

Microstructure Characterization of Nafion[®] HP JP as a Proton Exchange Membrane for Fuel Cell: Positron Annihilation Study

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Free volume size V_f and proton conductivity σ of a novel polymer electrolyte membrane were investigated as a function of temperature and relative humidity up to 140 °C and 80%, respectively. The free volume size V_f for Nafion[®] HP JP reflect the α -transition temperature at about 98 °C. In addition the free volume size V_f for Nafion[®] HP JP is smaller than that for Nafion[®] NRE212 membrane which leads to lower methanol permeability of the former membrane. The proton conductivity σ for Nafion[®] HP JP decreases with increase of temperature up to transition temperature due to free and bound water loss, then it starts to increase due to dynamic segmental motion. It increases for Nafion[®] HP JP with the increase of the relative humidity. A good correlation between V_f and σ was successfully established for both membranes which indicates that σ is governed by the free volume. In conclusion, Nafion[®] HP JP is a suitable membrane for a proton exchange membrane fuel cell application.

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1. Introduction

Fuel cells have been proposed to have potential to provide reliable future energy sources as they offer many advantages in energy production. In addition, they can be operated using many fuels either gases, such as hydrogen and natural gas or liquid fuels, such as methanol [1]. The electrolyte is the core of the fuel cell, which allows ions or protons to pass from anode to cathode and prevents the passage of electrons which in turn go through an external load. Proton exchange membrane fuel cells (PEMFCs) are under intensive research for being clean energy sources with high power density, which is essential for widespread applications in electric vehicles and residential power generation [2, 3]. PEMFC differs from most other fuel cells as it uses a solid polymer membrane as electrolyte, as opposed to a liquid electrolyte. This feature, along with the low operating temperature, makes it attractive for automotive applications [4]. However, many problems need to be solved before large scale commercialization such as high cost and thermal stability of the proton exchange membrane (PEM). Direct methanol fuel cell (DMFC) is also a PEMFC operating on methanol as fuel. It has a high energy density with respect to its volume, which allows for comparable efficiency with respect to traditional combustion engines. Proton conductivity, methanol permeability and membrane stability strongly affects the whole cell efficiency. The per-

fluorinated polymers, such as Nafion[®] membranes are the most commonly used membranes in DMFCs due to their high proton conductivity and stability [5]. On the other hand, the high methanol permeability of such membranes represents the major drawback. The methanol diffusion across PEM from the anode to the cathode in the DMFC results in loss of fuel, reduced cathode voltage and excess thermal load in the cell [6]. Therefore, it is necessary to find new materials with appropriate values of such performance-affecting parameters to serve as efficient PEMs for fuel cell applications.

The concept of free volume is critical in explaining and understanding the physical behavior of polymers. The free volume holes affect the mechanical, thermal and relaxation properties of polymers [7]. Positron annihilation lifetime (PAL) has been developed to be, probably, the most successful technique for the direct examination of free volume holes in polymers. Various techniques such as scanning tunneling microscopy (STM), neutron scattering and transmission electron microscopy (TEM) etc. are more sensitive to free volume holes with a size of 10 Å or larger [8]. Due to the small size of the positronium (Ps) probe (i.e. PAL technique) compared to other probes, PAL is particularly sensitive to small free volume holes with the order of angstrom magnitude ~ 1 Å. In addition, unlike other methods, PAL is able to determine the free volume holes in a polymer without being significantly interfered with by the bulk. It is well known that during fuel cell operation, the cell is heated up as a result of exothermic reactions of both electrodes. Temperature variation also affects relative humidity of the cell environment. These changes in operating conditions

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of the cell have strongly effects on the membrane performance. In PEMFC technology, the structures of free volume holes (size and its content) in the PEMs are vital because they are correlated to its transport properties such as ionic conductivity and fuel crossover [9]. Therefore, the aim of this work is to study the free volume hole size of the investigated membranes as a function of temperature and relative humidity which strongly affect the transport properties of PEM.

2. Experimental

Nafion[®] HP JP with 25 μm thickness produced by DuPont Japan while Nafion[®] NRE212 with thickness 50.8 μm , bought from DuPont, USA, is used as received. Table I summarizes some of the physical and chemical properties of both membranes under investigation [10]. Several drops of a carrier free solution of $^{22}\text{NaCl}$ were deposited and then evaporated on thin Kapton foil. Another piece of the foil was sealed over the first one to form a positron source. Nanostructure characterization for Nafion[®] HP JP and Nafion[®] NRE212 membranes was carried out using fast-fast coincidence PAL system with time resolution of 250 ps (full width at half maximum, FWHM). For each spectrum, more than 1.2×10^6 counts were collected and then analyzed by PALSfit3 [11] program. The source absorption by the Kapton foil was about 20% and was separated in the analysis of the lifetime spectra. It was found that three lifetime components for all spectra gave the best fitting with reduced chi-square ranging from 0.9 to 1.3. The third long-lived component τ_3 is characteristic to the *ortho*-positronium (*o*-Ps) pick-off annihilation. The PAL measurements were measured for both membranes under vacuum as a function of temperature up to 140 $^\circ\text{C}$ with a step of 10 $^\circ\text{C}$.

TABLE I

Characteristic properties as water uptake, IEC, degree of crystallinity X_c , methanol permeability P_m , tensile strength and proton conductivity of Nafion[®] HP JP and Nafion[®] NRE212 membranes measured under the same conditions. All the measurements except proton conductivity were done for both samples at 25 $^\circ\text{C}$ and 30% relative humidity.

Property	HP JP	NRE212
water uptake [%]	57.9 \pm 2.3	45.0 \pm 1.8
ion exchange capacity IEC [meq/g]	1.25 \pm 0.04	0.94 \pm 0.03
degree of crystallinity X_c [%]	47.3 \pm 2.7	27.3 \pm 2.6
P_m [cm^2/s] at methanol concentration of 2 M	5.6×10^{-7}	2.69×10^{-6}
tensile strength [MPa]	13.2	9.5
proton conductivity [S/cm] at 100% relative humidity	1.6×10^{-4}	3.0×10^{-3}

The proton conductivity σ measurements of Nafion[®] HP JP and Nafion[®] NRE212 membranes were done at

different temperatures using AC impedance spectroscopy over a frequency range from 50 Hz to 5 MHz (HIOKI LCR Hi-Tester, Model 3532, Japan). The proton conductivity σ is investigated in out of plane using the measured resistance R as [12]:

$$\sigma (\text{S/cm}) = \frac{L}{RA}, \quad (1)$$

where L is the thickness of the membranes and A is the effective area of the blocking electrode.

The effect of relative humidity on the nanostructure of both membranes was investigated using PAL spectrometer where dry N_2 gas from the cylinder is branched into two through two small rate flowmeters (10–100 ml/min). The output of the dry flowmeter circulates through a copper coil immersed in water at 30 $^\circ\text{C}$ to gain thermal equilibrium. On the other side, the output gas of the second flow meter is directed through the bottom of a copper tank filled with water in order that gas molecules can be humidified when exiting the top of the tank. Finally, both dry and humidified branches meet via a T-connector to go through the sample. Changing the ratio between dry and wet flow meters' rates changes the value of relative humidity (RH). The effect of RH on the nanostructure of both membranes was measured from 0 to 80% RH. For each point of RH, the PAL measurements were repeatedly performed until *o*-Ps parameters became almost constant.

3. Results and discussion

Free volume size was calculated from the *o*-Ps lifetime τ_3 and the Tao–Eldrup model [13, 14] as

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

where R is the radius of the spherical free volume, $R_0 = R + \Delta R$ and $\Delta R = 0.166$ nm is the thickness of the homogeneous electron layer within which positron of the *o*-Ps is supposed to annihilate [15]. The free volume size V_f is given as

$$V_f = 4\pi R^3/3. \quad (3)$$

Figure 1 shows the variation of *o*-Ps lifetime τ_3 and the free volume size V_f as a function of temperature for Nafion[®] HP JP and Nafion[®] NRE212 membranes. As shown from the figure, the free volume hole size expands with increase of temperature for both membranes. For Nafion[®] NRE212, an abrupt change in free volume size was noticed at ~ 70 $^\circ\text{C}$ which could be associated with α -relaxation of the polymer segments [16]. This temperature is known as glass transition temperature T_g at which the polymer exhibits phase transition from the glassy state to the rubbery state.

Thermal expansion coefficient α of the free volume which represents the fractional increase in the free volume hole size with increase of temperature [17] as:

$$\alpha = \frac{\Delta V}{V_0 \Delta T}, \quad (4)$$

where $\Delta V/\Delta T$ represents the slope of the straight line and V_0 is the initial free volume size, obtained by the

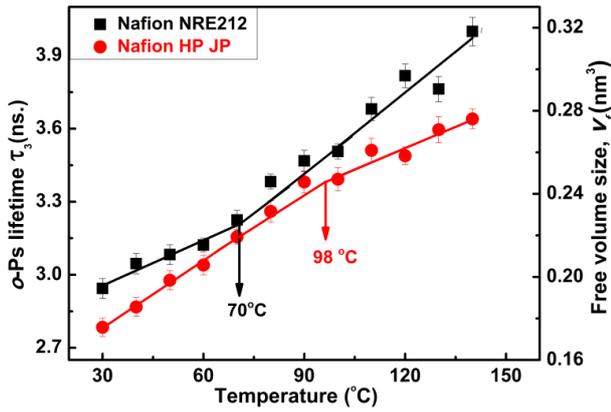


Fig. 1. The variation of *o*-Ps lifetime τ_3 as a function of temperature for Nafion[®] HP JP and Nafion[®] NRE212. The solid lines are the fitting of the experimental data to get the transition temperatures. The right axis ordinate represents the free volume size V_f .

intercept part of the Y-axis. The values of thermal expansion coefficients for Nafion[®] HP JP below and above T_g were found to be 7.01×10^{-3} and $3.87 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$, respectively, while for Nafion[®] NRE212 4.14×10^{-3} and $9.7 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$ for below and above, respectively. It was found that thermal expansion coefficient of free volume α for Nafion[®] NRE212 is larger than its value below T_g due to the long-range mobility of the main and side chain facilitated by a profound weakening of the electrostatic interactions within the ionic aggregates [18]. Similarly, for Nafion[®] HP JP a sudden change in free volume expansion with temperature was noticed at $\sim 98^\circ\text{C}$. A decrease in the thermal expansion coefficient above 98°C was also noticed which may be a result of stress relief of the membrane. The stress relief normally is caused by the rearrangement of the chains in a polymer with stress accumulated during its preparation [19]. In Nafion[®] HP JP, it is observed that the chain motions are more restricted (due to the small free volume holes) and more energy is required to activate the long range motions of the ionomer molecular chains, which is responsible for its higher α -relaxation temperature [16].

The variation of proton conductivity σ with temperature in the range from 30 to 140°C under vacuum is shown in Fig. 2 for Nafion[®] HP JP and Nafion[®] NRE212. The behavior of σ with temperature can be divided into two regions meeting at transition temperatures for both membranes. This inflection point can be also called T_g which happens to amorphous polymers. This can be connected to the α -relaxation of Nafion[®] which is associated with the onset of long-range mobility of both the main- and side-chains [16]. In the first region, below T_g , σ decreases with increase of temperature up to T_g due to the loss of surface and bound water gradually, leading to a decrease in the ionomer cluster order responsible for the proton transport. In the second zone, above T_g , σ increases with temperature. It was reported

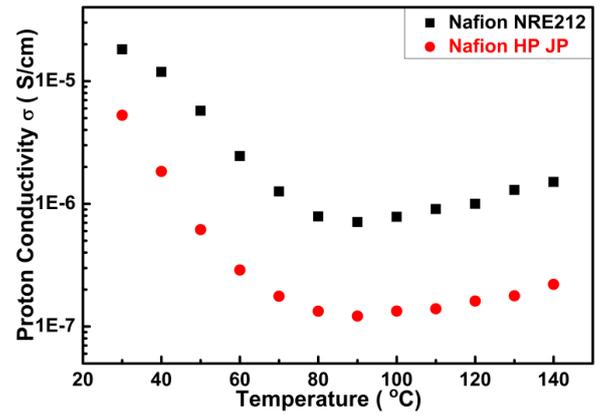


Fig. 2. The temperature dependence of proton conductivity σ for Nafion[®] HP JP and Nafion[®] NRE212.

that [20] the proton conductivity of a polymer electrolyte is strongly affected by segmental motion, which increases the free volume of the polymer and either allows the ions to hop from one site to another or facilitates the translational ionic motion. Increasing the amorphous region, causes the polymer chain to gain faster internal modes in which bond rotations produce segmental motion to inter- and intra-chain ion hopping that increases σ .

The effect of the free volume on the proton conductivity can be predicted. It can be expected that σ would increase with the increase of the thermal expansion coefficient of free volume. This conclusion applies for Nafion[®] HP JP as well as for Nafion[®] NRE212 and agrees quite well with the model suggested by Miyamoto and Shibayama [21]. This model is based on the assumption that the movement of ions is regulated by the amount and distribution of free volume, such that σ can be expressed as

$$\sigma = \sigma_0 \exp\left(-\frac{\gamma V_i^*}{V} - \frac{\Delta E a}{k_B T}\right), \quad (5)$$

where σ_0 is a constant, γ is a numerical factor used to correct the overlap of free volume and polymer segments, V_i^* is the critical free volume; the minimum free volume required for transport of an ion, E_a is the apparent activation energy at temperature below T_g and k_B is the Boltzmann constant. The correlation between proton conductivity and the free volume hole size for Nafion[®] HP JP and Nafion[®] NRE212 membranes is shown in Fig. 3. It was found that there is a strong correlation between proton conductivity and free volume size for both Nafion[®] HP JP and Nafion[®] NRE212 membranes below T_g . The deduced value of the critical hole size γV_i^* for Nafion[®] HP JP was found to be 0.3 nm^3 which is high compared to that in Nafion[®] NRE212 (0.114 nm^3), which explains the higher conductivity for Nafion[®] NRE212.

Figure 4 shows the variation of τ_3 with the change of RH for Nafion[®] HP JP and Nafion[®] NRE212 membranes at 30°C . It should be noticed that for both membranes, the values of τ_3 and V_f at 0% RH are almost

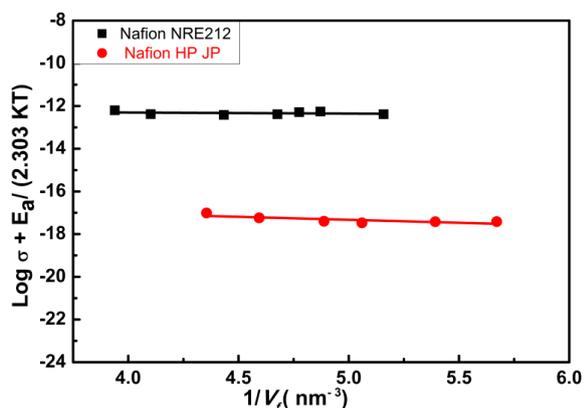


Fig. 3. The correlation between $\log(\sigma) + E_a/(2.303k_B T)$ and reciprocal o -Ps hole volume size ($1/V_f$) for Nafion[®] HP JP and Nafion[®] NRE212. The solid lines are the fitting of the experimental data.

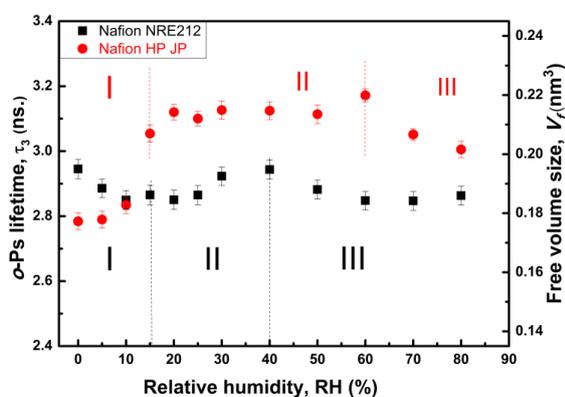


Fig. 4. The variation of o -Ps lifetime τ_3 as a function of relative humidity at 30°C. The right axis ordinate is the free volume size V_f .

the same as the obtained values at 30°C under vacuum (see Fig. 1), which supports the accuracy of the measurements. For both samples, the behavior of τ_3 and V_f with RH can be divided into three regions. For Nafion[®] NRE212, in the first region, at low RH, τ_3 and V_f are lower than their values for the dried membrane (at 0% RH) and continues to decrease within this region which is attributed to the filling of water molecules to the free volume holes [22]. In the second region, τ_3 and V_f start to increase with increase of RH which may be attributed to polymer plasticization due to higher water content inside the polymer [23]. In the third region, τ_3 returns to decrease that may be due to the absorption of larger amount of water that leads to more o -Ps annihilation events in the membrane aqueous phase while the value of τ_3 in pure water is almost 1.8 ns [22]. On the other hand, for Nafion[®] HP JP membrane, in the first region V_f starts to expand slightly from 0 to 10% RH then sharply increases, which means that plasticization

of this polymer occurs at lower values of RH than that of Nafion[®] NRE212 membrane. This may be regarded to its higher water uptake, IEC and reduced thickness. In the second region, the values of τ_3 and V_f increase but with lower dependence on RH than that of the first region. In the third region, the behavior is similar to that of Nafion[®] NRE212, where the value of τ_3 and V_f gradually decrease with relative humidity, but it should be observed that for Nafion[®] HP JP. The decrease in this region is sharper than that for Nafion[®] NRE212 which is due to the higher water uptake that means larger ratio of Ps annihilation occurring within the membrane aqueous phase.

4. Conclusions

PAL results showed that the free volume size of Nafion[®] HP JP is smaller than that of Nafion[®] NRE212 over the entire temperature range studied. Nafion[®] HP JP has lower methanol permeability than Nafion[®] NRE212, indicating that PEM formed from Nafion[®] HP JP will have a lower fuel cross-over than Nafion[®] NRE212 leading to better performance of Nafion[®] HP JP in the fuel cell. The higher value of T_g of Nafion[®] HP JP is in a good agreement with proton conductivity σ behavior. A strong correlation between σ and V_f has been achieved which indicates that proton conduction is governed by the free volume. The new Nafion[®] HP JP shows great potential for fuel cell applications.

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