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Positron Annihilation Techniques as probes for Investigation of the Polymer Electrolyte Membranes with Different Ion Exchange Capacities

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Abstract

The positron annihilation lifetime (PAL) experiments have been conducted on pure polyether sulfone (PES) and sulfonated polyether sulfone (SPES) with varying degrees of sulfonation, that is, varying ionic exchange capacities ($IEC=0.0, 0.75, 1.02, \text{ and } 1.40 \text{ meq/g}$) at room temperature. In addition, Doppler broadening of annihilation radiation (DBAR) measurements were performed simultaneously with PAL experiments. As IEC increases, the ortho-positronium ($o\text{-Ps}$) lifetime τ_3 declines until it reaches 0.75 meq/g , indicating a free volume size fall before leveling off. Conversely, the $o\text{-Ps}$ intensity I_3 falls off linearly as IEC rises, which could be because SO_3H inhibits positronium formation. The free volume sizes and distributions, calculated from the PALs spectra in sulfonated PES samples, reflected the relation between the free volume hole and the IEC . Sulfonated PES polymer has smaller free volume hole size and its distributions are narrower than unsulfonated PES. Sulfonated PES with SO_3H makes the S - (W -) parameters, deduced from DBAR, decrease (increase) linearly with increasing the IEC . The S -parameter decreases with the decrement of the Ps fraction corresponding to decreasing I_3 . The S - and W -parameters correlation shows linear dependence indicating that they have the same free volume or defect structure although their $IECs$ differ. The use of PALS to investigate the free volume and structure of these polymers is made possible by the advantageous production of Ps .

Key words: Positron annihilation spectroscopy, Free volume size, Positronium formation, Polyether sulfone, ion exchange capacity.

1. Introduction

In a matter of picoseconds, positrons introduced into a condensed material from a radioactive source first slow down to thermal energy. The positrons are guaranteed to reach most of the sample material by the mean implantation range, which varies between 10 and 1000 μm [1]. Following a period of thermal equilibrium, the positron annihilates into two γ -rays, each of which has a mass of 511 keV, by combining with an electron from the surrounding medium. Every material has a different average positron lifetime, which ranges from 100 to 500 ps [1]. A portion of the positrons mix with electrons during the slow down process to generate positronium (Ps) atoms, which get caught in atomic-sized holes. Ps can develop in a singlet state (*para*-positronium, *p*-Ps) or a triplet state (*ortho*-positronium, *o*-Ps), with a 3:1 ratio for each. Ps production likelihood is dependent on several physico-chemical characteristics [2]. Once produced, positronium is drawn into empty spaces, such as voids or free volume by the molecules in its surroundings. Since *p*-Ps have a lifetime that is too fast to be affected by this free volume factor, they annihilate with an intrinsic lifetime of 0.125 ns in most cases. On the other hand, *o*-Ps have a lengthy lifetime (140 ns in vacuum), and their positron has a good possibility of absorbing an electron from the surrounding medium and annihilating much faster. A pick-off annihilation rate is related to the overlap density of the surrounding electrons at the positron point [3, 4]. As a result, when *o*-Ps are trapped in smaller voids or smaller free volumes, their lifetime is shortened [5].

Doppler broadening of annihilation radiation (DBAR), positron annihilation lifetime (PAL), and angular correlation of annihilation radiation (ACAR) are the three experimental methods that comprise the field of positron annihilation spectroscopy (PAS). If one would like to know information about the positron density, data from the PAL approach can be used to determine the electron densities of the materials being studied. However, the ACAR and DBAR data allow for a quantitative investigation of the momentum density for two and one dimensions, respectively. Positron annihilation spectroscopy has become a potent tool for examining phase transitions, structural alterations, and microenvironmental changes in a range of systems. The PAS parameters are highly sensitive to these kinds of modifications, which makes them a promising tool for studying conformational, structural, and microenvironmental alterations in micellar and microemulsion systems [5]. Because it is exposed to vital information on the free volume size and its contents, the PAS also plays a significant role [6–8]. It offers helpful details regarding the electrical structure of the materials and the concentration of their flaws in liquids or solids [9]. In addition, the knowledge about the gas or liquid permeability of the materials is correlated with the free volume size [10].

An electrochemical device to produce electricity from hydrogen and oxygen is the polymer electrolyte fuel cell (PEFC) [11]. Protons in PEFC that have separated from hydrogen at the anode are transferred to the cathode via a hydrated polymer electrolyte membrane, where they combine with oxygen at the cathode to generate electricity and hot water. Due to the Grotthuss method of proton conduction [12], sulfonated polymers in their hydrated state have a high proton conductivity, making them the most popular polymer electrolyte membranes for PEFC.

An external electric current is extracted as the power produced by the chemical processes at the cathode and anode. For the generation of power for homes and vehicles, PEFC is a cutting-edge clean energy technology since it is extremely efficient and emits no hazardous pollutants. Because hydrogen and oxygen crossing the membrane reduce the cell's overall efficiency, the proton exchange membrane of a PEFC must function as a good gas barrier. Therefore, research into the polymer electrolyte membrane's gas penetration mechanism is crucial for the creation of PEFCs with high-performance. The free volume concept states that intermolecular open space, or free volume, which forms a route for gas diffusion, controls gas permeation in a polymer [13–15]. By using the PAL technique, one can examine the nanometer-sized free volume holes [16–18]. Our recent use of PAL technique on several ion-exchanged versions of Nafion, a perfluorosulfonic acid polymer membrane, has shown that gas penetration depends on the stiffness of the ionomer in addition to the free volume [19–21].

Positronium (Ps), the bonded state between a positron and an electron, must form for applying the PAL technique for studying the free volume in polymers [22–24]. Three positron states are found in polymers containing Ps. These states are lifetimes τ_1 , τ_2 and τ_3 with their relative intensities I_1 , I_2 , and I_3 , respectively; they are spin antiparallel *para*-positronium (*p*-Ps) with a lifetime $\tau_1 \sim 125$ ps, free positrons lifetime $\tau_2 \sim 450$ ps, and spin parallel *ortho*-positronium (*o*-Ps) $\tau_3 \sim 1$ –10 ns. The polymer investigations place special emphasis on the *o*-Ps component (τ_3 & I_3), which is closely related to the free volume hole size and contents [25–26]. The Tao-Eldrup model [27, 28] gives the following relationship, in spherical approximation, between the average radius R of free volume holes and lifetime τ_3 as

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

where the thickness ΔR of the homogeneous electron layer. The positron in *o*-Ps annihilates at this thickness, where $\Delta R = 0.166$ nm and $R_o = R + \Delta R$ [29]. To compute the free volume hole size V_{Ps} , use the formula:

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

Positrons, localized at defect and/or free volume or not, eventually annihilate with electrons, primarily producing annihilation two γ -rays as required by the conservation of energy-momentum process during annihilation. Because of the thermalization of the positrons, the total energy of the annihilation γ -rays is given by $2m_oC^2 - E_B$, where E_B is the binding energy of the electron and m_oC^2 is the electron rest mass energy (ignoring chemical potentials and the thermal energies). When the annihilation pair is connected to a net center of mass energy, the entire energy is not split equally between the two γ -rays. The deflection of one γ -ray from the center energy of $m_oC^2 - E_B/2$ to the deflection of the other is determined by the formula $\Delta E = (1/2)\Delta P_L C$, where P_L is the positron-electron momentum's longitudinal component along the direction of γ -ray emission. A detector oriented in the same direction will record both downshifted and upshifted γ -rays since the emission of γ -rays is random. This results in a

generalized broadening of DBAR spectra, and analyzing this broadening offers a sensitive approach to investigating the surrounding electronic environment of the annihilation locus [30]. The percentage of valence electrons participating in the annihilation process rises when positrons localize in free volume or/and defects as opposed to core electrons. The distribution of the momentum with the annihilating electrons shifts to smaller momenta as a result of the valence electrons' much lower momentum, which is represented by the *S*-parameter in the DBAR spectrum. On the other hand, the distribution of the momentum for the core electrons can be obtained by analyzing the tail region of the DBAR curve (*W*-parameter). It is well known that the *W*-parameter is sensitive to the substances in the vicinity of the positron annihilation site. The high-energy area, which deviates from the annihilation energy of 511 keV, is mostly contributed to by the core electrons with high momenta [31].

The susceptibility of the PAS parameters to conformational and structural changes in the surrounding medium [7] and its nondestructive nature, which allows for highly sensitive measurements without disturbing the studied samples [5], are two features of PAS that make them particularly appealing for our studies. So, in this paper, we discuss the applicability of PALS to the study of the nanostructure of the free volume deduced from PAL and the DBAR parameters for polyether sulfone (PES) and sulfonated polyether sulfone (SPES) based on experimental data on those with different chemical structures, such as different ion exchange capacity (*IEC*). Due to their greater heat resistance and lower cost compared to perfluorosulfonic acid, sulfonated aromatic polymers such as SPES with large *IEC* are gaining a lot of attention as proton-conducting membranes.

2. Experimental set-up and data analysis

The chemical structures of sulfonated polyether sulfone (SPES) and polyether sulfone (PES) are depicted in Fig. (1). Japan's Sumitomo Chemical Co. provided the PES and SPES with *IECs* of 0.75, 1.02, and 1.40 meq/g. On a thin piece of Kapton foil (7 μm thick), approximately 20 μCi of aqueous $^{22}\text{NaCl}$ was deposited to provide the positron source. After the $^{22}\text{NaCl}$ spots dried, they were covered with another Kapton foil that was comparable, adhered together using epoxy glue, and then kept under vacuum for 24 hours. About 10% of positron source will be absorbed by Kapton foils which will contribute to the short lifetime components (τ_1 & τ_2), and the PAL spectra analysis did not distinguish this absorption. A standard fast-fast coincidence system was used to evaluate the PAL measurements under vacuum at room temperature [19–21]. The PAL spectrum of the thick Kapton foils has been measured to compute the time resolution of the system. It appears that the Kapton polymer is the only one lacking a long-lived component, or *Ps* yield [32-33]. The time resolution of the PAL technique was determined to be 240 ps (full width at half maximum, FWHM) using the RESOLUTION software [34]. To do PAL measurements at room temperature (about 30 $^{\circ}\text{C}$), the sandwich of membrane/positron-source/membrane was wrapped in Al foil.

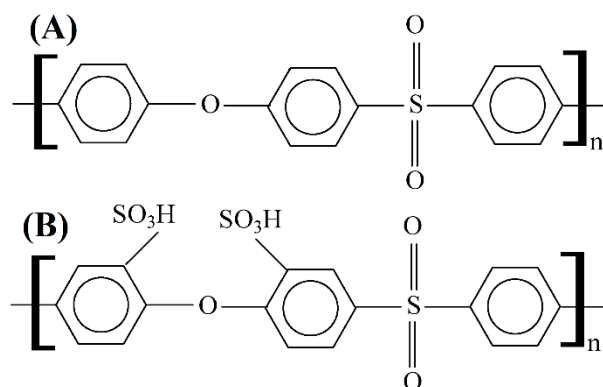


Figure (1): Chemical structures of (A) polyether sulfone (PES) and (B) sulfonated polyether sulfone (SPES).

Three lifetimes, denoted as τ_1 , τ_2 , and τ_3 , together with their intensities I_1 , I_2 , and I_3 , respectively, are often present in the positron annihilation lifetime spectrum of a molecular material. These intensities represent the fraction of annihilation events for each component. Using the PALSfit program [35], each lifetime spectrum with more than two million counts was broken down into three lifetime components to determine the *o*-Ps lifetime τ_3 and its intensity I_3 . In the data analysis, source correction was not used. Using certified reference material (NMIJ CRM 5601-a), the validity of our measurements and data analysis was guaranteed [36, 37]. Additionally, for all these PAL spectra, the average and distribution of the τ_3 are computed using the MELT program [38]. The constant value of 10^{-5} was assigned to the entropy weight parameter (α). Figure (2) displays an example of the positron annihilation lifetime spectra for PES and SPES.

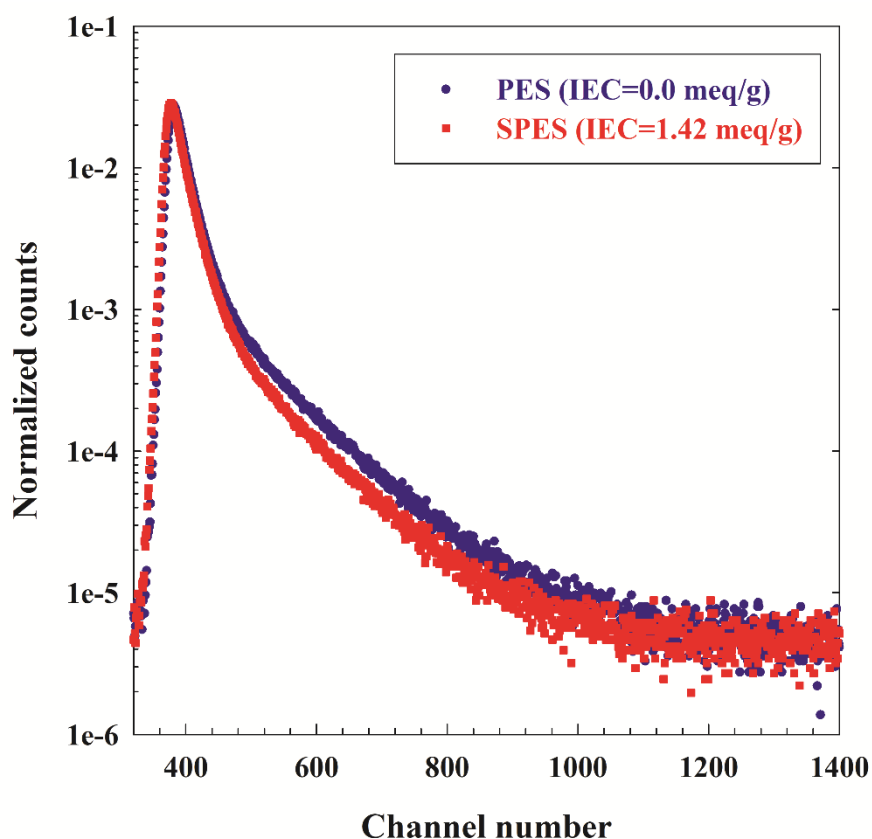


Figure (2): The positron annihilation lifetime spectra for PES and SPES polymers at room temperature.

The measurement of the Doppler broadening annihilation radiation (DBAR) was performed simultaneously with the PAL measurement using energy γ -spectroscopy. The mean component of this γ -spectroscopy is a high purity germanium (HPGe) detector with an energy resolution of 1.35 keV at γ -line 622 keV for ^{137}Cs . Thus, the momentum resolution of present spectroscopy is $4.31 \times 10^{-3} m_0c$ (one keV = 3.913868 milliradian), which corresponds to the energy resolution of approximately 1.1 keV at the 511 keV annihilation peak. The DOPPLERFIT [39] program was used to examine each DBAR spectra, and S - and W -parameters were then retrieved. As indicated in Fig. (3), the S - and W -parameters are defined as the ratio of the areas under the low momentum [$510.1\text{-}511.9$ keV ($|P_L| < 3.5225 \times 10^{-3} m_0c$)] and high momentum [$503\text{-}507$ keV ($15.66 \times 10^{-3} < |P_L| < 31.31 \times 10^{-3} m_0c$)] in the DBAR spectrum to all of the entire annihilation regions (photo peak around 511 keV). The momentum density at low (high) momentum is measured by the S - (W -) parameter, respectively.

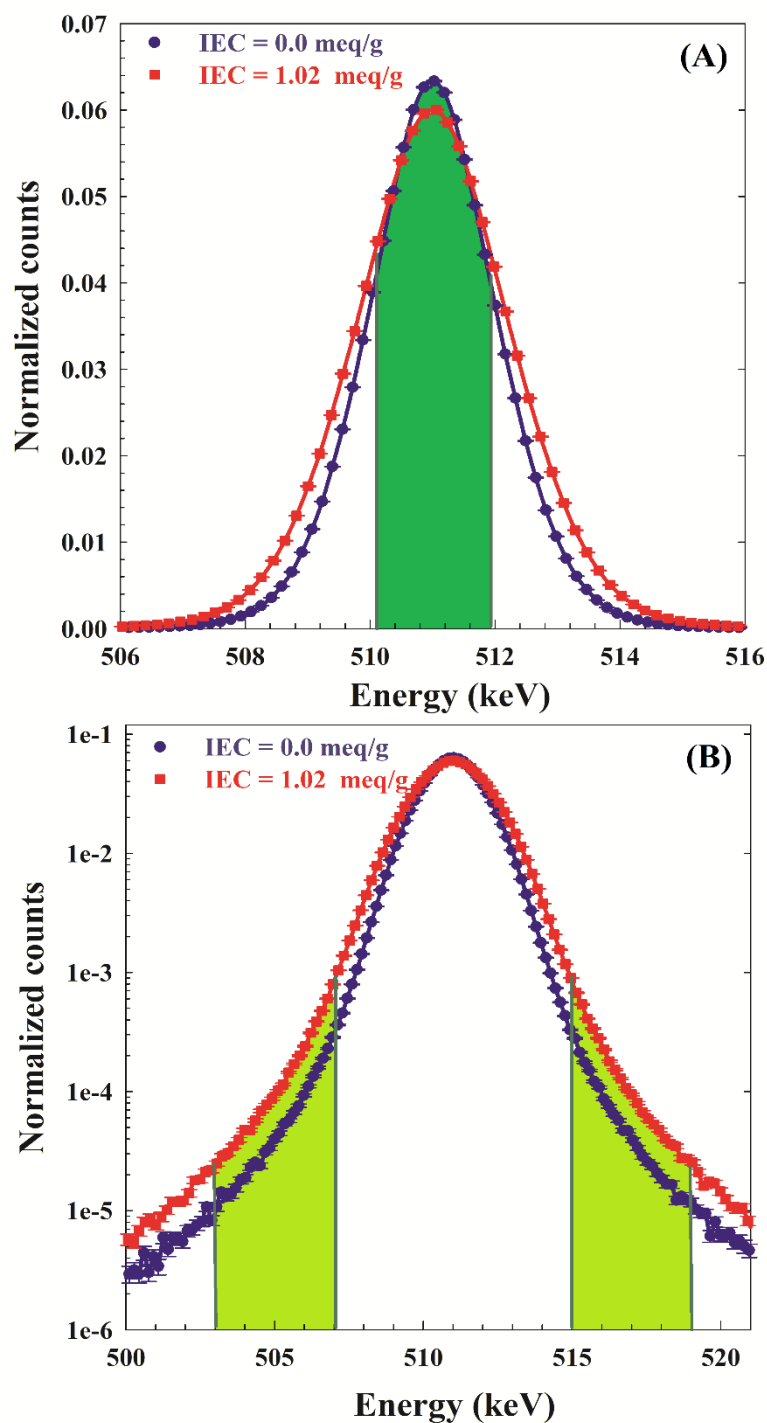


Figure (3): The Doppler broadening of annihilation radiation spectra for PES and SPES polymers showing (A) the S -parameter range (green) and (B) the W -parameter range (yellow) at room temperature.

3. Results and Discussion

It was discovered that three lifetime components provided the most acceptable standard deviations and the optimum variance ratio. Para-positronium (p -Ps) and direct annihilation of positrons are the primary causes of the short-lived component ($\tau_1 \sim 0.125$ ns, $I_1 = 20 - 35\%$) and

the intermediate component ($\tau_2 = 0.37 - 0.46$ ns, $I_2 = 50 - 65$ %), respectively. Because of the potential for the creation of positron and Ps compounds that affect both, a thorough examination of these two components is challenging. Pick-off annihilation of the *o*-Ps in free volume holes is responsible for the long-lived component ($\tau_3 = 2.04 - 1.87$ ns, $I_3 = 12.5 - 16.5$ %).

The *o*-Ps lifetime τ_3 and its intensity I_3 for polyether sulfone (PES) polymers are plotted against the ion exchange capacity in Fig. (4). Equations [1, 2] were utilized to calculate the free volume hole size, or scale, at the right ordinate, where the *o*-Ps is trapped. The error bars fit inside the symbol's dimensions. The figure makes it evident that the incorporation of SO₃H into pure PES reduces the τ_3 , i.e., V_{Ps} . Nevertheless, when the IEC, or the concentration of SO₃H in PES, increases, the V_{Ps} remain relatively constant. Sulfonation's reduction of the free volume hole is consistent with the findings of Lu et al. [40], who found that the addition of SO₃H to PES polymer chains raised the glass transition temperature because it enhanced intermolecular ionic contact.

As the concentration of SO₃H in PES increases, that is, as the IEC value increases, the *o*-Ps intensity I_3 drops linearly [Fig. (4)]. This showed that the SO₃H in the SPES hindered the creation of positronium, which is consistent with data from Mogensen [1], who reported that 0.28 percent of positronium is blocked by H⁺. According to the spur reaction hypothesis of Ps synthesis, Ps is created in the terminal positron spur through a reaction between a positron and one of the electrons that have been ionized and freed from the molecules of the polymer by the energetic positron itself [1, 41, 42]. Many processes and parameters in polymers can affect the generation of Ps, such as positron and/or electron escaping from the spur, positron and/or electron scavenging, trapping of Ps in a free volume hole, and electron-ion recombination [1, 35]. A noteworthy result relevant to the current work is that in polymers, the Ps yield is dramatically decreased upon the addition of a particular electron acceptor, such as SO₃H. The captures and scavenges of electrons from the spur that would recombine with the positron to generate Ps, causing the effect known as suppression of Ps generation. [1, 22, 43, 44]. It is possible that in the sulfonated membranes, the -SO₃H group inhibits the production of Ps, which leads to decrease in the I_3 of PES during sulfonation with high IECs. The benzene ring that the -SO₃H group substitutes becomes both electron-deficient and electron accepting because it is an electron-removing substituent [45-47].

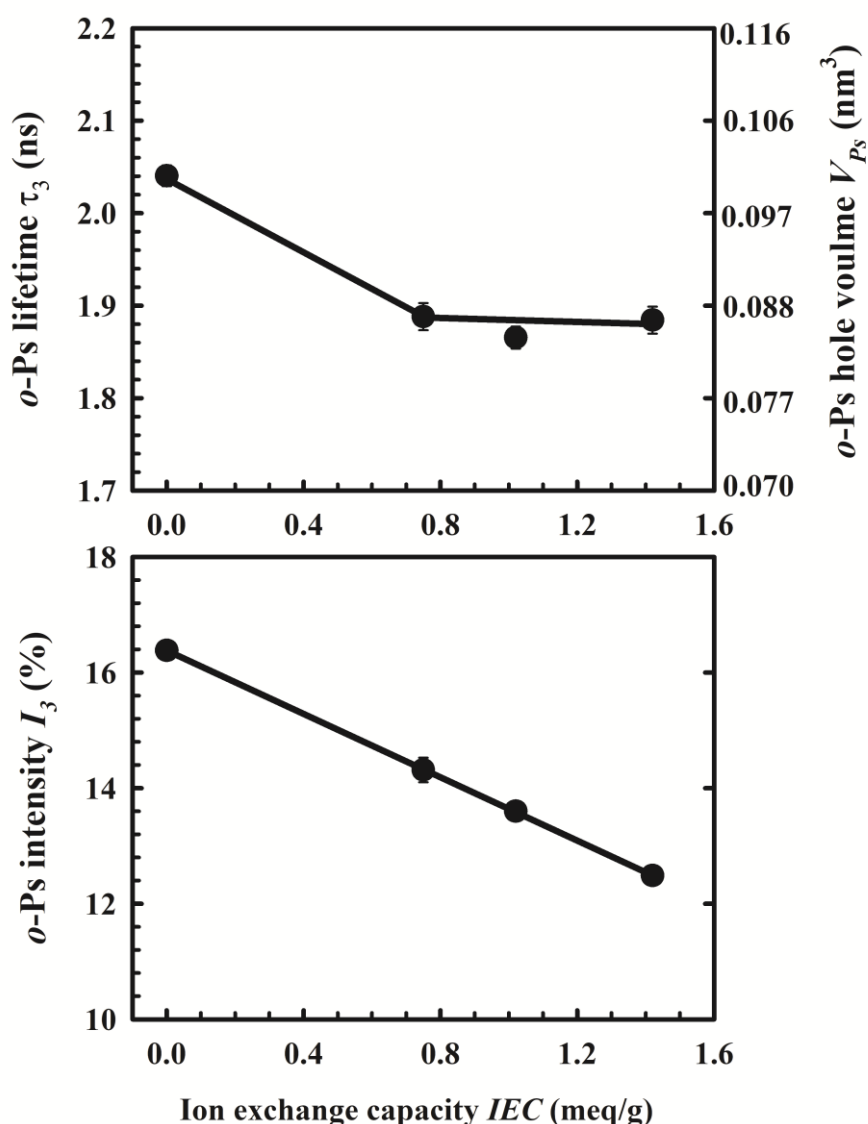


Figure (4): The o -Ps lifetime τ_3 and its intensity I_3 as a function of the ion exchange capacity IEC for polyether sulfone (PES) polymers. The scale at the right ordinate is the free volume hole size in which the o -Ps is trapped. The error bars are within the size of the symbol.

Remarkably, in SPES with different concentrations of sulfonation groups (i.e., different IEC up to 1.42 meq/g) and with $-SO_2-$ in its chemical structure, the strength of $-SO_3H$ in inhibiting Ps production is significantly lessened; I_3 of the present membrane is reduced from $I_3 = 16.4$ to 12.5% at the $IEC = 0$ to 1.42 meq/g, respectively, by just 4%. Hirata et al. [48] investigated the polymers after incorporating them with p-dibromobenzene or p-dichlorobenzene. They discovered that whereas the dihalogenated benzenes had no influence on the Ps yield in polysulfone, which includes SO_2 in their chemical structure as $(-O-C_6H_4-C(CH_3)_2-C_6H_4-O-C_6H_4-SO_2-C_6H_4-)_n$ while p-dibromobenzene or p-dichlorobenzene prevented Ps generation in polycarbonate (PC). The addition of diphenyl sulfone ($C_6H_5-SO_2-C_6H_5$) to PC containing dihalogenated benzenes promotes the synthesis of Ps, according to research using this compound of polysulfone which included SO_2- groups in its chemical structure [48]. Anti-

inhibition refers to the occurrence of regaining Ps production that has been repressed by an inhibitor [1, 2, 49]. It is brought on by an electron acceptor that poorly traps the spur electrons despite competing with the inhibitor for them. The Ps formation is regained because the positron can still remove the electrons that are stuck on the anti-inhibitor. Therefore, the anti-inhibition impact of $-\text{SO}_2-$ involved in Ps creation is also responsible for the enhancement of the formation of Ps in SPES, even at high concentrations of the $-\text{SO}_3\text{H}$ group. Specifically, by trapping on $-\text{SO}_2-$, the spur electrons that would otherwise be caught by substituted rings with $-\text{SO}_3\text{H}$ become accessible for Ps production.

Studying the free volume distribution that the MELT algorithm can infer from PAL spectra is fascinating [38]. The lifetime distribution of τ_3 (free volume V_{Ps} distribution) for PES and SPES with varying IEC is displayed in Fig. (5). In comparison to sulfonated poly(ether sulfone) SPES, the distribution of lifetime or free volume for pure poly(ether sulfone) PES is broader. The distribution showed how positronium generation changed with IEC , with a decreasing region under the peak as IEC increased. Additionally, the free volume drops and shifts to a smaller free volume size upon SO_3H sulfonating the PES, which is consistent with the earlier finding. Conversely, the peak center of the o -Ps lifetime distribution for sulfonated PES ($IEC = 0.75$ - 1.42 meq/g) remained unchanged, despite the distribution becoming broader as the IEC increased due to the competing effects of SO_3H -induced inhibition and SO_2 -induced anti-inhibition. The region of loose packing in PES is densified by the addition of SO_3H , which intensifies the molecular interactions.

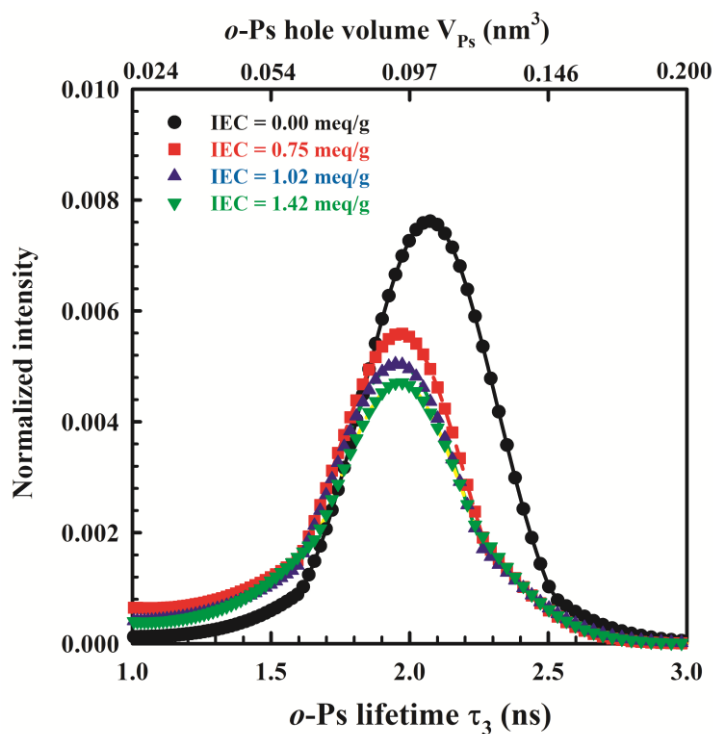


Figure (5): The o -Ps free volume size distributions at different IEC 's. The scale at the top ordinate is the free volume hole size in which the o -Ps is trapped.

The 511 keV annihilation peak's sharpness is measured by the S -parameter. Positrons and Ps have a higher probability of annihilating electrons are located at the outer orbital of atoms with lower kinetic momentum or/and are located at the wall of the free volume holes, especially in an amorphous region of the membrane. This results in a smaller perturbation to the γ -ray energy of the annihilation, which raises the S -parameter. This is true whether o -Ps annihilate in free volume holes or positrons annihilate in vacancies. Nevertheless, the absence of free volume holes lowers the S -parameter value because it raises the chance of annihilation of positrons with inner electrons that have low kinetic momentum linked to lattice atoms, which causes annihilation to be perturbed [2]. Consequently, an increment in the S -parameter denotes a rise in the number and/or size of free volumes concentrated. Figure (6) displays the variation of the S -parameter and W -parameters with the IEC for PES. The S -parameters and W -parameters of sulfonated PES with SO_3H drop and rise linearly with increasing IEC , respectively. Assume for the moment that the positronium generated in the samples is the primary factor influencing the S -parameter. Simply by offering a second positron interaction mechanism to rival the previously discussed positronium formation in pure PES, increasing IEC will result in a decrease in positronium formation. The S -parameter's behavior is consistent with the results of Mohamed et al. [48, 49], who stated that as the positronium fraction (I_3) rises, the S -parameter also rises.

When there is only one defect type with a variable concentration in metals or semiconductors and the slope of the line is a characteristic feature of the defect type, a linear relationship between the S -parameters and W -parameters could occur if the regions used for the calculation of the parameters are adjacent [51]. Similar circumstances may arise during the examination of a polymer sample in which positrons annihilate from various polymer states. If the percentage of annihilation from a particular state fluctuates mostly for the cost of annihilation from other states, then there may be a linear relationship between the S - and W -parameters. Figure (7A) displays the S - W plot for PES and SPES with varying IEC . This picture makes it evident that, in the SPES samples, W -parameter relies linearly with S -parameter, indicating that, despite the membranes with varied $IECs$, all the membranes exhibit the same kind of free volume or defect. The S -parameter exhibits a comparable pattern across all samples to the I_3 , indicating a parallel formation probability for both o -Ps and p -Ps. The S -parameters are consistent with positron annihilation at low momentum [1]. The S -parameter and I_3 exhibit a substantial association, as predicted by theoretical considerations, as illustrated in Fig. (7B). The explanation for this link can be given by considering the contribution of the o -Ps (high Doppler shifts \sim high momentum) and the p -Ps (low Doppler shifts \sim low momentum) annihilations to the total annihilation peak shape of coupled free positron.

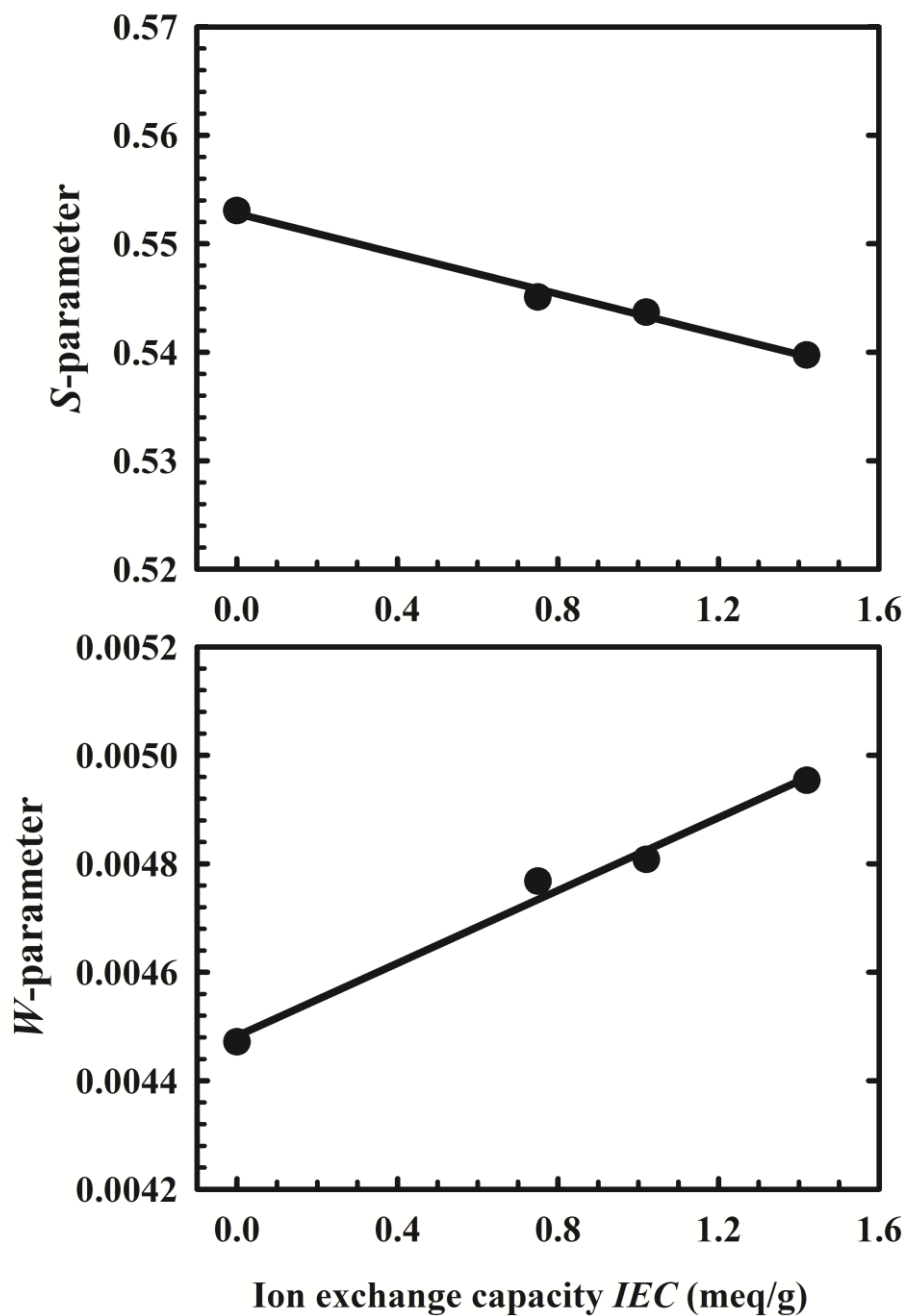


Figure (6): The *S*- and *W*-parameters, deduced from DBAR, as a function of the ion exchange capacity *IEC* for polyether sulfone (PES) polymers.

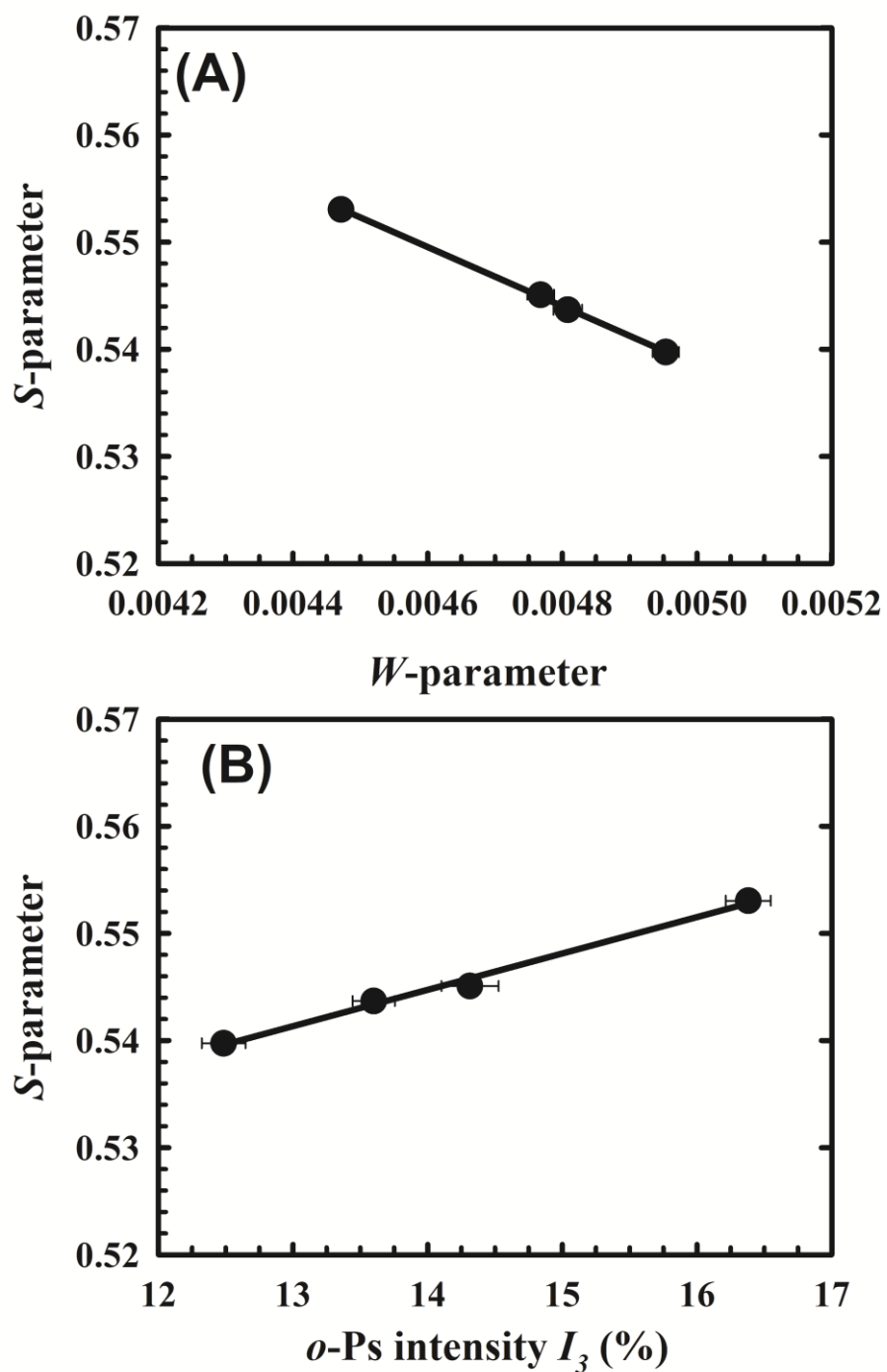


Figure (7): The correlation between S -parameter and both of (A) W -parameters and (B) o -Ps intensity I_3 for polyether sulfone (PES) polymers with different IEC.

4. Conclusion

Based on the previous discussion, one can conclude that:

- (1) The sensitivity of PAS to structural changes in membranes with varying *IEC* is exemplified by positron annihilation data.
- (2) The region of loose packing in PES is densified by strengthening the molecular connections with the injection of SO_3H (increasing *IEC*).
- (3) Ps preferentially forms in sulfonated aromatic polymer electrolytes with $-\text{SO}_2-$ in their structures, even though Ps creation can be virtually completely blocked in those with large *IECs*. This is because $-\text{SO}_2-$ has an anti-inhibition action.
- (4) Despite having differing *IECs*, the relation between the *S*-parameter and the *W*-parameters demonstrates a linear dependence, suggesting that the defect or/and the free volume structure is the same for all the samples.
- (5) Because Ps forms favorably, PALS can be applied to demonstrate the free volume properties, which are connected to the mechanism of gas penetration in polymers like SPES that have $-\text{SO}_2-$ in their chemical structures.

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