Structure of Porous Vycor Glass 
and Its Adsorption Characteristics of Water —
An Application of Positron Annihilation Method

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Abstract. Positron lifetimes in porous Vycor glass have been measured. There are four lifetime components, and the fourth component has been assigned to o-Ps annihilation in large pores of radius 34 Å. The intensity \( I_4 \) has been correlated to a specific surface area, but the value obtained from \( I_4 \) by the Monte Carlo method is smaller than that obtained by the BET method. From variations in \( (\tau_4, I_4) \) against the kinetics of adsorption of water vapor, a rough picture of water adsorption is presented.

Index Headings: Positron lifetime measurement – Porous glass

It has been well known that o-Ps in solid materials diffuses within its lifetime a certain distance which is about \( 1-3 \times 10^{-6} \) cm depending upon the substance [1]. If the substance contains a sufficient amount of defects, pores or grain boundaries, some fraction of o-Ps may escape into these free volumes before annihilation and may survive a longer time in it. The lifetime of o-Ps in these free volumes might be controlled by two factors, namely, pick-off annihilation at the surface of pores and reaction or conversion of o-Ps with something like surface active species.

It is expected from this particular feature that the positronium annihilation method might be used to elucidate the structure and surface state of porous materials. The present paper is a preliminary report on an application of the positron annihilation method to the study of structure of porous Vycor glass and its adsorption characteristics of water.

Experimental Procedure

Porous Vycor glass (PVG), Corning Code No. 7930, was used in this study. The surface area of PVG determined by a BET method using nitrogen adsorption was observed to be \( 154 m^2/g \) [2]. The pore volume measured by a displacement method with Hg and He was 0.26 ml/g, so that pore radius was determined to be 34 Å [2].

A rod of PVG was cut into two pieces of thickness 3 mm. These were, after being washed with hot nitric acid and distilled water and subsequently dried in vacuum, placed in a glass tube for positron lifetime measurement with the positron source between them. About 20 \( \mu \)Ci of \( ^{22} \text{NaCl} \) infolded in a thin nickel foil was used as the positron source.

The lifetime of positrons has been measured with a conventional fast-slow coincidence apparatus which had an effective linear range of about 250 nsec. The
time resolution of this apparatus is less than 0.5 nsec at full width at half maximum of Co-60 prompt peak for $^{22}$Na energy selection. It took about 4 days to obtain a lifetime spectrum with good statistics of coincidence counting rates, drift of the apparatus being negligibly small. The data of the lifetime spectra have been analyzed by the method of least squares.

**Results and Discussion**

A typical lifetime spectrum is shown in Fig. 1. There are four lifetime components. The 1st component is assigned to annihilation of free positrons and p-Ps. The 2nd component can be assigned to the annihilation of o-Ps in the glass, because its lifetime ($\tau_2 = 1.7$ nsec) agrees well with the values so far reported for o-Ps lifetime in bulk silica [3]. The 3rd and 4th components are undoubtedly assigned to o-Ps in defects or pores, because their lifetimes are considerably longer than $\tau_2$.

Referring to the works of Perkal and Walters [4], and Chuang and Tao [3] who have measured positron lifetimes in silica gel and molecular sieves, it seems reasonable to assign the 4th component to o-Ps in large pores with the radius of 34 Å for the present sample.

It is difficult to make assignment of the 3rd component, but we tentatively assign it to o-Ps in small free volumes of several angstrom in diameter or micro cracks, since this assignment can explain the experimental results, as will be shown later.

The lifetime of the 4th component ($\tau_4$) decreased when oxygen was introduced into the sample tube as is shown in Table 1. This can be explained by the well known reaction scheme between o-Ps and O$_2$ gas filled in the pores

$$\text{o-Ps} + \text{O}_2 \rightarrow [\text{PsO}_2]^n \rightarrow 2\gamma + \text{O}_2 \quad (1)$$

and this result agrees with our previous assignment that this component is attributed to o-Ps in the large pores.

The relative intensity of the 4th component, $I_4$, is about 3–4 %, and the “escape probability” of o-Ps to pores $I_4/(I_2 + I_3 + I_4)$ nearly equals to 0.15. It is principally possible to estimate the mean separation of the pores, if we assume that the migration of o-Ps can be expressed by diffusion equation, as was done by Brandt et al. [1]. As it is quite difficult to solve the equation for the probability of o-Ps escape into pores for the present case, we have tried to simulate o-Ps migration by the Monte Carlo method using a simplified model, as illustrated in Fig. 2, in which we assume that the shape of the pore could be cylindrical and the pore could be situated at the core of each square pillar cell (model A) or hexagonal pillar cell (model B). The o-Ps produced in the substance diffuses

**Table 1. Interaction of Ps with O$_2$ in PVG**

<table>
<thead>
<tr>
<th>Degassed at 200°C (5 x 10$^{-5}$ Torr)</th>
<th>O$_2$ 155 Torr</th>
<th>O$_2$ 588 Torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2nd Compt. $\tau$</td>
<td>$1.66 \pm 0.04$</td>
<td>$1.69 \pm 0.1$</td>
</tr>
<tr>
<td>$I$</td>
<td>$16.9 \pm 1.0$</td>
<td>$10.5 \pm 0.9$</td>
</tr>
<tr>
<td>3rd Compt. $\tau$</td>
<td>$5.34 \pm 0.11$</td>
<td>$4.8 \pm 0.2$</td>
</tr>
<tr>
<td>$I$</td>
<td>$5.8 \pm 0.33$</td>
<td>$5.6 \pm 0.6$</td>
</tr>
<tr>
<td>4th Compt. $\tau$</td>
<td>$53.1 \pm 2.0$</td>
<td>$36.1 \pm 1.0$</td>
</tr>
<tr>
<td>$I$</td>
<td>$3.8 \pm 0.2$</td>
<td>$5.4 \pm 0.2$</td>
</tr>
</tbody>
</table>

Fig. 1. Positron lifetime spectrum of PVG degassed 5 h at 200°C. Time scale is 0.424 nsec/channel. The solid lines show each component calculated by the method of least squares.