Degradation process of fuel cell membrane observed by positron

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Abstract. To investigate degradation process due to radicals in fuel cell membrane by means of positron annihilation spectroscopy, three kinds of radicals, HO•, H• and O2•− are produced through water radiolysis. The results show that the cluster structure and proton conductivity was greatly affected by reductive radicals. This is because the oxidative radical is responsible for the dissociation of sulfonic group, whereas the reductive radical breaks down the cluster in the membrane and disrupts proton conduction, which is consistent with solution analysis.

1. Introduction

Elucidation of degradation process of polymer electrolyte membrane (PEM) for fuel cell is very important to develop a better membrane. In practical fuel cell operation, generation of radicals such as hydroxyl radical (HO•), hydrogen radical (H•) and peroxo radical (HOO•) is reported and these are regarded as the sources of degradation. [1] We have investigated the influence of radical species such as HO•, H•, superoxide anion (O2•−) on Nafion®-117. [2] Nafion produced by DuPont is known as a most representative perfluorinated sulfonic acid membrane and is well investigated. [3] This membrane has polytetrafluoroethylene (PTFE) backbone and side chain terminated with sulfonic group through two ether bonds. Aggregation of hydrophilic sites, sulfonic groups, forms clusters and such clusters are connected each other with channels where hydrated proton can be transferred, which is known as a cluster-network model and is most widely referenced, though other models have been proposed. [3] Ortho-positronium (o-Ps) as well as positron has been thought to be a sensitive probe to find structural change in soft materials. To evaluate a free volume with positron, it should be taken into account that positron may annihilate in a special place due to local electric field relevant to functional group, followed by localization of o-Ps, and the deduced free volume size might not reflect overall property of the material. However, such character would be attractive in turn, if such a local place is closely relating to the function of material. Indeed, based on the cluster-network model, which would be valid for a water volume fraction less than 0.5, and taking into account that the time-dependent S-parameters for PTFE and Nafion®-117, the lifetime of o-Ps in swelling process and the evaluated space size based on the lifetime of o-Ps, it could be found that o-Ps stays in the space made up of side chains and hydrophobic backbone, and the change of its lifetime reflects the change of cluster structure. [4] In the followings, the influences of three kinds of radicals on two kinds of PEMs are shown by using positron annihilation spectroscopy.

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2. Experimental setup

Two kinds of perfluorinated membranes, Nafion®-117 and Aquivion® H87-10 produced by Solvay Solexis, were adopted as PEM (Figure 1). Chemical form of Aquivion® is similar to that of Nafion® but has shorter side chain, and it also has clusters. [5] Both kinds of membranes were exposed to HO•, H• and O2• radicals which were produced through water radiolysis due to γ-irradiation. [2] Absorbed dose was ranged from 0.1 kGy to over 1 MGy. The number of generated radicals depends on absorbed dose and it can be evaluated based on G-value. In case of 1 MGy, the concentration of HO• dose and it can be evaluated based on G-value. In case of 1 MGy, the concentration of HO• is evaluated to be about 0.5 mol/liter. Production rate of these radicals is HO• : H• : O2• ~ 2 : 1.2 : 1 for the same dose. Nafion® was stacked in atmosphere with 6 sheets and Aquivion® was with 10 sheets as the samples. All the membranes were pre-treated with sulfuric acid and hydrogen peroxide solution to remove impurities. [2] We regarded proton conductivity as an index of degradation and this was measured by using 4-probe AC impedance meter. Na-22 of 1 MBq was used as a positron source and sandwiched with the samples.

3. Results and Discussion

3.1. Proton conductivity

Dependencies of proton conductivities on absorbed dose for Nafion®-117 and Aquivion® H87-10 are shown in Figure 2. Up to 100 kGy, no significant change was observed for both kinds of membranes. Above 100 kGy, the proton conductivity, σp, was decreased for the samples exposed to H• and O2•, whereas σp of the sample exposed to HO• did not decrease significantly. Taking into account of the number of HO• being almost twice that of other radicals, it is found that the reductive radicals such as H• and O2• caused more serious damage on the membrane rather than oxidative radical, HO•.

3.2. Positron annihilation lifetime spectroscopy

Figure 3 shows the dose-dependencies of lifetime and relative intensity of o-Ps for Nafion®-117 exposed to different radicals. There were no significant changes in the lifetime of o-Ps below 100 kGy, but it decreased drastically for the samples exposed to H• and O2•, whereas for the sample exposed to HO• it was only scattered. As the lifetime of o-Ps reflects the size of cluster [4], these results show that the cluster structure was not influenced significantly by HO•, but damaged heavily by the reductive radicals above 100 kGy. The dose-dependencies of the relative intensity of o-Ps for the samples exposed to reductive radicals were very similar to those of lifetime. The relative intensity of o-Ps in the sample exposed to HO• started decreasing from a lower dose region but the decreasing rate with respect to dose was less. These results show that the damage due to radical reactions clearly depends on radical species. HO• does not reduce the cluster size but decreases the number of the space o-Ps can stay or deprives positron of chance to form o-Ps, whereas other radicals reduce the cluster size and decrease the number of the space o-Ps can stay. Along with the solution analysis [2], it can be concluded that HO• brings about the dissociation of side chain and the cluster structure remains without serious damage. On the other hand, other radicals are thought to cause destruction of cluster above 100 kGy. As the behaviors of proton

![Figure 1. Chemical form of Nafion® and Aquivion®.](image1)

![Figure 2. Proton conductivity vs. absorbed dose. ●: HO•, □: H•, Δ: O2•.](image2)
conductivity and the lifetime of $o$-Ps with respect to dose are quite similar, the serious damage is thought to be brought by the disruption of proton conduction channel due to destruction of cluster. Figure 4 shows the results for Aquivion®. The lifetime of $o$-Ps for Aquivion® is a little longer than that for Nafion® in spite of the shorter side chain, which is probably due to the longer interval of side chain than that of Nafion®. With respect to the diameter of the space where $o$-Ps stayed, it was reduced roughly from 0.7 nm, which is equivalent length between sulfonic group and backbone, to 0.65 nm for Nafion® exposed to reductive radicals. Corresponding dropping of the diameter for Aquivion® was from 0.72 nm to 0.64 nm. Both behaviors of lifetime and relative intensity of $o$-Ps showed similar dose-dependencies to those of Nafion®, but there were slight differences. Decrease of the relative intensity of $o$-Ps at a higher dose range in Aquivion® exposed to HO• was less compared to that in Nafion®. Aquivion® was also more affected by the reductive radicals than the oxidative radical and the structural change caused by the reductive radicals seemed to progress from a lower dose range compared to Nafion®. However there was no remarkable difference in proton conductivity. In case of Aquivion®, it seems that successive structural change takes place so as not to lose proton conduction ability.

Figure 3. Lifetime and relative intensity of $o$-Ps for Nafion®-117 exposed to different radicals. Solid and open circles represent lifetime and relative intensity, respectively.

Figure 4. Lifetime and relative intensity of $o$-Ps for Aquivion® H87-10 exposed to different radicals. Solid and open circles represent lifetime and relative intensity, respectively.

3.3. Energy spectrum analysis
As the fraction of $o$-Ps is less than 10 %, the momentum of free annihilation electron is dominantly reflected on S-parameter. As the location of $o$-Ps is limited to the space formed with backbone and side chains, major free annihilation is probably taking place near there, i.e. around sulfonic group. Figure 5 shows the ratios of the Doppler broadened spectra of PTFE (Aldrich; powder 100 micron) and Aquivion® to Nafion® obtained by coincident Doppler broadening measurements. Each spectrum was normalized by the area of higher energy side of photopeak. The shapes of energy spectrum of Nafion® and Aquivion® were almost same, whereas annihilation with a larger momentum electron was
more likely to take place in PTFE, indicating that the dominant free annihilation in perfluorinated sulfonic acid membrane is taking place near sulfonic group, probably oxygen and hydrogen bond, since some water molecules are bonded to sulfonic group through hydrogen bond even in dry state. Thus sulfonic group is an attractive site for positron. Figure 6 shows dose-dependencies of S-parameter for Nafion® exposed to different kinds of radicals. The S-parameter of the sample exposed to HO• was slightly decreased with increase of dose, whereas it remarkably increased for the sample exposed to H• in a higher dose region. Decreasing of S-parameter would be attributed to either the increase of annihilation with energetic electrons belonging to C-F bond or the decrease of annihilation with electrons relevant to hydrogen bond. Such change is thought to be brought by the lost of sulfonic group due to HO•. Increasing of S-parameter can be understood in such a way that the destruction of cluster leads to the dispersion of sulfonic groups along with associated water molecules, and eventually free annihilation with a lower energy electron relevant to hydrogen bond would increase. In the sample exposed to O2•−, a similar behavior to the samples exposed to H• was expected but there was no significant dependency on absorbed dose. The radicals produced at the instance of scission would react with abundant oxygen or oxygen radical and eventually the scission site would be terminated with an oxygen, leading to the suppression of annihilation with the electrons belonging to hydrogen bond and C-F bond. In γ-irradiated Nafion® in dry state, there was a reverse correlation between proton conductivity and S-parameter, and cross-linking was thought to happen between neighboring sulfonic groups. [4] In dry state, HO• radicals would be generated from bound water to sulfonic group. However there was no such correlation between S-parameter and proton conductivity for the sample exposed to HO• in water. This indicates that water greatly influences on the degradation process caused by radicals.

4. Conclusion
Degradation process of PEM caused by different kinds of radicals was investigated by positron annihilation spectroscopy. The catastrophic damage was brought by reductive radicals, i.e. destruction of cluster structure was more severe rather than loss of sulfonic group in cluster for proton conductivity. Such degradation processes due to structural change were able to be drawn by positron annihilation spectroscopy.

Acknowledgement
This work was supported by NEDO.

References
[1] Danilczuk M, Coms F D and Schlick S 2009 J. Phys. Chem. B 113 8031
[2] Uegaki R, Akiyama Y, Tojo S, Honda Y and Nishijima S 2011 J. Power Sources 196 9856
[3] Mauritz K A and Moore R B 2004 Chem. Rev. 104 4535
[4] Honda Y, Aoyagi Y, Tojo S, Akiyama Y and Nishijima S 2013 Material Sci. Forum 733 53
[5] Halim J, Buchi F N, Haas O, Stamm M and Scherer G G 1993 Electrochimica Acta 39 1303