Positron annihilation study of acryl amide/poly (metha acrylic acid) membrane

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Abstract. Gamma irradiation posses a serious role for casting the membranes. Acryl amide /poly (methacrylic acid) membrane was synthesized under γ-radiation effect. The structure of the membrane was characterized by FTIR, thermo-gravimetric analysis and the scanning electron microscope. The properties of the membranes were also investigated in terms of proton conductivity and positron annihilation lifetime (PAL) parameters. On the basis of the values of the long-lived components in the lifetime spectra, the size of the free volume and their intensity were calculated. The positron lifetime study on these irradiated casted membranes shows that the cross-linking and degradation within the membrane matrix affect the free volume content and hence the microstructure.

1. Introduction
Positron annihilation spectroscopy has been established as a powerful probe for the determination of free volume hole sizes in the polymer [1]. Recent investigations in membrane materials and film systems have been reported mainly in the bulk using conventional positron annihilation lifetime technique [2-4]. The automotive fuel cell represents perhaps the largest volume of all potential fuel cell applications and has also set some of most challenging requirements for component performance, durability and cost. Currently, there is much ongoing research for developing non-perfluorinated polymers with better performance and lower cost as alternative PEM materials. The aim of this work was to obtain low-cost membrane specifically for fuel cell use. The specific aim was to determine whether Acrylamide / Polymeth-acrylic Acid Membrane could be developed that would give a competitive performance to an established Nafion membrane in a fuel cell.

2. Experimental
2.1 Materials and Sample Preparation
Acrylamide of purity 98.5% was supplied by Merck, Germany. Poly (meth acrylic acid) and powdered activated carbon (PAC) was commercially purchased from local company OPTCo, Egypt. 10 % of Acrylamide was solvated in doubly distilled water with the addition of 1% of phosphoric acid, 1% poly methacrylic acid, 0.5% of phathalic anhydride (which is used as a plastisizing agent)...
and powdered activated carbon at different ratios 0.1, 0.2 and 0.3% to the acrylamide. The content of the sealed vial was heated at 80°C for 3 hours. The viscous solution was poured into clean and dry glass Petri dish. The Petri dish content was subjected to γ-rays from a 60Co source with different doses (10 & 20 KGY). Evaporation of the irradiated soft gelatinous mixture at dried ambient temperature for 48 hours.

2.2. Positron annihilation lifetime spectroscopy

The positron annihilation lifetimes (PAL) of the membranes were determined by detecting the prompt γ-ray (1.28 Mev) from the nuclear decay that accompanies the emission of a positron from the 22Na radioisotope and the subsequent annihilation γ-rays (0.511 Mev). A conventional fast-fast coincidence circuit of PAL spectrometer with a time resolution 240 Ps was used to record all PAL spectra. The PAL spectra containing 1.5x10^6 counts were analyzed into three components (τ_1, τ_2, and τ_3) and their intensities (I_1, I_2, and I_3) using PALSfit program [5].

2.3. Characterization

FTIR spectra were obtained with Mattson 1000, Pye-Unicam, England. Fourier transform infrared spectrophotometer. Thermo-gravimetric analysis (TGA) was recorded on a thermal analysis system at a heating rate of 10 °C/min. Proton conductivity measurements were derived from AC impedance spectroscopy measurements over a frequency range of 50 to 10^6 Hz with an oscillating voltage of 50–500mV, using a system 3532 Hioki bridge LCR hitester. Each membrane sample was cut into sections 2.5 cm×2.0 cm prior to being mounted in the cell. The sample was equilibrated at 100% RH at ambient atmospheric pressure and clamped between two electrodes. The proton conductivities of the samples were measured through the membrane and were calculated from the impedance data, using the following relationship: σ=I/RS where σ is the proton conductivity (in S/cm), I is the membrane thickness, S is the area for protons to transport through the membrane (in cm^2) and R is derived from the intersection of the semicircle on a complex impedance plane with the Re (Z) axis.

3. Results and discussion

3.1. FT-IR characterization

Figure 1 shows strong bands at 1040–910 cm⁻¹ that belong to asymmetric stretching vibrations of the P–OH group and at 1150 cm⁻¹ that corresponds to P–O stretching. At higher poly phosphoric acid ammonium salt ratio, the P–O–H vibration at 930 cm⁻¹ becomes stronger indicating the existence of excess acidic protons. Additionally, phosphoric acid units give rise to broad bands with medium intensity at 1700–1590 cm⁻¹ and 2850–2750 cm⁻¹ [figure 1 b]. The band broadening around 3100 cm⁻¹ is due to the hydrogen bonding network which is necessary for proton conduction.

3.2. Thermo-gravimetric analysis

The thermogram could be divided into 5 divisions as shown in figure 2. The first division described the membrane stability upon raising the temperature (working temperature of the membrane). The Second division explained the slow weight decrease upon raising the temperature. The third division described the convex zone regarding to temperature axe. The fourth division described the abrupt change of weight by temperature raising up, via which 0.1% PAC membrane, the temperature range was 320–370 while it expanded to a range of 320–380°C for 0.3% PAC-membrane. The weight loss through this division showed similar loss of weight for 0.1 and 0.3% PAC membrane which was 13%. The fifth division showed a weight reduction to 52% from the original weight for 0.1% PAC while it was 50% for 0.3% PAC. This loss of weight has occurred up to 550 °C.
3.3. Scanning electron microscope
SEM shows all the particles appeared to be tightly packed, evenly distributed carbon aggregates in figure 3 (a) which is explained by their diffusion onto deepest layer of matrix. Whitish zones have been seen and the disappearance of black and white may due to cross-linking between poly phosphoric acid ammonium salt and poly meth acrylic acid. By increasing the PAC content [figure 3 (b)], it can be seen larger content of PAC aggregate diffused into the net polymer while exceeding scattered regularly over the membrane surface.

![Figure 3: Scan Electron Microscope](image)
Figure 3: Scan Electron Microscope a) 20 KGY and 0.1 % PAC; b) 20 KGY and 0.2 % PAC.

3.4. Proton conductivity
Table 1. shows that, the casted membrane with different PAC ratio and doses has relatively good proton conductivity values ranging from 1.46 to 3.14 mS/cm compared to Nafion (70 mS/cm).
Table 1: The proton conductivity for casted membrane with different PAC ratio and doses

| Samples | PAC ratio | Dose KGy | Proton conductivity (mS/cm) |
|---------|-----------|----------|-----------------------------|
| 1       | 0.1       | 10       | 2.70                        |
| 2       | 0.2       | 10       | 1.46                        |
| 3       | 0.3       | 10       | 0.31                        |
| 4       | 0.1       | 20       | 1.80                        |
| 5       | 0.2       | 20       | 2.09                        |
| 6       | 0.3       | 20       | 2.90                        |

3.5. Positron lifetime studies

Table 2 shows the positron annihilation parameters for casted membrane with different PAC ratio and doses. The o-Ps lifetime $\tau_3$, and its intensity $I_3$, decreased for the sample irradiated with 10 KGy with increasing PAC concentration. The decrease in $\tau_3$ is related to the change in the free volume as a result of the formation of new bonds or cross linking. The decrease in $I_3$ reflects a decrease in the number of free volume holes fits well with increase in cross linking. While at 20 KGy, the increase in o-Ps lifetime due to chemical degradation and agglomeration of free volume hole size. This means that the casted membrane with different PAC concentration at 10 KGy had a good characteristics compared with the irradiated sample at 20 KGy.

Table 2: The positron annihilation parameters for casted membrane

| Sample | PAC ratio | Dose KGy | Lifetime $\tau_3$(ns)  | Intensity $I_3$ | Free volume(A°³) | Fractional free volume |
|--------|-----------|----------|------------------------|-----------------|-------------------|------------------------|
| 1      | 0.1       | 10       | 1.70±0.022             | 4.90±0.121      | 70.27             | 3.44                   |
| 2      | 0.2       | 10       | 1.68±0.027             | 4.21±0.128      | 68.33             | 2.88                   |
| 3      | 0.3       | 10       | 1.61±0.024             | 5.03±0.156      | 62.20             | 3.13                   |
| 4      | 0.1       | 20       | 1.62±0.015             | 9.20±0.167      | 63.09             | 5.00                   |
| 5      | 0.2       | 20       | 1.62±0.028             | 3.94±0.134      | 63.51             | 2.50                   |
| 6      | 0.3       | 20       | 1.68±0.015             | 2.11±0.122      | 67.86             | 1.44                   |

4. Conclusion

Acryl amide /poly (methacrylic acid) membrane was synthesized under $\gamma$-radiation effect. The casted membranes with different PAC ratio and doses has relatively good proton conductivity values ranging from 1.46 to 3.14 mS/cm compared to Nafion (70 mS/cm). The positron lifetime study on these irradiated casted membranes shows that the cross-linking and degradation within the membrane matrix affect the free volume content and hence the microstructure.

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5. References

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