



Short communication

Effect of humidity and temperature on polymer electrolyte membrane (Nafion 117) studied by positron annihilation spectroscopy

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ABSTRACT

Polymer electrolyte fuel cells (PEMFC) have emerged as portable power source for future transportation and home based systems. Over the past years perfluorosulfonated cation exchange membranes have been used as solid polymer electrolyte in fuel cells, however, humidity control and water management have remained major issues in the area of stack development. Local drying that results in the changes in the local conductivity behavior and physical failure of the membrane is one of the key issues to be addressed in detail. It is therefore necessary to estimate these changes precisely to evaluate the membrane behavior during the fuel cell operation. Positron annihilation spectroscopy offers a very sensitive probe to the determination of polymer free-volume as well as electronic state of the polymer. In the present study we studied Nafion 117 with varying temperature and humidity using positron annihilation spectroscopy. The *ortho*-positronium lifetime (*o*-Ps, i.e., τ_3) which gives the size of the free-volume holes inside the polymer was determined. It was found that the *o*-Ps lifetime increases for relative humidity between 40% and 60% and thereafter it decreases in the temperature range of 62–95 °C. When the inversion point at which the *o*-Ps lifetime is the maximum was plotted with actual vapor pressure, it was observed that it has a logarithmic behavior with the ordinate intercept of 1 ns. This indicates that at higher temperature the membrane has larger free-volume holes; and also at higher temperature a larger vapor pressure is essential to saturate the membrane. Above this point the clusters expand and the free-volume hole size decreases. This also indicates the optimum vapor in the cell to be maintained during the fuel cell operation. The studies also indicated that there is a correlation between *o*-Ps lifetime and the hydrogen crossover current density under the similar temperature and humidity condition.

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1. Introduction

Polymer electrolyte fuel cells (PEMFC) have emerged as portable power source for the variety of applications mainly for transportation and domestic power pack. Perfluorosulfonated membranes, especially Nafion, have been used as a solid polymer electrolyte (SPE) in PEMFC. The proton (H_3O^+) transport through this membrane gets severely influenced by the water content, reflected in the increase of resistivity with the drying of the membrane, therefore water content of the membrane is very important for proton transport [1,2]. Thus humidity control and water management has remained a major issue in the fuel cell stack development. Vast amount of research has been carried out on methods to improve

the humidification [3–5]. Precise control of humidity with temperature over the flow field channels is the key issue and has been dealt from engineering point of view.

The effect of temperature and humidity on the structure of the membrane is also very important aspect, local swelling and deswelling would result in mechanical failure of the membrane thus complicating the issue of humidity control. Therefore, it is necessary to study the detail effect of temperature and humidity on the microscopic structure of the membrane, especially the cluster and free-volume hole sizes. The effect of humidity on cluster sizes has been reported [6 and references therein], however, the effect on the free-volume hole sizes in the amorphous region of the polymer is needed to be studied in detail under the actual/simulated fuel cell conditions.

Positron annihilation spectroscopy has been established as a powerful probe for the determination of free-volume hole sizes in the polymer, and has been supported by number of studies conducted using a variety of physicochemical techniques such as nuclear magnetic resonance (NMR), Mossbauer, infrared, X-ray

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diffraction and K-edge absorption fine structure, neutron scattering, relaxation studies, etc. [7–12] and in the past it has been used to study polymer electrolyte membranes [13].

Positron is an anti electron, in nature it is produced by decay of some radionuclide, e.g., ^{22}Na which decays via β^+ to ^{22}Ne . The ^{22}Ne formed is in the excited nuclear state and decays by emitting 1275 keV γ -ray within 3 picosecond (ps) of the positron emission. Since time scale of 3 ps is very short as compared to typical lifetime of positron (>100 ps) in condensed matter, this signal is taken as a birth of positron. On entering into a condensed matter such as Nafion, it diffuses through the lattice and thermalises in a few picoseconds, much shorter than its mean lifetime in the medium. After thermalization, the positron either annihilates via free annihilation or forms a bound state with an electron, i.e., a neutral entity called positronium (Ps). In case of two gamma annihilation the positron annihilate to give rise to two 511 keV γ -rays, detection of one of the γ indicated the death of the positron. The time duration, i.e., from the birth of the positron till its annihilation (death of positron) is called lifetime of positron. The annihilation rate (inverse of lifetime) of positron/Ps reflects the electron density of its environment, e.g., the higher the electron density such as in the case of smaller free-volume holes, the faster is its annihilation rate and the shorter is lifetime. Therefore, positron/Ps lifetime measurement provides information about the electron density at the annihilation site. The Ps atom has two spin states; one is *ortho*-Ps (*o*-Ps) in which the spins of the positron and electron are parallel, and the other is *para*-Ps (*p*-Ps), in which spins are anti parallel. *p*-Ps decays into two photons (511 keV) with intrinsic lifetime of 0.125 ns. *o*-Ps has an intrinsic lifetime of 142 ns in the vacuum free space, however, in the condensed matter *o*-Ps annihilates predominantly with an electron of the medium having opposite spin, and this process of annihilation is called “pick-off” process, and the *o*-Ps also annihilates into two photons and its mean lifetime is reduced to a few ns. The most important property of *o*-Ps is its preferential trapping into free-volume holes, which have lower electron density. In the absence of any chemical interaction such as oxidation or paramagnetic quenching, the annihilation rate of *o*-Ps is proportional to the extent of overlap between positronium wave function and the pick-off electron wave function in the bulk. Smaller free-volume holes facilitate larger overlap and faster annihilation rate and smaller lifetime and *vice versa*. The relationship between *o*-Ps lifetime (τ_3) and average radius R of free-volume holes in spherical approximation is given by the Tao–Eldrup model [14,15] as

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

where, $\Delta R = 0.166$ nm is the thickness of the homogenous electron layer in which the positron in *o*-Ps annihilates in the pick-off annihilation process [16]. The free-volume size $V_{\text{FV, Ps}}$ in nm^3 is calculable as

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

In Nafion the effect of different amount of water in the membrane changes the free-volume hole size in the membrane has been reported earlier [13]. In the present work, we investigated the effect on the lifetime of *o*-Ps with the changes in humidity and temperature in the temperature range from room temperature up to 95 °C and humidity from 8% to 100%.

2. Experimental

Nafion 117 was purchased from Aldrich was used for this study. Samples pieces (2.5 cm dia coupons) were pretreated by successive boiling in 3% H_2O_2 solution, Milli-Q water, 1 M sulfuric acid solution and Milli-Q for 1 h each followed by air drying at room temperature.

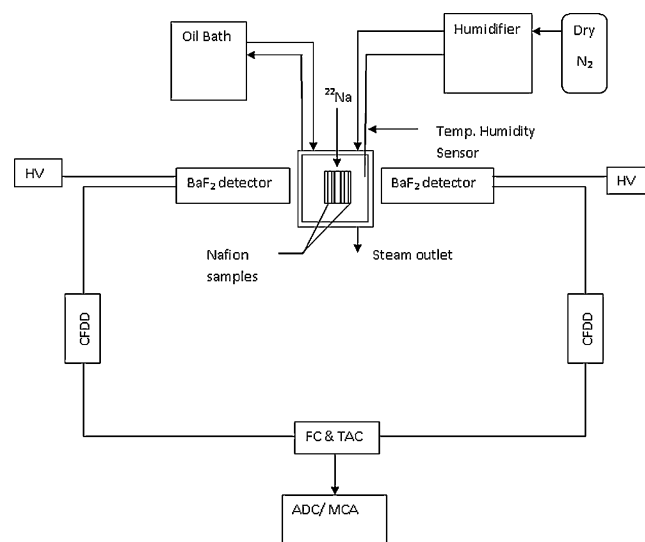


Fig. 1. Schematic representation of the positron annihilation spectrometer and the humidification arrangement. HV, high voltage supply to detector; CFDD, constant fraction differential discriminator; FC, fast coincidence; TAC, time to amplitude converter; ADC, analogue to digital converter; MCA, multichannel analyzer.

The ^{22}Na source (1 MBq in Kapton) was sandwiched by six pieces of Nafion samples in order to ensure that all the positrons emitted enter into the membrane samples (Fig. 1). The sample was loaded into a specially designed humidity and temperature control cell. The cell chamber was heated using oil bath whereas nitrogen gas bubbled through water at constant temperature and this humidified gas was supplied to the heated sample chamber. Humidity was maintained by controlling the humidifier temperature and the humidified gas was heated to the same temperature as that of the chamber before it was administered into the sample chamber. The membrane samples were equilibrated overnight to equilibrate at constant temperature and humidity. Lifetime spectra was measured using positron annihilation spectrometer that had resolution of 276 ps, about 3.5 million counts were accumulated under the spectra. The spectra were deconvoluted using POSITRONFIT program to get the *o*-Ps lifetime [17].

3. Results and discussion

The change of *o*-Ps lifetime (τ_3) along with the free-volume size with vapor pressure is plotted in Fig. 2A and B. The free-volume size is seen to increase with the vapor pressure and temperature. The free-volume size increases with vapor pressure at constant temperature and goes through a maxima thereafter it decrease slightly as shown by arrow in Fig. 2A. This maximum lifetime at a given vapor pressure is plotted in Fig. 2B on logarithmic scale.

The increase of the *o*-Ps lifetime at constant vapor pressure indicates the increase in the free-volume hole size with temperature is due to the polymer expansion and/or increase in the polymer chain flexibility [18]. The difference between the *o*-Ps lifetime between different temperatures at constant vapor pressure is large at low vapor pressures (Fig. 2A). At low vapor pressures and at high temperature the free-volume size is higher due to the thermal expansion of Nafion, however, at lower vapor pressure and lower temperatures the polymer chains are not flexible enough thus resulting in smaller free-volume holes. As the vapor pressure increases the water going into cluster region acts as a plasticizer thereby allowing the polymer chains to reorient and expand to form clusters thus increasing the free-volume hole size and reducing the difference in the free-volume hole size between lower and higher temperature. The whole process can be visualized based on

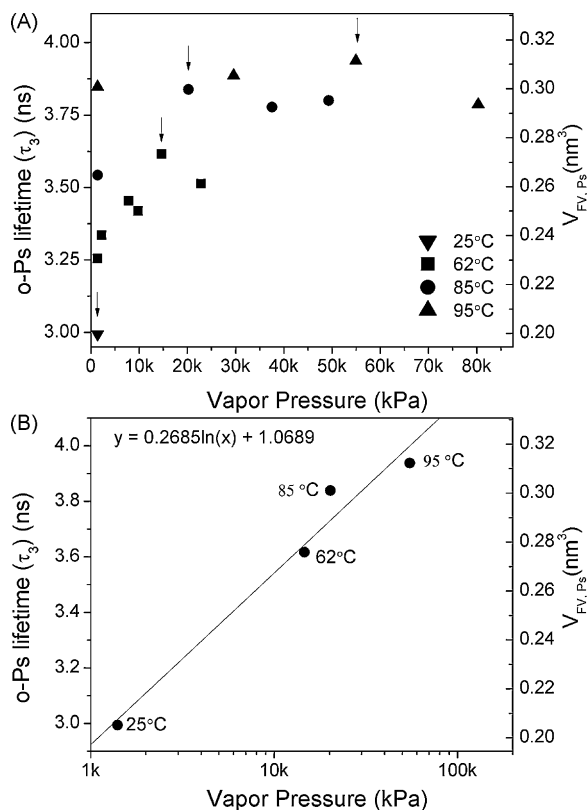


Fig. 2. (A) Change of *o*-Ps lifetime/volume of free-volume hole with vapor pressure at different temperatures. (B) Linear relation between the highest *o*-Ps lifetime at a given temperature in (A) indicated by arrows with vapor pressure. The statistical error on lifetime is within the symbol.

the cluster model [19,20]. According to this model, the absorption of water would lead to larger cluster formation as observed from SAXS & SANS studies [21]. The SAXS and SANS looks at the cluster region whereas, Ps would probe the amorphous region or free-volume hole in the amorphous region besides clusters. This is corroborated by the increase of number of sulfonic acid groups/cluster with increase in water content [19]. On further increase in the vapor pressure the cluster undergoes further expansion and channel formation and thus the size chains have to accommodate the expanded cluster that results in the decrease in the free-volume hole size [13]. The logarithmic relation with the vapor pressure as seen in Fig. 2B, and the maximum lifetime at a given vapor pressure (Fig. 2A) is indicative of the membrane microstructure having the largest free-volume hole sizes. A minimum of this vapor pressure at a given temperature (indicated by arrows in Fig. 2A) maybe required for the operation of the fuel cell.

It will be noteworthy to mention that the larger free-volume holes in the Nafion may indicate larger gas crossover in the fuel cell, which is one of the major issue regarding the peroxide formation leading to membrane degradation as well as lowering the efficiency of the stack. In order to test the correlation between the *o*-Ps lifetime and fuel crossover in the fuel cell, we compared our results from this study with that of the reported by Inaba et al. [22] (Fig. 3A and B) In order to compare the data we have plotted *o*-Ps lifetime/free-volume shown in Fig. 2A up to maximum value is plotted with the corresponding vapor pressure in Fig. 3A and H_2 crossover data by Inaba et al. in the same data range in Fig. 3B. The *o*-Ps lifetime as well H_2 crossover current density shows similar trend over the temperature and humidity range, even though Ps is localized in the free-volume holes. This indicates that free-volume plays an important role in the diffusion of fuel in Nafion

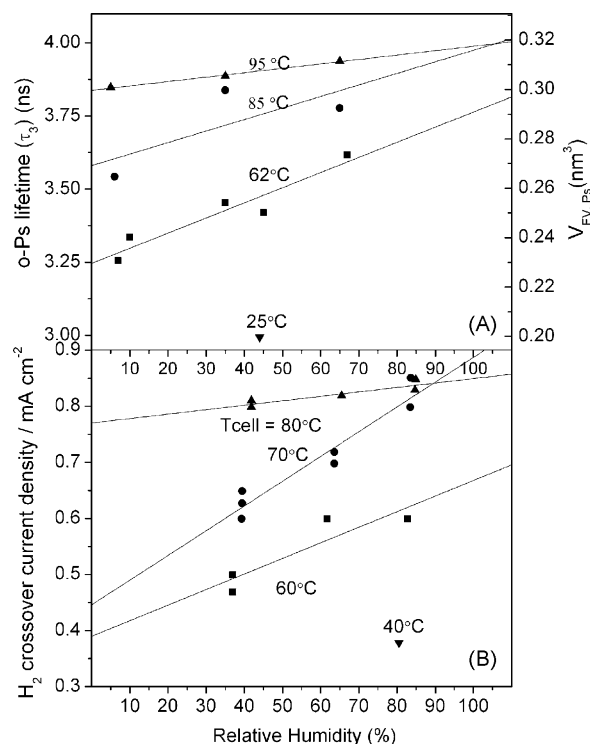


Fig. 3. (A) Change of *o*-Ps lifetime with relative humidity, (B) H_2 crossover current density with relative humidity. (B: Reprinted from Publication, [22] with permission from Elsevier).

membranes. However, there is a little difference between the free-volume changes and gas diffusion behavior of the membrane. This indicates that there could be different channel available for gas diffusion, e.g., cluster region. Therefore, it is necessary to take into account both the effect of cluster and amorphous region in gas diffusion behavior of the membrane.

4. Conclusion

In conclusion we can say that, the Nafion free-volume hole size increases with increase in temperature at constant vapor pressure. At constant temperature the increase in humidity/vapor pressure leads to larger free-volume holes possibly due to the plasticizing effect of water in the cluster region and thereafter the free-volume hole decrease due to expansion of clusters/channels. This indicates that there is a minimum vapor pressure to be maintained at a given temperature in order to operate the fuel cell. It is also necessary to take into account the gas diffusion at the given humidity and temperature. The similar trend of fuel crossover as well as *o*-Ps lifetime also indicates the role played by free-volume in the gas diffusion through Nafion.

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