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Positron annihilation lifetime study of graft-type fluorinated polymer electrolyte membranes

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Abstract. Positron annihilation lifetime spectroscopy (PALS) measurements were performed on polymer electrolyte membranes (PEMs) synthesized by radiation-induced graft polymerization of styrene into crosslinked-polytetrafluoroethylene (cPTFE) films and subsequent sulfonation. The base cPTFE and polystyrene grafted films were also measured as references. The cPTFE based PEM was found to have free-volume holes with different radius of 0.28-0.30 nm and 0.44-0.45 nm. The larger holes may be located in PTFE amorphous regions, while the smaller ones are considered to exist in both PTFE crystallites and poly(styrene sulfonic acid) grafts containing no water. Introduction

There has been increasing interest in polymer electrolyte membrane (PEM) fuel cells for vehicles and other applications [1]. As one of the problems during fuel cell operation, gas fuels such as hydrogen and oxygen permeate through a PEM, resulting in degradation of the fuel cell performance. In order to clarify this gas-leak mechanism, a few researchers have studied on free-volume holes in Nafion membrane being the most widely used PEM [2-3].

Recently, as Nafion-alternative low-cost materials, much attention focused on PEMs prepared by a radiation grafting method [4]. So far, however, little is known about free-volume holes in these radiation-grafted PEMs. In this study, we performed the positron annihilation lifetime spectroscopy (PALS) measurement on the graft-type PEMs based on crosslinked-polytetrafluoroethylene (PTFE) films [5] to obtain information about the size and location of microvoids in them.

Experimental

Synthesis of the PEMs was carried out as already reported [3]. We used, as a base material, a 42-μm thick film of PTFE crosslinked with an electron beam at 100 kGy. The film was pre-irradiated with 15-kGy γ-ray in an Ar atmosphere at room temperature, and then immersed in a styrene monomer at 60 °C for 4 h. After the grafting reaction, the film was immersed in toluene to extract any excess styrene. The degree of grafting (DOG) was given by:

$$\mathrm{DOG}\ (\%) = 100\ (W_g - W_o) / W_o, \quad (1)$$

where W_g and W_o denote weights of the grafted and base films, respectively. For sulfonation, the grafted film was immersed in 0.2 M chlorosulfonic acid / 1,2-dichloroethane mixture at 50 °C for 6 h. Finally, the obtained PEM was rinsed with pure water and then dried in a vacuum oven.

PALS measurements were performed with a ^{22}Na positron source using a fast-fast coincidence spectrometer having time resolution of 225 ps. A stack of about 10 PEM samples was set on each side of the source to ensure positron annihilation only in the samples. As references, the virgin cPTFE and

grafted films were also measured in a similar way. The obtained PALS spectra with about 10^6 counts were analyzed by PATFIT program.

Results and discussion

The PALS spectra for all the samples were decomposed into four lifetime components with a good variance of the fit. Components i =1, 2, 3, 4 are assumed to be due to para-positronium, free positrons, and two types of ortho-positronium (*o*-Ps) in different regions, respectively. Table 1 shows the lifetimes, τ_i, and intensities, I_i, of Components i=2, 3, 4. In the case of the virgin cPTFE film irradiated at 15 kGy, Components 3 and 4 are attributed to *o*-Ps in the free-volume holes in PTFE crystallite and amorphous regions, respectively [6]. Next is considered the grafted film having a DOG of 27%. Here, it is accepted that the radiation-induced grafting of styrene proceeds from generated radicals, which should exist in the interfacial areas between PTFE crystalline and amorphous regions. Compared with the base cPTFE film, both τ_4 and I_4 of the grafted film were smaller. This observation indicates that the polystyrene graft chains elongated into the amorphous regions, leading to decrease of the size and number of free-volume holes. The similar result was reported for the other polystyrene-grafted film based on poly(tetrafluoro-ethylene-*co*-hexafluoropropylene) [7]. On the other hand, I_3 increased from 6.4 to 16%. In a previous study [8], the *o*-Ps lifetime in polystyrene was reported to be 1.94 ns, which is near τ_3 for a cPTFE film. Accordingly, Component 3 should include *o*-Ps in polystyrene grafts as well as in inherent PTFE crystallites.

Now, let us discuss the results for PEMs being our main concern. For a PEM in a dried state, I_2 remarkably increased from 37 to 60%, in comparison with the grafted film. This would be because, as is well known, positrons were easy to be trapped in negatively-charged sulfonic acid groups, and then annihilated from a free state [9]. Large increase of I_2 inevitably lowered both I_3 and I_4.

Table 1 Positron annihilation lifetime and intensities for various samples

Samples	DOG (%)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	I_2 (%)	I_3 (%)	I_4 (%)
cPTFE film	0	0.39	1.8	4.2	39	6.4	19
Grafted film	27	0.41	2.0	3.8	37	16	11
PEM (dried)	27	0.40	2.1	4.5	60	10	3.0
PEM (fully hydrated)	27	0.39	2.0	4.3	61	10	2.9

Regarding the lifetime, τ_4 increased from 3.8 to 4.5 ns, which can be explained as follows. In the grafted film, the polystyrene graft chains should be somewhat entangled with amorphous PTFE chains. In contrast, the hydrophilic PSSA graft regions in the PEM tend to be phase-separated thoroughly from the hydrophobic PTFE amorphous ones owing to the significant difference of chemical property. By the phase-separation behavior, the graft chains that had originally existed in the PTFE amorphous regions moved out. Consequently, these amorphous regions were more vacant, resulting in higher τ_4. When the dried and fully-hydrated PEMs were compared, there was little difference neither in lifetimes nor intensities. From the *o*-Ps lifetime, τ (ns), the free-volume hole radius, R (nm), was calculated by the following Tao-Eldrup equation:

$$\tau = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \quad (2),$$

where ΔR denotes a fitted empirical electron-layer thickness (=0.166 nm). The R values corresponding to τ_3 and τ_4 were estimated to be 0.28-0.30 nm and 0.44-0.45 nm, respectively.

Finally, we mention the location of these different-size holes. Fig. 1 shows a possible structure model of the hydrated cPTFE PEM. The larger free-volume holes for Component 4 are undoubtedly in PTFE amorphous regions. On the other hand, the smaller holes for Component 3 should be in both PTFE crystallites and PSSA grafts. The latter, in general, is believed to retain absorbed water to form ionic clusters. However, based on the above fact that wetness of the PEM had no effect on PAL results, the microvoid- containing domains in PSSA grafts may not be hydrated. Namely, such water-free domains could exist near PSSA graft-chain roots along the crystallites, where PTFE semi-crystalline chains perhaps repel water molecules. The findings obtained in this study will help us for further understanding of the gas-permeation mechanism.

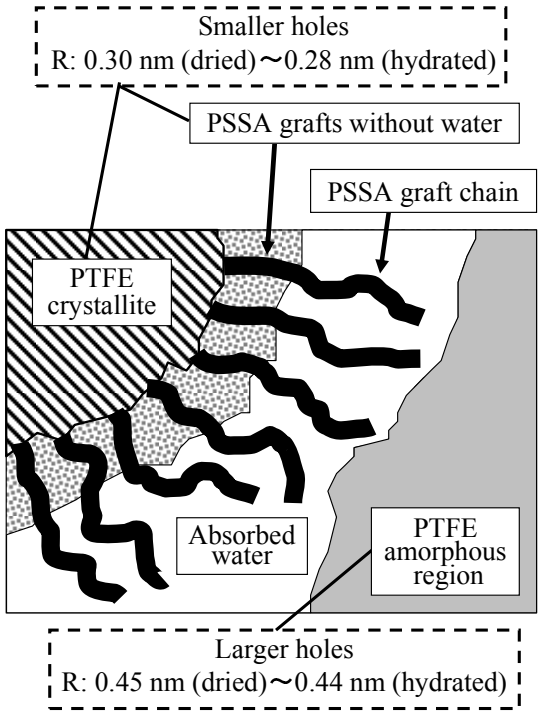

Fig. 1 Possible structure model of a PEM.

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