Free Volume, Glass Transition, and Electrochemical Properties of PVA/SSA Proton Exchange Membrane Studied by Positron Annihilation Spectroscopy

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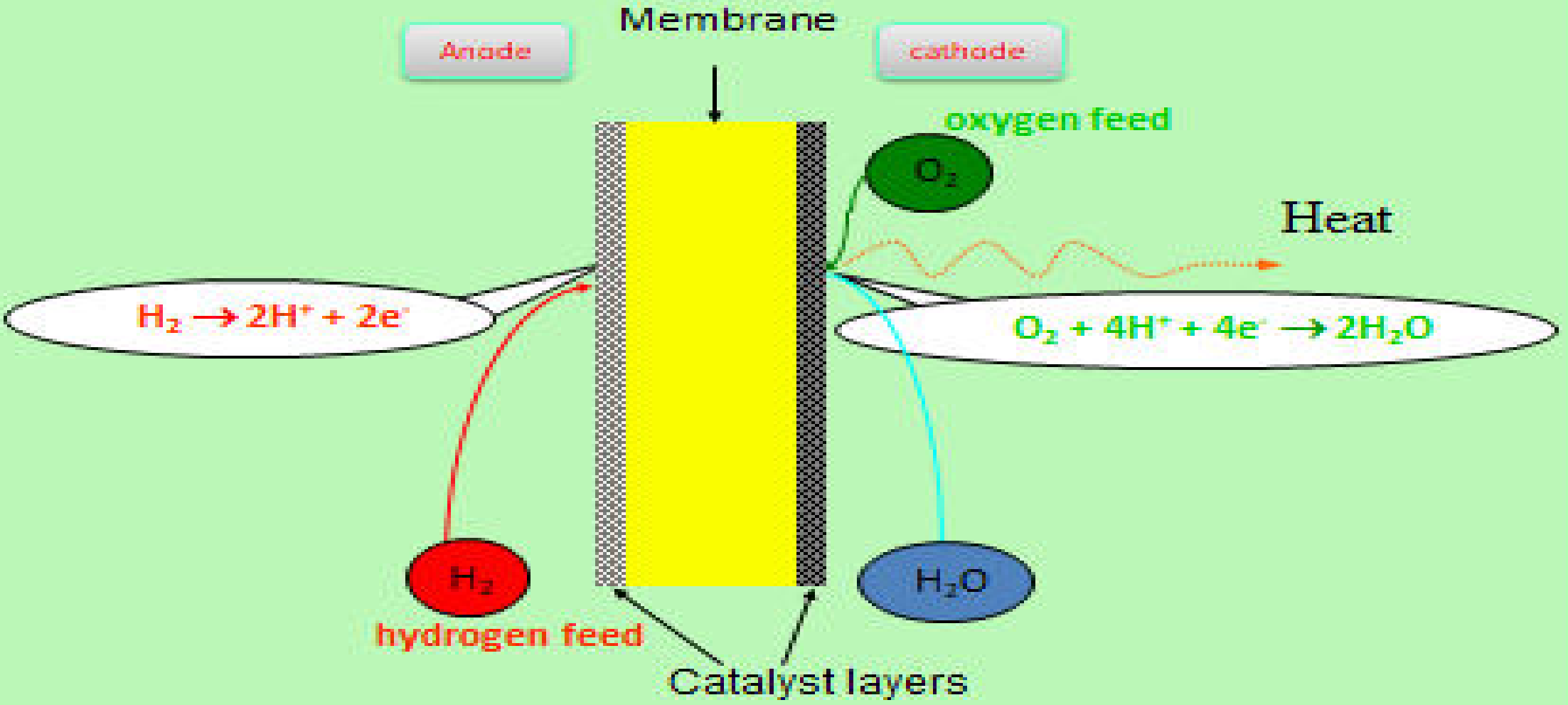
Outlines

- Introduction
- Experimental
- Results and Discussions
- Conclusions

The GOAL

The goal of this research is to develop Polymer Electrolyte Assembly (MEA), making them efficient with lower production costs than other produced nowadays.

What is a Fuel Cell?



Why is Fuel Cell Technology Important

1. Direct energy conversion
2. .Fuel cells are Quiet
3. Fuel cells are clean
4. Fuel cells are environmentally safe.

Fuel Cell Types

Fuel Cell Types

generally distinguished by type of electrolyte and conducting ion:

fuel cell type	temp.	anode reaction	conducting ion	cathode reaction
SOFC (Solid Oxide FC)	≈1000°C	$H_2 + O^{-2} \rightarrow H_2O + 2e^-$	$\leftarrow O^{-2}$ (Y-stabilized ZrO_2)	$\frac{1}{2} O_2 + 2e^- \rightarrow O^{-2}$
MCFC (Molten Carbonate FC)	≈650°C	$H_2 + CO_3^{-2} \rightarrow H_2O + CO_2 + 2e^-$	$\leftarrow CO_3^{-2}$ (alkali carbonates)	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{-2}$
PAFC (Phosphoric Acid FC)	≈200°C	$H_2 \rightarrow 2H^+ + 2e^-$	$H^+ \rightarrow$ (H_3PO_4)	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
PEMFC (H^+ Exchange Membrane FC)	≈80°C	$H_2 \rightarrow 2H^+ + 2e^-$	$H^+ \rightarrow$ (solid polymer)	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$
DMFC (Direct Methanol FC)	≈80°C	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H^+ \rightarrow$ (solid polymer)	$1.5\, O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$
AFC (Alkaline FC)	≈80°C	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$\leftarrow OH^-$ (KOH)	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

- high-temperature fuel cells (SOFC, MCFC):
  - → temperature required to obtain sufficient electrolyte conductivity
  - → ability to oxidize CO and to use CH_4 reactant via *internal reforming*
- low/medium-temperature fuel cells:
  - → temperature maximum dictated by H_2O-loss (no conductivity without H_2O)
  - → require clean H_2: CO-tolerance of ≈1% for PAFC and <<100ppm for others; CO_2-free O_2/air for AFCs (carbonate formation: pH change, precipitation)

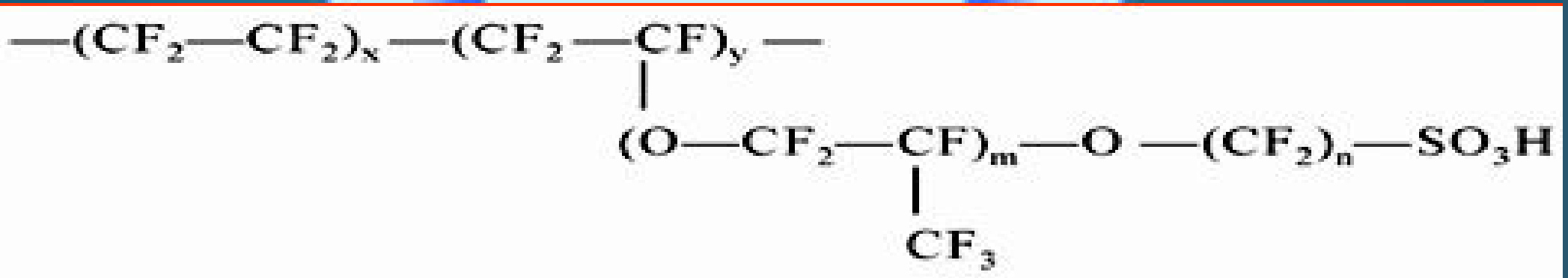
Polymer Electrolyte Membranes (PEM)

Polymer Electrolyte Membrane is the heart of fuel cell system. It is consist of copolymer materials which include proton conductor units. Usually sulfonic acid groups (SO_3H) are utilized.

Requirements for PEM

- Low cost material.
- High protonic conductivity for large current densities and low internal resistance.
- Mechanical integrity and structural strength, to minimize deformation under tension.
- High wateruptake to prevent localized drying.
- Low Methanol and gas permeability.

Nafion®



Advantages

*Stable in both oxidative and reductive environments

*Excellent proton conductor (**0.07 - 0.23 S cm^{-1} at 100 % RH**) 1M H_2SO_4 σ = 0.08 S cm^{-1}

Nafion Disadvantages

*High cost

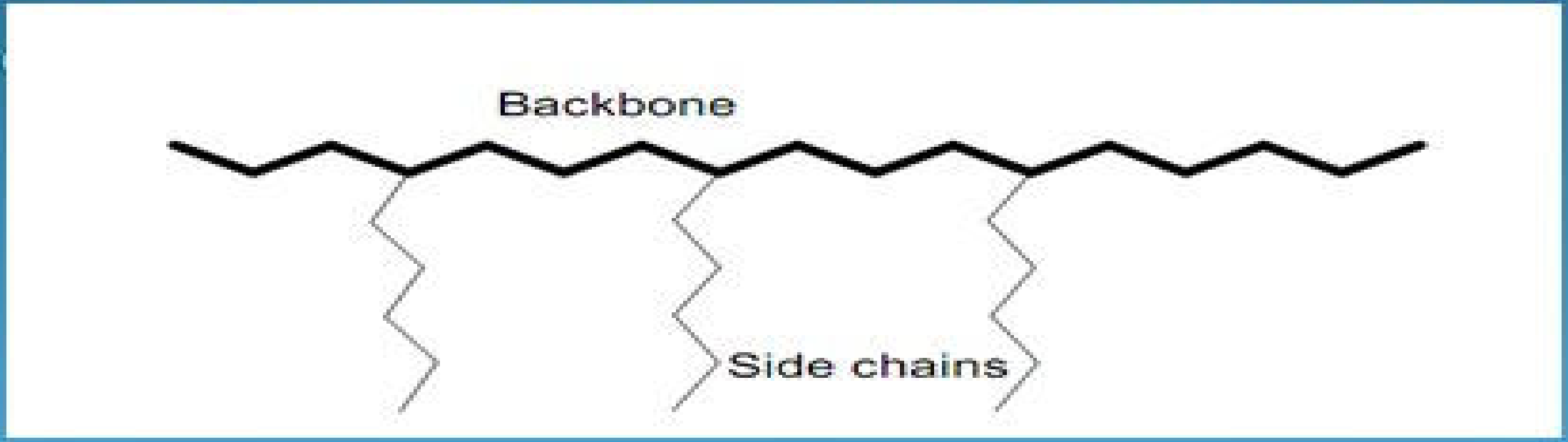
*Structural instability at temperatures above 100°C

* Lower conductivity at lower relative humidity

*High methanol crossover

Grafting copolymer

To prepare PEM we need to hanging of sulfonic group into the base polymer, so we need host polymer for hanging sulfonic group by grafting



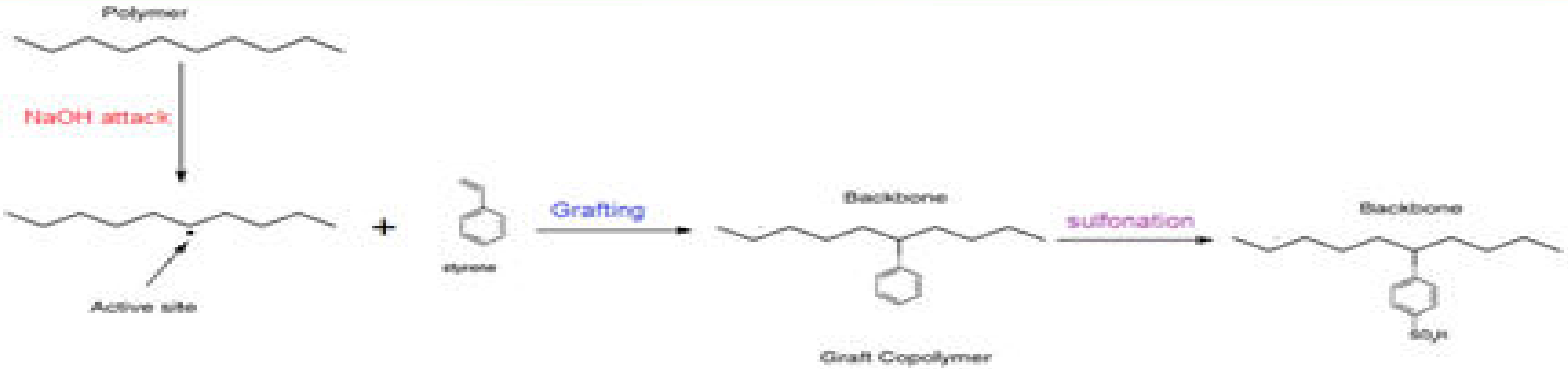
Grafting parameters

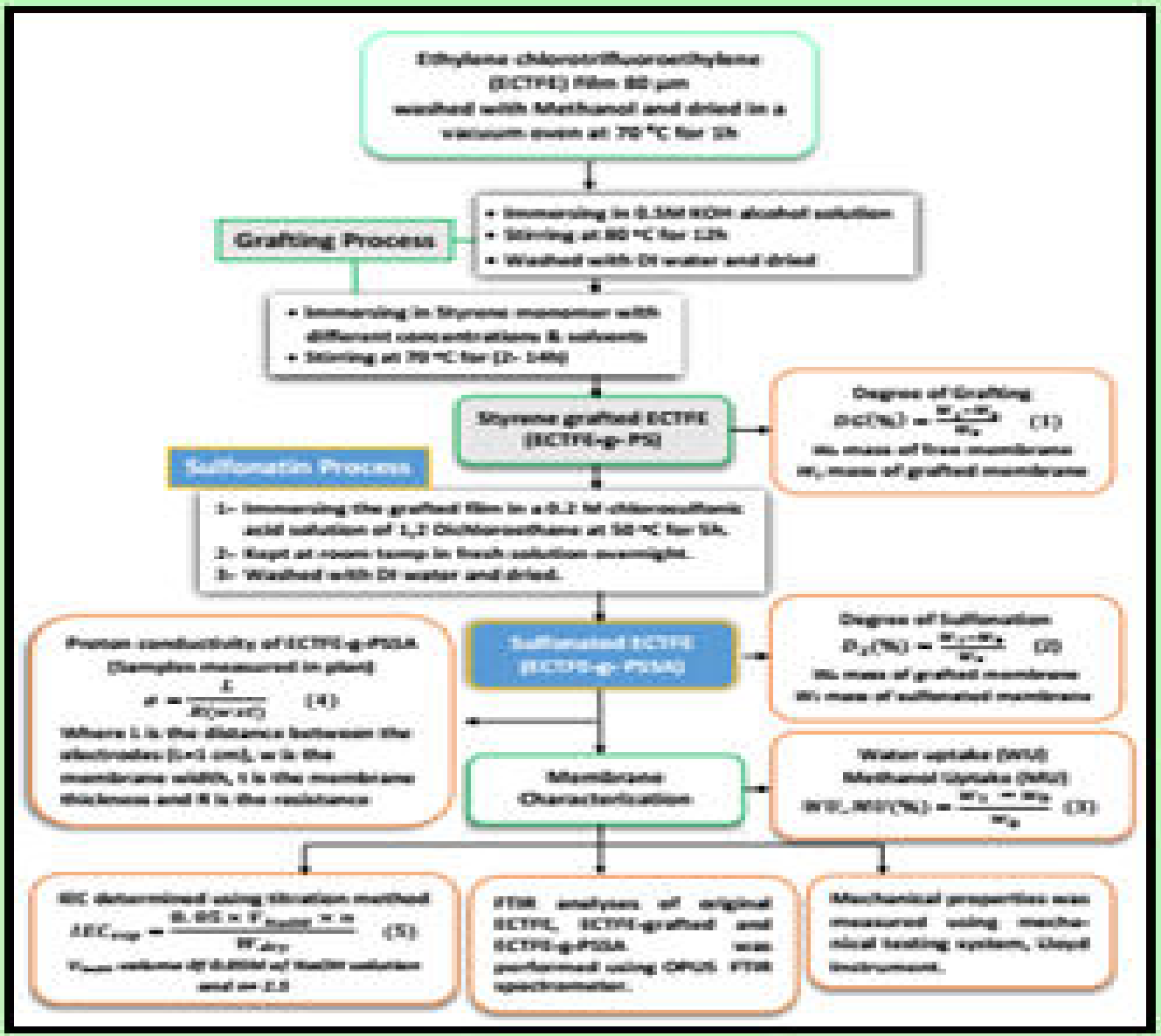
grafting yield gravimetrically determined as the percentage of weight increase ECTFE film after grafting reaction using the following equation :

$$D.O.G(\%) = \frac{M_1 - M_0}{M_0} (\%)$$

Sulfonation

Sulfonation is the final step for the preparation of polystyrene- based membranes for fuel cell applications. In this reaction a sulfonic acid group is added to an aromatic ring.





Overview showing grafting, sulfonation, and characterization of ECTFE-g-PSSA membranes

Results and Discussion

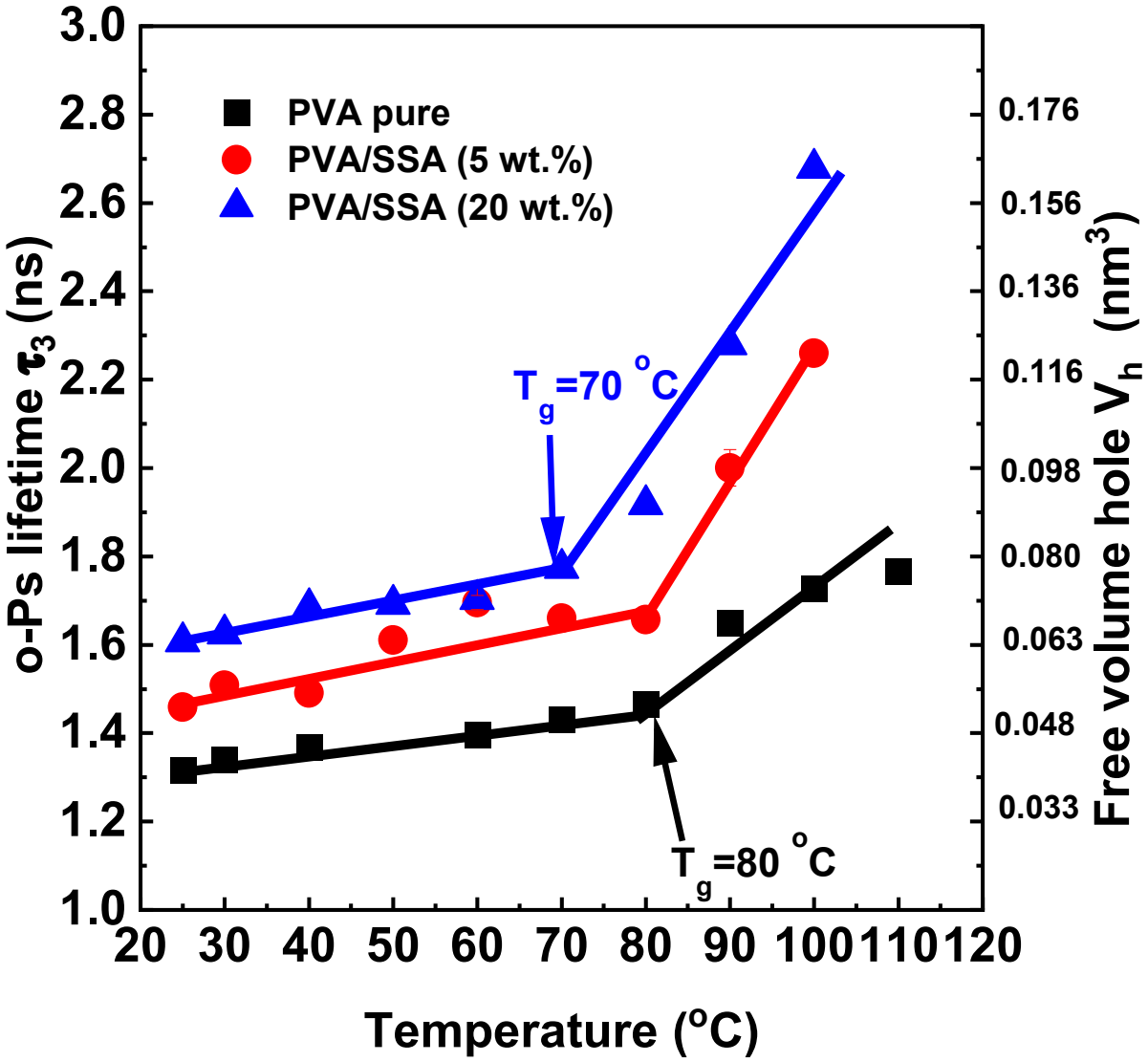
PALS results of crosslinked PVA as a function of SSA content

SSA content (wt.%)	τ_3 (ns)†	I_3 (%)¥	V_h (nm^3)*
0	1.166±0.011	25.012±0.173	0.0294±0.00698
5	1.170±0.011	18.235±0.193	0.0297±0.00698
10	1.151±0.010	16.113±0.187	0.0284±0.00639
15	1.216±0.010	14.825±0.187	0.0328±0.00642
20	1.285±0.010	11.523±0.195	0.0376±0.00677
25	1.330±0.010	8.231±0.190	0.0408±0.00703
30	1.337±0.011	8.410±0.201	0.0414±0.00789

†*The o-Ps lifetime obtained from PAL spectra using PALSfit program.*

¥*The o-Ps intensity obtained from PAL spectra using PALSfit program.*

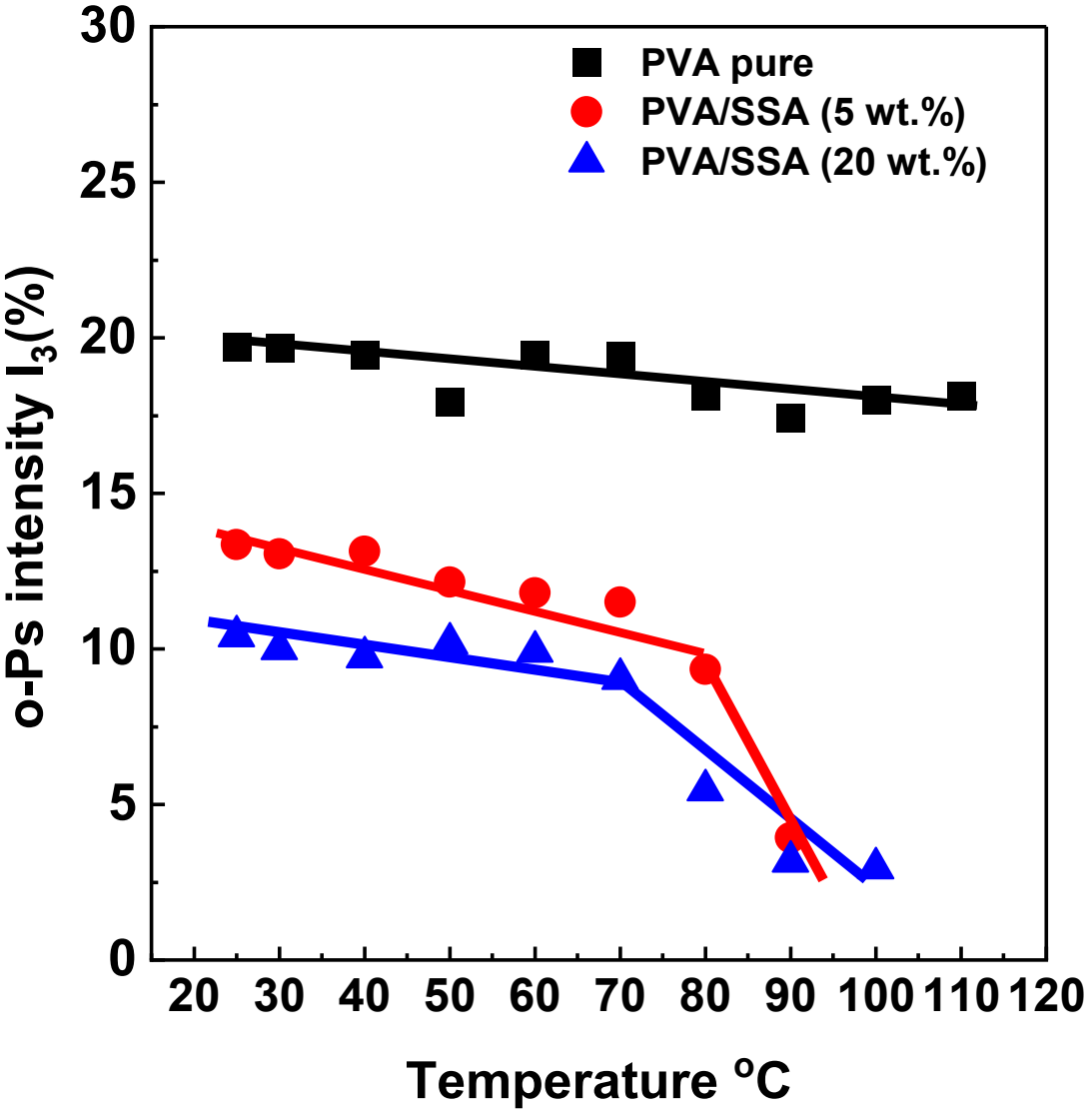
V_h* **is free volume size obtained using Eq. (9) and the relation $V_h = 4\pi R^3/3$.



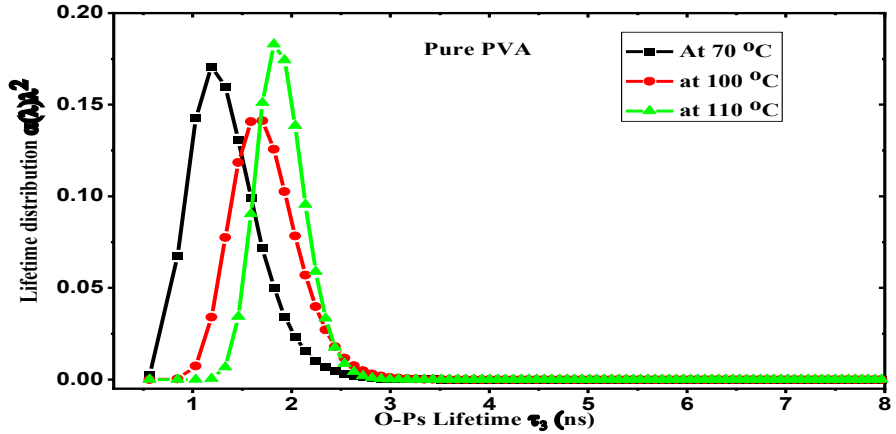
The o-Ps lifetime τ_3 as a function of temperature in the crosslinked PVA/SSA membranes. The right axis presents the free volume hole V_h calculated using Tao-Eldrup model and the relation $V_h = 4\pi R^3/3$. The error bars are within the symbol size.

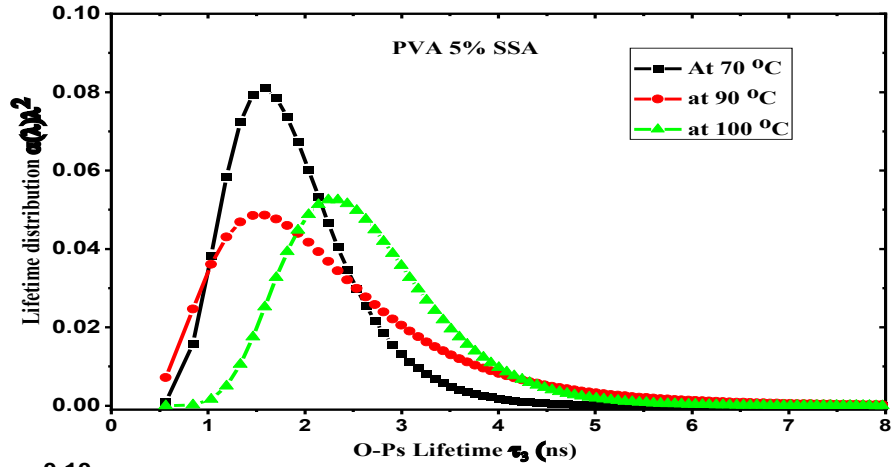
Thermal expansion coefficient (α) of free volume obtained from PAL data below and above the glass transition temperature (T_g) in pristine PVA and crosslinked PVA/SSA contents.

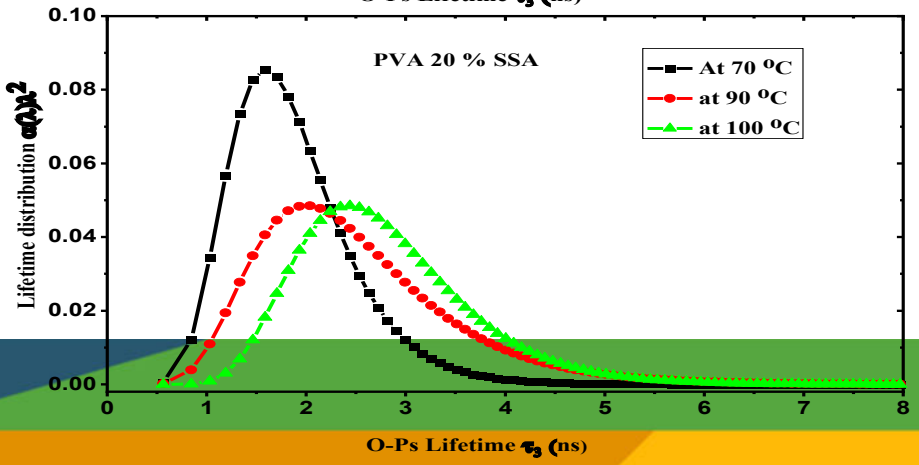
Samples	$\alpha_{before\ Tg}$ ($^oC^{-1}$)*	$\alpha_{after\ Tg}$ ($^oC^{-1}$)*
Pure PVA	$5x10^{-3}$	$188x10^{-3}$
PVA/SSA (5 wt.%)	$7x10^{-3}$	$375x10^{-3}$
PVA/SSA (20 wt.%)	$24x10^{-3}$	$429x10^{-3}$



The o-Ps intensity I_3 as a function of temperature in the crosslinked PVA/SSA membranes. The error bars are within the symbol size.







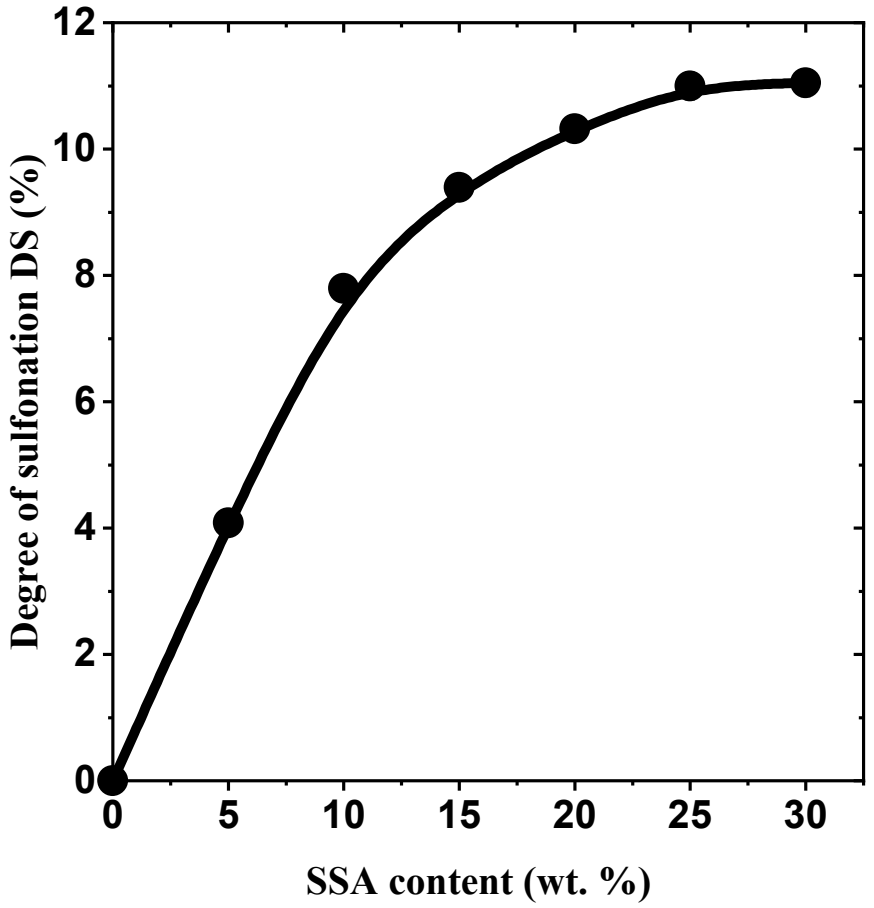
Normalized o-Ps lifetime distribution for the crosslinked PVA/SSA membranes at different temperatures calculating using LT9.0 program.

IEC values at different additive of SSA wt.% in crosslinked PVA membrane

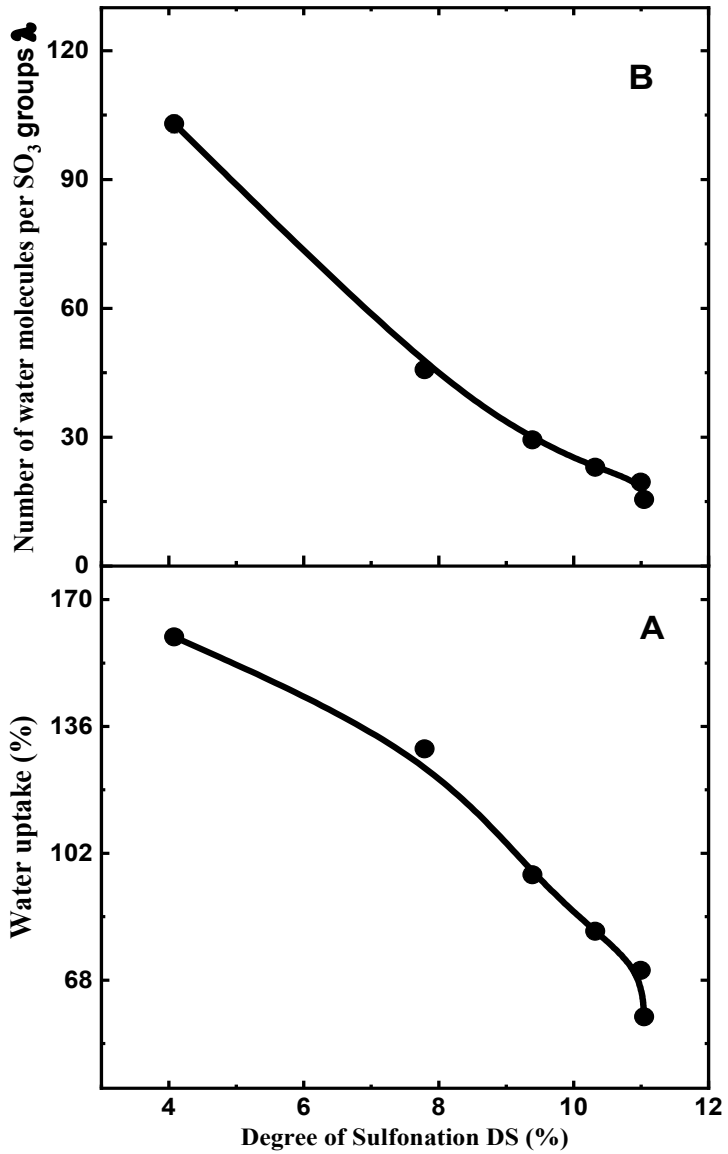
SSA (wt.%)	IEC (meq/g)
5	0.863±0.016
10	1.580±0.027
15	1.820±0.025
20	1.956±0.028
25	1.991±0.020
30	2.085±0.021

Mechanical properties versus degree of sulfonation DS in the crosslinked PVA/SSA membranes.

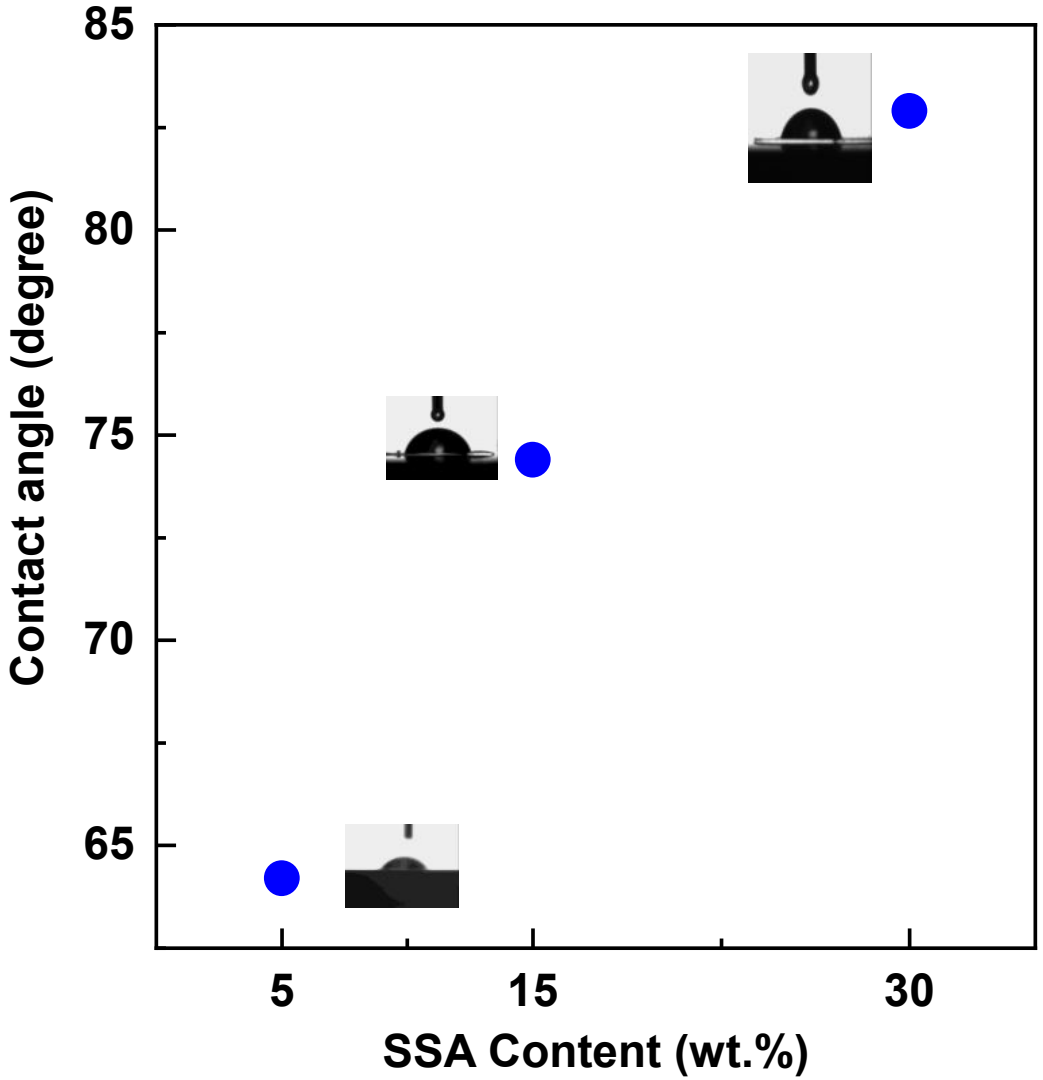
Degree of sulfonation DS (%)	Tensile strength (MPa)	Elongation at break (%)
0	59.00±0.5	17.4±0.4
4.08	6.00±0.4	10.2±0.3
7.79	61.02±0.6	10.1±0.2
9.39	62.05±0.4	7.4±0.1
10.32	38.01±0.3	7.3±0.099



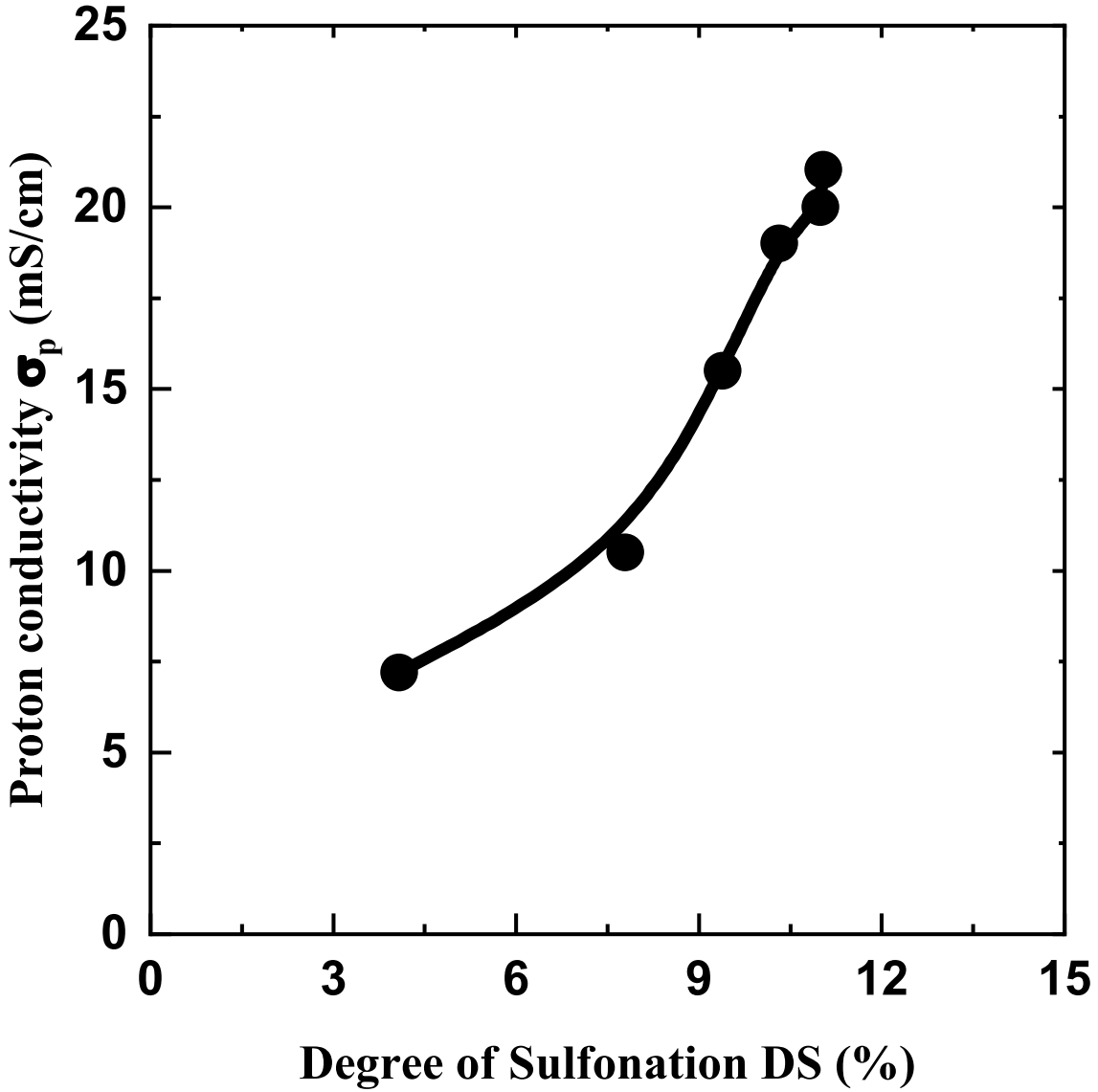
Degree of Sulfonation (DS) % as function of SSA content wt.% for crosslinked PVA/SSA membranes at room temperature 25 ^{o}C. The error bars are within the symbol size.



(A) Water uptake and (B) Number of water molecules per SO_3 groups λ versus DS in crosslinked PVA/SSA membranes measured at room temperature 25 ^oC. The error bars are within the symbol size.



Contact angle results of crosslinked PVA/SSA membranes as function of SSA content (wt.%) measured at room temperature 25 °C. The error bars are within the symbol size.



Proton conductivity σ versus DS in crosslinked PVA/SSA membranes measured at room temperature 25 °C and relative humidity of about 100%. The error bars are within the symbol size.

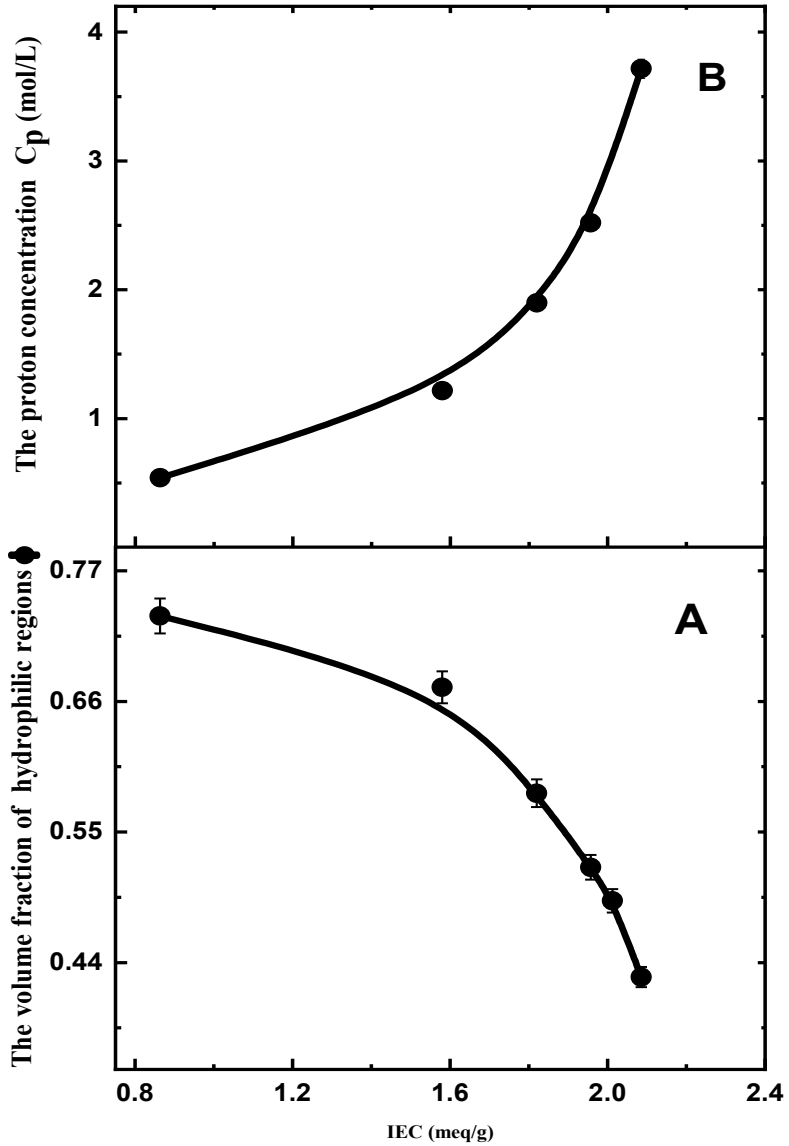


Fig. (8): (A) The volume fraction of the hydrophilic regions Φ and (B) the proton concentration *Cp* versus ion exchange capacity IEC in the crosslinked PVA/SSA membranes at room temperature 25 ^{o}C and relative humidity of about 100%.

Conclusions

- **The solution casting method was used to successfully prepare crosslinked proton exchange PVA/SSA membranes for use in fuel cell applications.**
- **The electrochemical properties had been examined by measuring many parameters. The degree of sulfonation (SO_3 content) was found to increase with increasing SSA content wt.%.**
- **Two contradiction phenomena have been observed, first water uptake was found to decrease with increasing degrees of sulfonation.**
- **On the contrary, both IEC and proton conductivity were found to increase with rising DS. The contradiction phenomena of water uptake, IEC, and proton conductivity was investigated further by using Nernst Einstein equation of proton conductivity which proves to decrease of the membrane hydrophilicity as a function of SSA content wt.%.**

Conclusions (cont.)

- **Besides, the contact angle measurements enhance the Nernst Einstein findings.**
- **The positron annihilation lifetimes results showed that as the D.S increases, the size of the free volume hole increases.**
- **By studying the free volume hole size as a function of temperature, one could conclude that the glass transition temperatures of the crosslinked PVA/SSA membranes were declined as a function of SSA content wt.% as the crystallinity of the membranes decreased by increasing SSA content wt.%.**


thank you!