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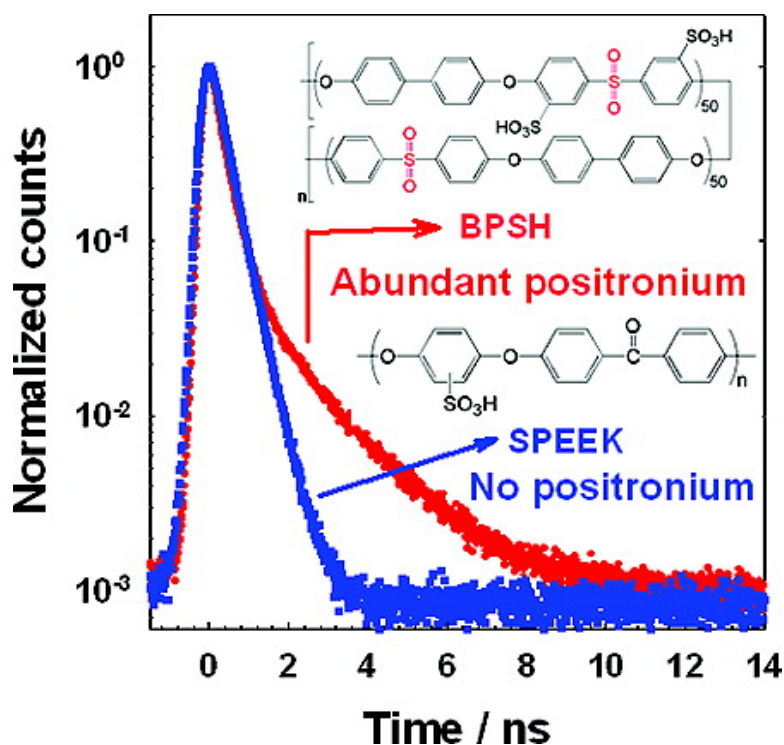
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## Positronium Formation in Aromatic Polymer Electrolytes for Fuel Cells

Y. Kobayashi,<sup>\*,†</sup> Hamdy F. M. Mohamed,<sup>‡,§</sup> and A. Ohira<sup>‡</sup>

NMIJ, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan, and FC-Cubic, National Institute of Advanced Industrial Science and Technology, Tokyo 135-0064, Japan

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We measured the yield of positronium (Ps) in sulfonated aromatic proton conducting membranes for the polymer electrolyte fuel cell (PEFC) with and without  $-\text{SO}_2-$  in their chemical structures by positron annihilation lifetime spectroscopy (PALS). It was observed that Ps formation is almost totally inhibited in the polymers without  $-\text{SO}_2-$  such as sulfonated poly(ether ether ketone) (SPEEK). On the other hand Ps favorably forms in those with  $-\text{SO}_2-$  as sulfonated polyether sulfone (SPES), which is due to the anti-inhibition effect of  $-\text{SO}_2-$ . The high probability of Ps formation in these polymers enables the study of the free volume and the mechanism of gas permeation by PALS.

The polymer electrolyte fuel cell (PEFC) is an electrochemical device to generate power from hydrogen and oxygen.<sup>1</sup> In PEFC protons dissociated from hydrogen at the anode are transported through a hydrated polymer electrolyte membrane to the cathode, where they react with oxygen to form water. Sulfonated polymers that exhibit high proton conductivity in the hydrated state due to the Grotthuss mechanism of proton conduction<sup>2</sup> are the most frequently used polymer electrolyte membranes for PEFC. The power resultant from the chemical reactions at the anode and cathode is extracted as an external electric current. Being highly efficient with no emission of harmful chemicals, PEFC is a leading future clean energy technology for residential and transportation power generation. The proton conducting membrane of PEFC is required to be a good gas barrier, because the crossover of hydrogen and oxygen across the membrane has a negative impact on the overall efficiency of the cell. Thus the study of the gas permeation mechanism in the polymer electrolyte membrane is of considerable technological importance for the development of high performance PEFC.

According to the free volume model, gas permeation in a polymer is governed by intermolecular open space or free volume that provides a pathway for gas diffusion.<sup>3–5</sup> One can probe the nanometer sized free volume holes with positron annihilation lifetime spectroscopy (PALS).<sup>6–9</sup> Recently we have applied PALS to a perfluorosulfonic acid polymer membrane, Nafion, in different ion-exchanged forms, and suggested that gas permeation is dependent not only on the free volume but also on the stiffness of the ionomer.<sup>10–12</sup>

Application of PALS to the study of free volume in polymers relies on the formation of positronium (Ps), the bound state between a positron and an electron.<sup>13</sup> In polymers

with Ps formation, there exist three states of positrons characterized by lifetimes  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  with the corresponding relative intensities  $I_1$ ,  $I_2$  and  $I_3$ , respectively; these are spin antiparallel *para*-positronium (*p*-Ps) with  $\tau_1 \sim 125$  ps, free positrons with  $\tau_2 \sim 450$  ps, and spin parallel *ortho*-positronium (*o*-Ps) with  $\tau_3 \sim 1\text{--}10$  ns. The longest-lived *o*-Ps component with lifetime  $\tau_3$  and intensity  $I_3$  is of particular importance for the polymer studies because the lifetime  $\tau_3$  is closely connected to the average free volume hole size.<sup>13</sup> The relationship between lifetime  $\tau_3$  and average radius  $R$  of free volume holes in spherical approximation is given by the Tao–Eldrup model<sup>14,15</sup> as

$$\tau_3 = 0.5 \left\{ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right\}^{-1} \text{ (ns)} \quad (1)$$

where  $R_0 = R + \Delta R$  and  $\Delta R = 0.166$  nm is the thickness of the homogeneous electron layer in which the positron in *o*-Ps annihilates.<sup>13</sup> The free volume size  $V_{\text{FV,Ps}}$  in  $\text{nm}^3$  can be calculated as

$$V_{\text{FV,Ps}} = 4\pi R^3/3 \quad (2)$$

In the  $\text{H}^+$  form of Nafion NRE212, about 7% of the positrons form *o*-Ps, and the free volume hole size can be reliably determined from the *o*-Ps lifetime.<sup>10</sup> However, in certain polymers Ps hardly forms and the longest-lived component is of little intensity ( $I_3 \sim 0$ ).<sup>16</sup> PALS is not applicable to probing the free volume in such polymers. In this paper we discuss the applicability of PALS to the study of the free volume and gas permeation in nonfluorinated aromatic proton conducting membranes for PEFC based on experimental data on those with different chemical structures. Sulfonated aromatic polymers with large ion exchange capacity (IEC) are receiving much attention as proton-conducting membranes because of their lower cost and higher heat resistance than perfluorosulfonic acid membranes.<sup>17</sup>

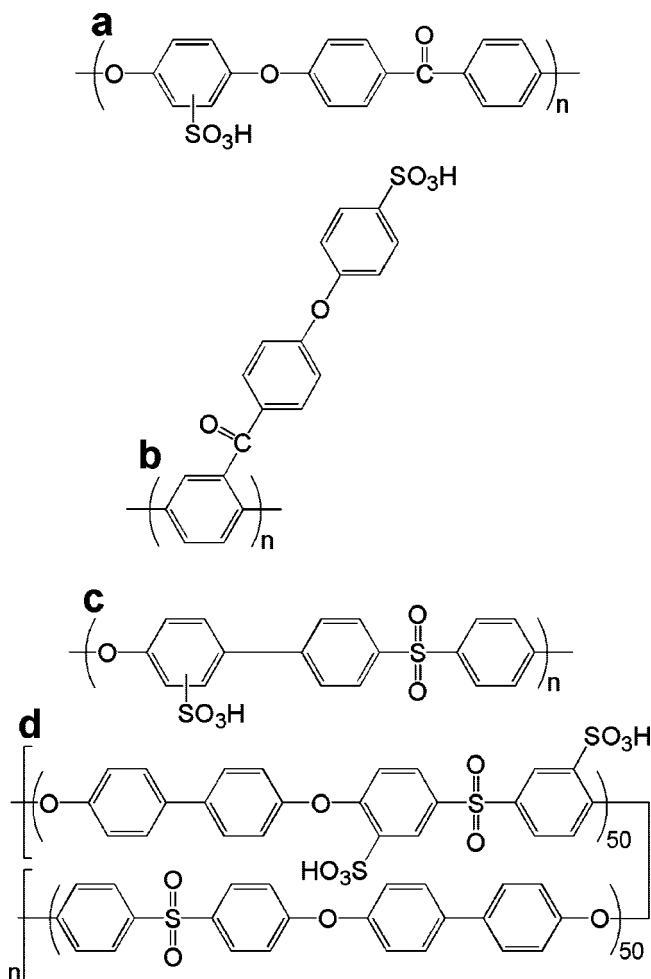
Chemical structures of the polymers studied in this work are shown in Figure 1. Sulfonated poly(ether ether ketone) (SPEEK) with an IEC of 1.87 mequiv/g was synthesized by sulfonation

\* Corresponding author. Tel: +81-29-861-4886. Fax: +81-29-861-4622. E-mail: y-kobayashi@aist.go.jp.

<sup>†</sup> NMIJ.

<sup>‡</sup> FC-Cubic.

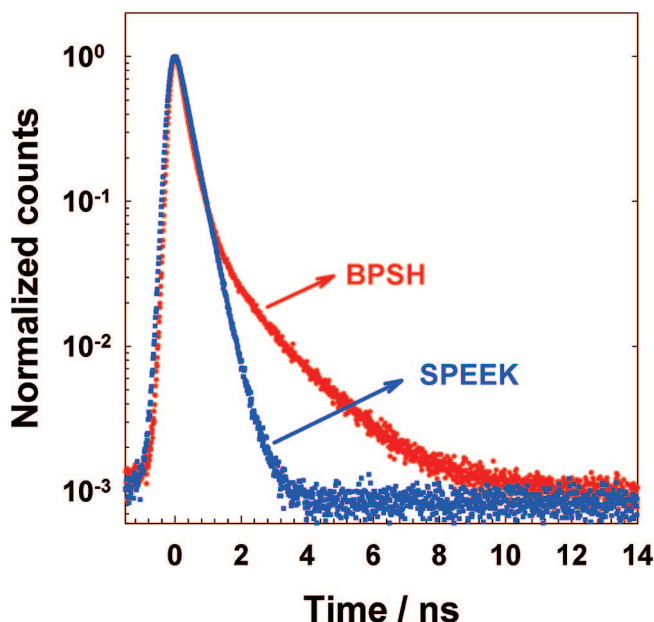
<sup>§</sup> Visiting from Physics Department, Faculty of Science, Minia University, P.O. Box 61519, Minia, Egypt.



**Figure 1.** Chemical structures of sulfonated aromatic polymer electrolytes for PEFC studied in this work: (a) sulfonated poly(ether ether ketone) (SPEEK); (b) sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP); (c) sulfonated polyether sulfone (SPES); (d) biphenol-based sulfonated poly(arylene ether sulfone) (BPSH). For all the structures the number of the repeating units with  $\text{SO}_3\text{H}$  depends on IEC and varies from one sample to another.

of commercial PEEK from Goodfellow with concentrated sulfuric acid as reported by Kobayashi et al.<sup>18</sup> Sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP) with IEC's of 2.00 and 2.80 mequiv/g were from Prof. Rikukawa of Sophia University. Sulfonated polyether sulfone (SPES) with IEC's of 0.75, 1.02, and 1.40 mequiv/g were supplied by Sumitomo Chemical Co., Ltd. Biphenol-based sulfonated poly(arylene ether sulfone) (BPSH) with an IEC of 1.60 mequiv/g was synthesized by direct aromatic nucleophilic substitution polycondensation.<sup>19,20</sup> The IEC's of all the sulfonated polymers were determined by back-titration. For comparison, poly(ether ether ketone) (PEEK) and polyether sulfone (PES) without sulfonation were also studied.

Positron lifetime measurements were conducted using a fast-fast coincidence system with a time resolution of 280 ps fwhm at room temperature under vacuum.<sup>10–12</sup> A 0.37 MBq  $^{22}\text{Na}$  positron source sealed between two Kapton films with a thickness of 7.5  $\mu\text{m}$  was sandwiched between two stacks of polymers each with a thickness of 1 mm. Each lifetime spectrum containing over 2 million counts was analyzed using the PALSfit program<sup>21</sup> into three lifetime components to deduce lifetime  $\tau_3$  and relative intensity  $I_3$  of the longest-lived *o*-Ps component. No source correction was



**Figure 2.** Positron lifetime spectra of SPEEK with IEC = 1.87 mequiv/g and BPSH with IEC = 1.60 mequiv/g.

applied in the data analysis. The validity of our measurements and data analysis was ensured with a certified reference material (NMIJ CRM 5601-a).<sup>22</sup>

Positron lifetime spectra of BPSH (IEC = 1.60 mequiv/g) and SPEEK (IEC = 1.87 mequiv/g) are shown in Figure 2. The presence of the longest-lived *o*-Ps component is very clear for BPSH, whereas the long-lived component is hardly visible in the spectrum for SPEEK. Thus the Ps formation in sulfonated aromatic polymers with large IEC's varies considerably from one structure to another. The lifetime  $\tau_3$  and corresponding relative intensity  $I_3$  of all the polymers studied are listed in Table 1. It is seen in this table that no Ps forms in SPEEK with IEC = 1.87 mequiv/g despite  $I_3$  being as high as 21% for PEEK without sulfonation (IEC = 0 mequiv/g). We also note that  $I_3$  is less than 1% in SPPBP with IEC = 2.00 and 2.80 mequiv/g.

The spur reaction model of Ps formation states that Ps is formed by a reaction between a positron and one of the electrons, ionized and liberated from the polymer molecules by the energetic positron itself, in the terminal positron spur.<sup>23–28</sup> Ps formation competes with other processes such as positron and electron scavenging, electron–ion recombination, positron and electron escaping from the spur, trapping of Ps in a free volume hole, etc., so that the yield of Ps in a polymer is dependent on a number of parameters. An important observation relevant to the present work is that the addition of a certain electron acceptor such as *p*-dichlorobenzene and *p*-dibromobenzene causes a marked reduction in the Ps yield in a polymer.<sup>29</sup> Such a phenomenon is called inhibition of Ps formation and is due to the scavenging and capture of spur electrons, which would otherwise recombine with the positron to form Ps, by the electron acceptor.<sup>13,23,28–33</sup> The dramatic decrease of  $I_3$  of PEEK upon sulfonation and very little Ps formation in SPPBP with high IEC's suggest that the  $-\text{SO}_3\text{H}$  group in sulfonated polymers is an inhibitor of Ps formation no matter whether it is in the main chain or in the side chain. The  $-\text{SO}_3\text{H}$  group is an electron withdrawing substituent, and the benzene ring substituted by it becomes electron deficient and electron accepting.<sup>34</sup>

**TABLE 1: *o*-Ps Lifetime  $\tau_3$  and Its Intensity  $I_3$  in Sulfonated Aromatic Polymer Electrolytes for PEFC with Different Chemical Structures and Ionic Exchange Capacities (IEC's)<sup>a</sup>**

polymer	IEC/mequiv g <sup>-1</sup>	$\tau_3$ /ns	$I_3/\%$
sulfonated poly(ether ether ketone) (SPEEK)	0.00 (PEEK)	1.87 ± 0.01	21.2 ± 0.3
	1.87		~0
sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (SPPBP)	2.00		<1.0
	2.80		<1.0
sulfonated polyether sulfone (SPES)	0.00 (PES)	2.04 ± 0.01	16.4 ± 0.2
	0.75	1.89 ± 0.01	14.3 ± 0.2
	1.02	1.87 ± 0.01	13.6 ± 0.2
	1.42	1.88 ± 0.01	12.5 ± 0.2
biphenol-based sulfonated poly(arylene ether sulfone) (BPSH)	1.60	1.94 ± 0.01	20.9 ± 0.2

<sup>a</sup> The uncertainties are those obtained in the data analysis, taking account of only counting statistics.

Interestingly, the strength of  $-\text{SO}_3\text{H}$  in suppressing Ps formation is appreciably weakened in SPES (IEC = 0.75, 1.02, 1.42 mequiv/g) with  $-\text{SO}_2-$  in its chemical structure;  $I_3$  of this polymer is reduced from  $I_3 = 16.4\%$  at IEC = 0 mequiv/g to  $I_3 = 12.5\%$  at IEC = 1.42 mequiv/g only by 4%. In our previous study<sup>29</sup> on the effect of adding *p*-dichlorobenzene and *p*-dibromobenzene to polymers, it was found that whereas the Ps formation in polycarbonate is inhibited by the dihalogenated benzenes, they do not have any effect on the Ps yield in polysulfone  $\{(-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-)_n\}$ . Further experiments using diphenyl sulfone ( $\text{C}_6\text{H}_5-\text{SO}_2-\text{C}_6\text{H}_5$ ) as a model compound of the  $-\text{SO}_2-$  structure of polysulfone revealed that the addition of this compound to polycarbonate containing the dihalogenated benzenes increases the Ps formation.<sup>29</sup> Such a phenomenon of recovering Ps formation suppressed by an inhibitor is called anti-inhibition.<sup>13,23,29</sup> It is caused by an electron acceptor that competes with the inhibitor for the spur electrons but traps them only weakly. The electrons trapped on the anti-inhibitor are still able to be extracted by the positron, thereby the Ps formation is recovered.<sup>13,23,29</sup> Our previous study convincingly shows that  $-\text{SO}_2-$  in diphenyl sulfone and polysulfone is an anti-inhibitor of Ps inhibited by the dihalogenated benzenes. We consider that the favorable formation of Ps in SPES, in spite of high degrees of sulfonation, is also due to the anti-inhibition effect of  $-\text{SO}_2-$  involved in it. Namely the spur electrons otherwise captured by  $-\text{SO}_3\text{H}$  substituted rings are made available for Ps formation by trapping on  $-\text{SO}_2-$ . We note in Table 1 that  $I_3$  in BPSH (IEC = 1.60 mequiv/g) with  $-\text{SO}_2-$  is also high and over 20%.

Apart from the intraspur reactions, free volume has an influence on the yield of Ps in a polymer. For example, decrease of Ps formation with increasing crystallinity has been observed for several polymers.<sup>35,36</sup> If the low values of  $I_3$  in SPEEK (IEC = 1.87 mequiv/g) and SPPBP (IEC = 2 and 2.8 mequiv/g) were due to the absence of free volume with a sufficient size for the localization of Ps, their gas permeability would be extremely small. We measured oxygen permeabilities in SPEEK (IEC = 1.87 mequiv/g) and SPPBP (IEC = 2.8 mequiv/g) at 80 °C and found that they are  $7.2 \times 10^{-15}$  and  $1.36 \times 10^{-14}$  cm<sup>3</sup> cm cm<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, respectively. These values are comparable to those of Nafion NRE212 with a significant amount of free volume.<sup>10–12</sup> Therefore the large variations of Ps formation in sulfonated polymer electrolyte membranes with high proton conductivity among different chemical structures are attributed to the inhibition effect of  $-\text{SO}_3\text{H}$  and anti-inhibition effect of  $-\text{SO}_2-$  but not to differences in free volume.

In conclusion, although Ps formation can be almost totally inhibited in sulfonated aromatic polymer electrolytes with large IEC's, Ps favorably forms in those with  $-\text{SO}_2-$  in their structures. This is due to the anti-inhibition effect of  $-\text{SO}_2-$ .

The favorable formation of Ps enables the application of PALS to the study of the free volume and the mechanism of gas permeation to such polymers as BPSH and SPES with  $-\text{SO}_2-$  in their chemical structures.

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