.

Conclusions

The electrical conductivity of the irradiated sample was higher by three orders of magnitude than that of unirradiated one at room temperature. For temperature dependence, Arrhenius plot for irradiated samples have two slopes. The slopes at lower and higher temperatures show the new protonic conduction with fluorocarbon and peroxy radicals produced by gamma-ray irradiation and existing proton conduction with sulfonate group.

References

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[3] Almeida S.H., Kawano Y., Polym. Degrad. Stab., 1998;62:291-297