Heinz Maier-Leibnitz Zentrum

12th International Workshop on Positron and Positronium Chemistry
28 August - 1 September 2017, Lublin, Poland

Free volume of PVA/SSA proton exchange membrane studied by positron annihilation lifetime spectroscopy

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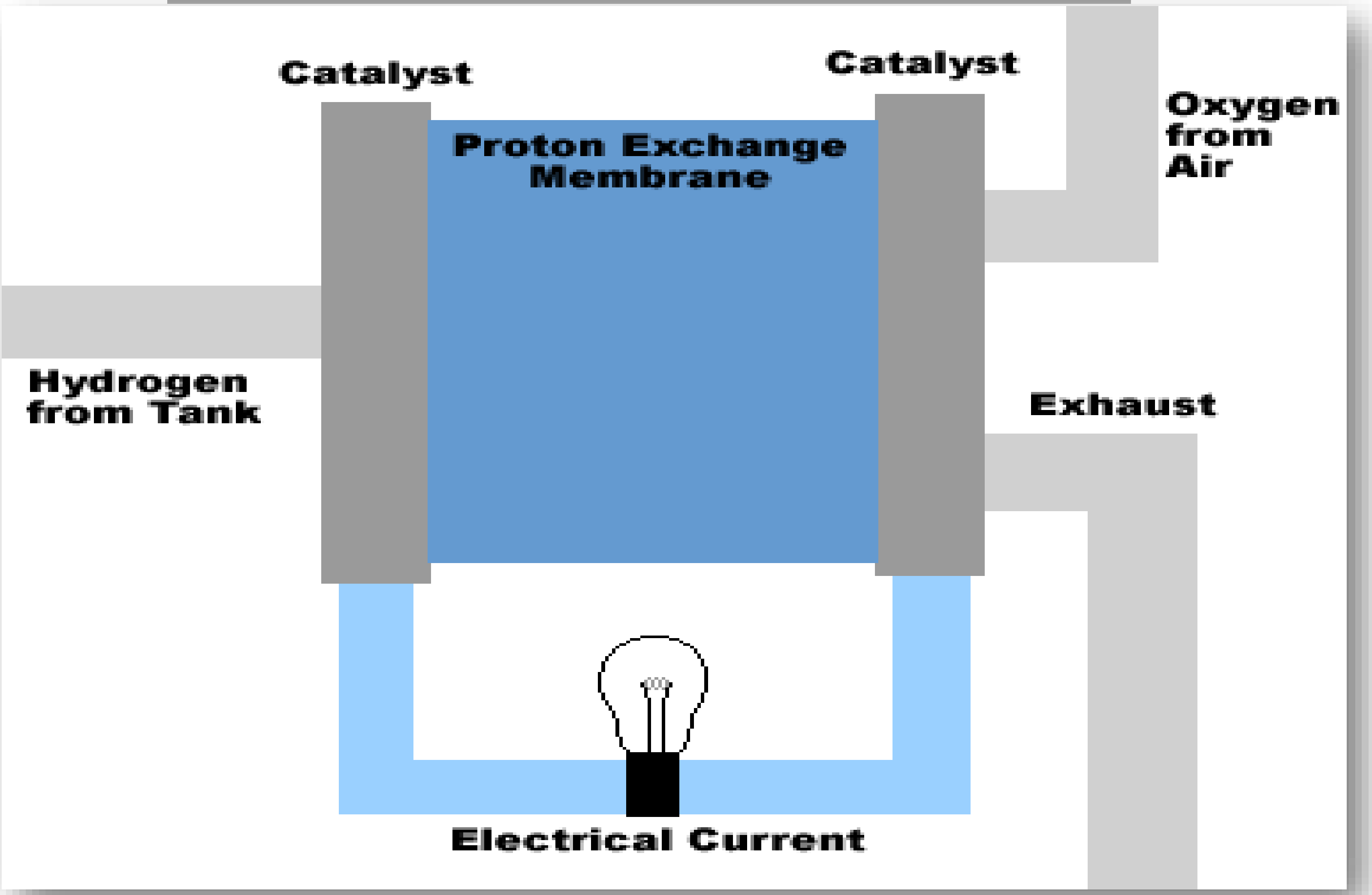
Aim of the Work

- Preparation of low-cost Proton exchange membranes for fuel cell applications.
- Characterization the properties of the prepared membrane (Thermal stability,, Proton conductivity and Ion exchange capacity) .
- studying the relationship between the free volume sizes and the tensile strength of the prepared membranes.
- Studying the free volume hole size using (positron annihilation lifetime technique) PALS at different humidity.

HOW DOES PEMFC WORK ?



https://energy.gov/eere/fuelcells/fuel-cell-animation

Membrane Preparation.

- The crosslinked Polyvinyle alcohol (PVA)/ sulfosuccinic acid (SSA) proton exchange membrane was prepared using casting method PVA (10 wt %) was dissolved in deionized water under stirring at 80 ^{o}C for 6 h.
- Different weights of SSA 5-30 wt% added to the PVA homogenous solution to obtain membranes with different wt% of SSA. The solution kept under stirring for 24 h at room temperature.
- Casting the solution then pored onto Teflon Petri dish then the excess water solvent was evaporated in a vacuum oven
- After the evaporation, PVA/SSA polymer membranes were cross-linked thermally at 100 $^{\circ}$C for 1 h and then were stored in bags for further testing.

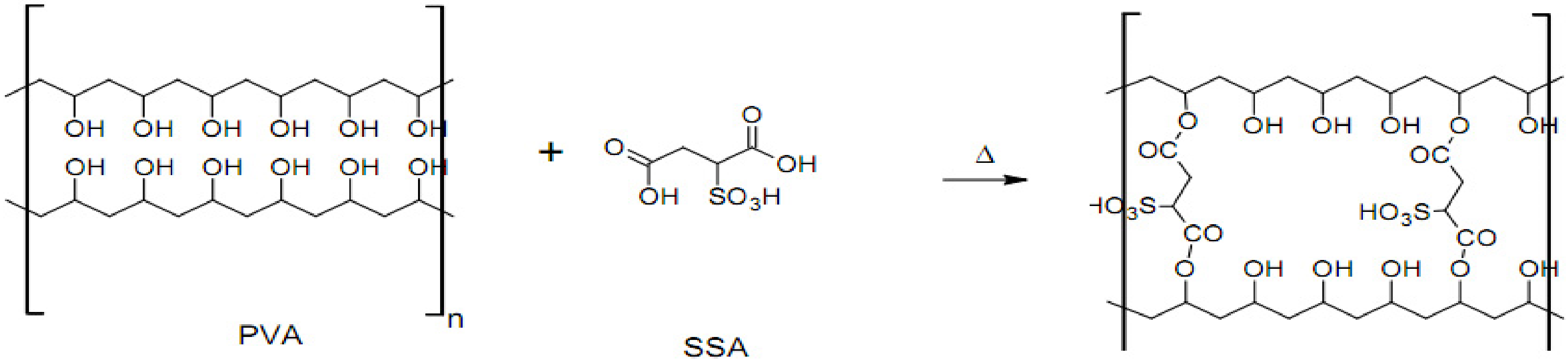


Fig.(1). PVA/SSA reaction mechanisms.

Thermal gravimetric analysis (TGA).

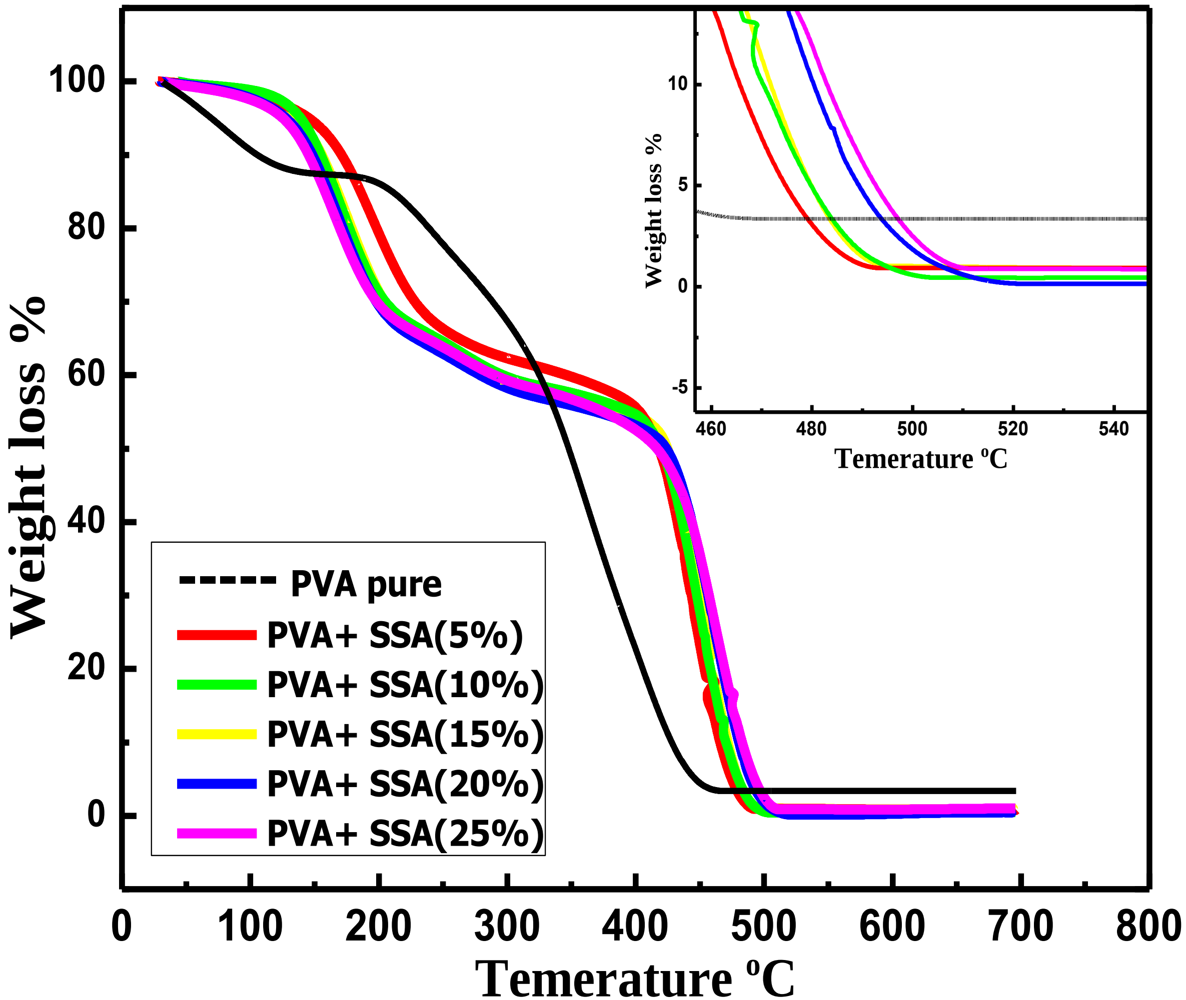


Fig.(2). TGA spectrums for PVA with different concentrations of SSA.

Ion Exchange Capacity (IEC)

$$IEC_{exp} = \frac{0.05 \times V_{NaOH} \times n}{W_{dry}} \quad (meq/g)$$

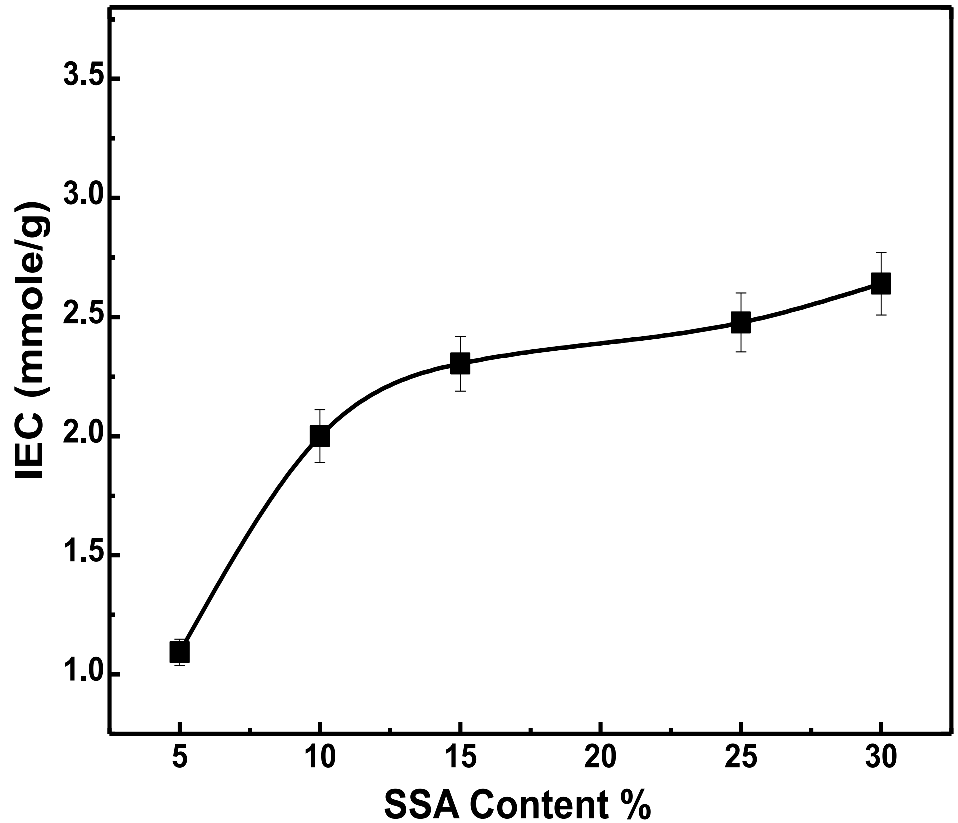


Fig. (3). Ion exchange capacity (IEC) of PVA/SSA membrane as a function of SSA concentration .

The proton conductivity of PVA/SSA membranes.

Impedance spectroscopy

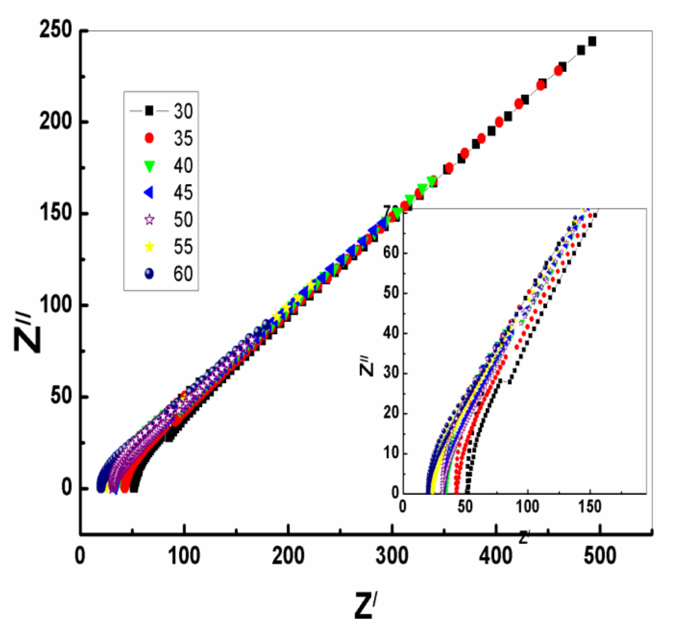


Fig. (4.a). A C impedance spectra of PVA /SSA 5 (W/W)%at different temperature

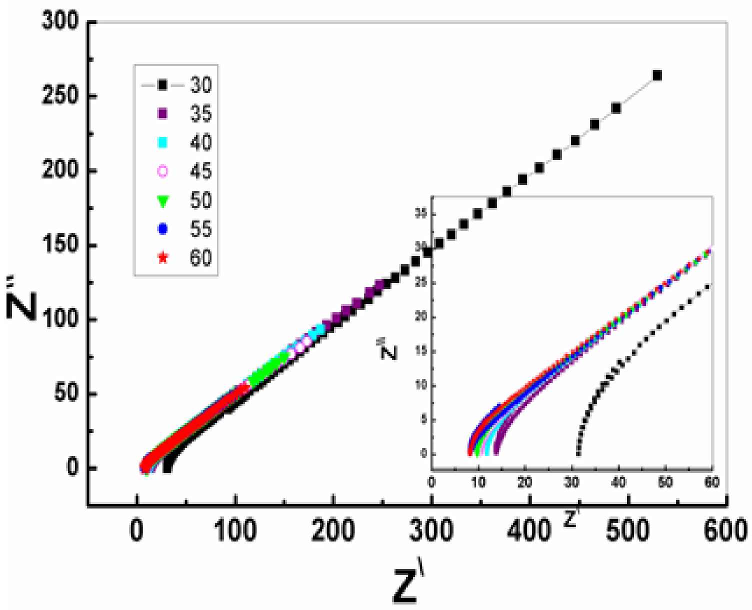


Fig. (4.b). A C impedance spectra of PVA /SSA 30 (W/W)%at different temperature

$$\sigma = \frac{L}{RA}$$

- where L is the thickness (cm) of the membranes.
- A is the area of the blocking electrode (cm^2).

The proton conductivity of PVA/SSA membranes.

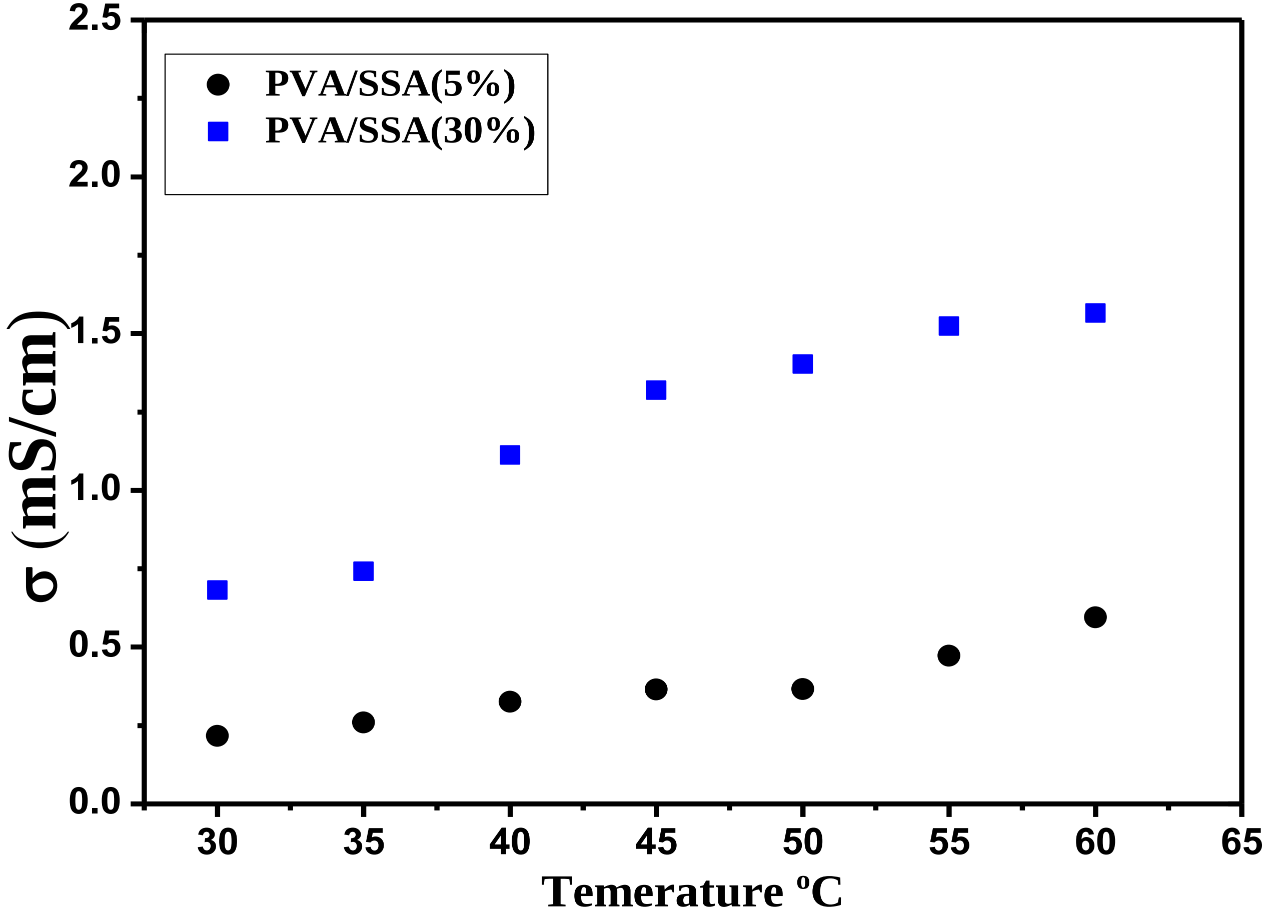


Fig. (5). The conductivity of PVA with different concentrations of SSA at different temperature

Free volume & Tensile strength.

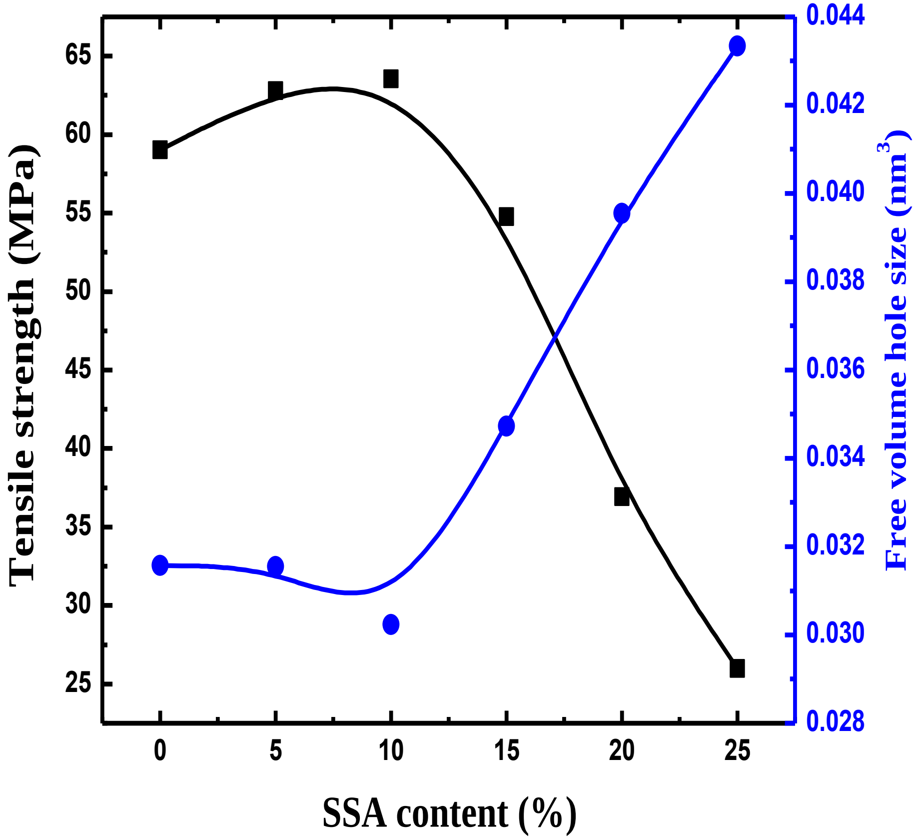


Fig. (7) Tensile strength and free volume hole size of PVA/SSA membrane as a function of SSA concentration at room condition.

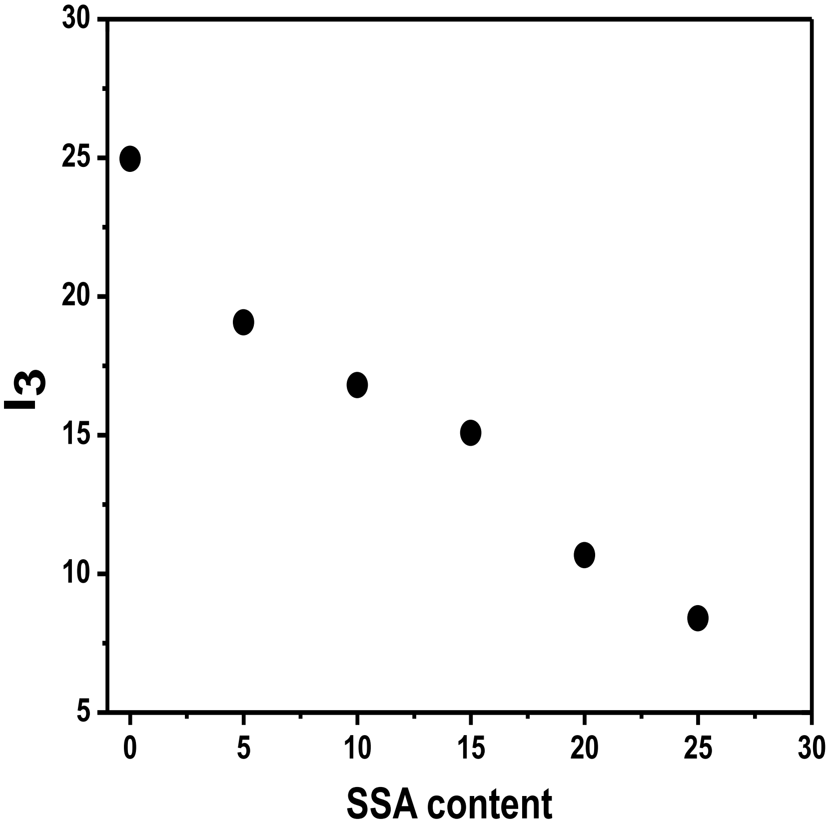


Fig. (8) Intensity I3 of PVA/SSA membrane as a function of SSA concentration at room condition.

See:

Kobayashi, Y., H.F.M. Mohamed, and A. Ohira,. The Journal of Physical Chemistry B, 2009. **113**(17): p. 5698-5701.

Free volume & Humidification time

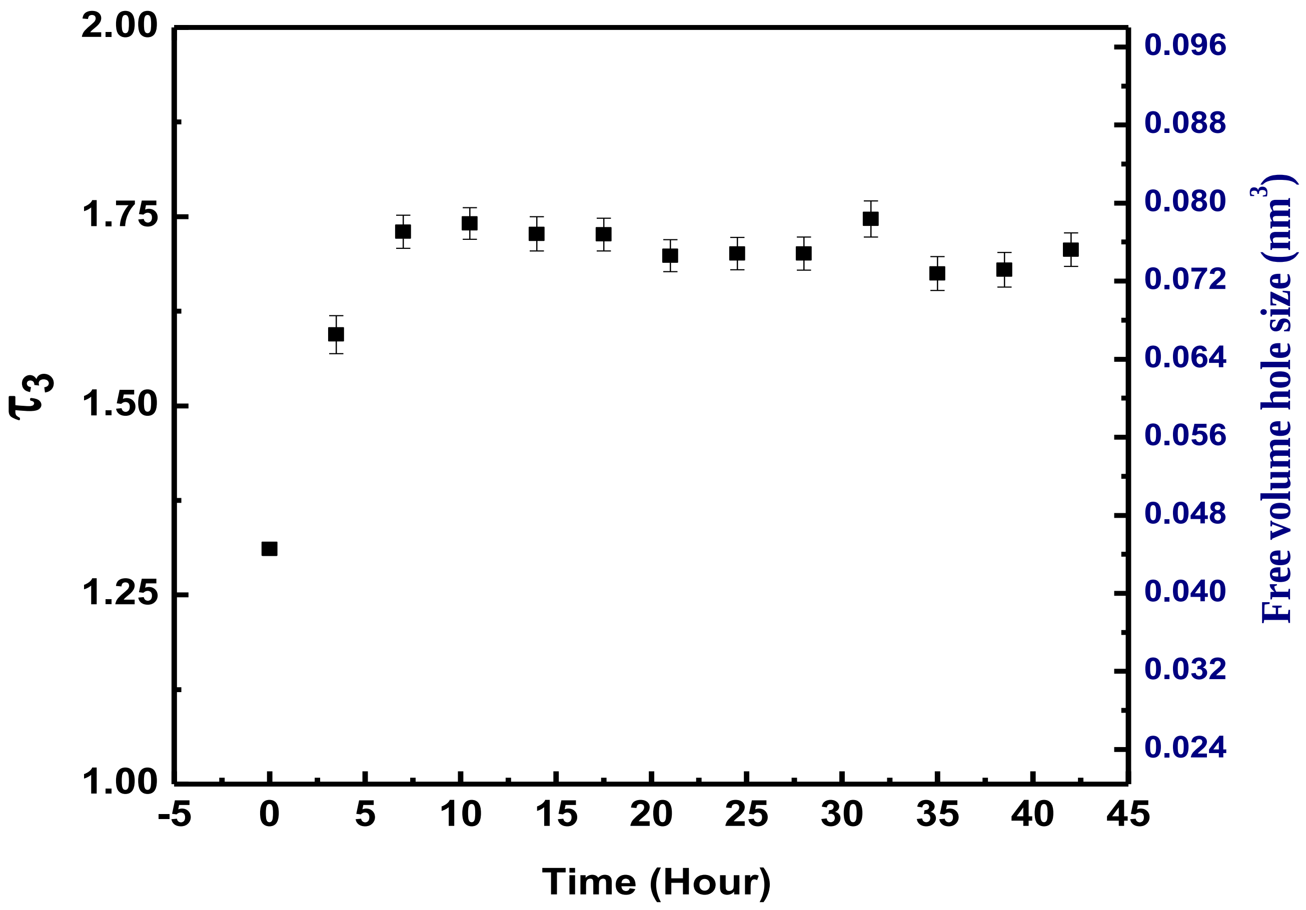


Fig. (6) ortho Positronium lifetime t_3 of PVA/SSA (15%) as function of time at Humidity 80% RH.

Free volume & Humidity

Humidity-Induced Plasticization and Antiplasticization of Polyamide 6: A Positron Lifetime Study of the Local Free Volume

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Received 30 August 2000; accepted 2 August 2001

RH (%)	$\Delta m_w/m_p$ (%)	N_w (nm^{-3})	T_g (°C)	τ_3 (ps)	v (Å^3)	Δv_g (Å^3)
0	0.00	0.00	54	1693	70.0	0
11	1.60	0.58	31	1641	65.0	−9.5
32	2.65	0.95	13	1595	61.7	−16.0
45	3.20	1.15	4	1610	62.9	−19.4
55	4.15	1.49	−2	1650	66.0	−18.5
75	5.90	2.12	−13	1707	71.1	−17.7
90	8.40	3.02	−20	1801	79.2	−12.9
100	10.00	3.60	−25	1942	92.1	−1.90

Conclusions

- ✓ PVA/SSA was successfully prepared as a Polymer electrolyte membranes (PEMs) for fuel cells.
- ✓ SSA improved the thermal stability of the PVA/SSA membranes.
- ✓ Proton conductivity increases with increasing the temperature at the PVA/SSA membranes.
- ✓ There is a correlation between the tensile strength and the free volume hole sizes.
- ✓ (PALS) was used to determine the size of free volume at different humidity for PVA/SSA membranes, its found that the free volume size is slightly decreased at low humidity and duplicated at high humidity (more than 30 % RH).
- ✓ PVA/SSA membranes displayed excellent thermal, high proton conductivity and mechanical properties, so PVA/SSA are considered for use in DMFCs

Thank you