Tuning intermolecular interactions of SiO_2-TiO_2-PBC Nanocomposite Membranes with Cation

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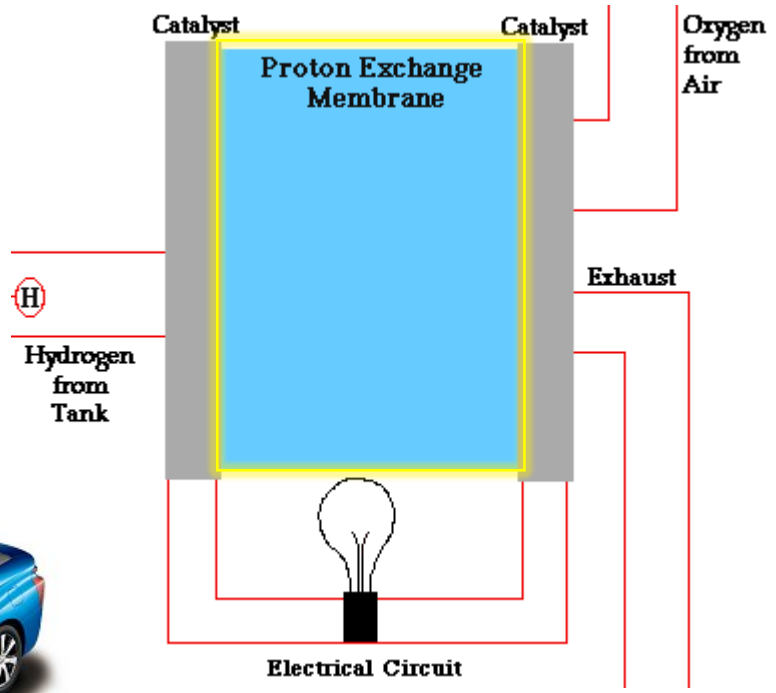
Background

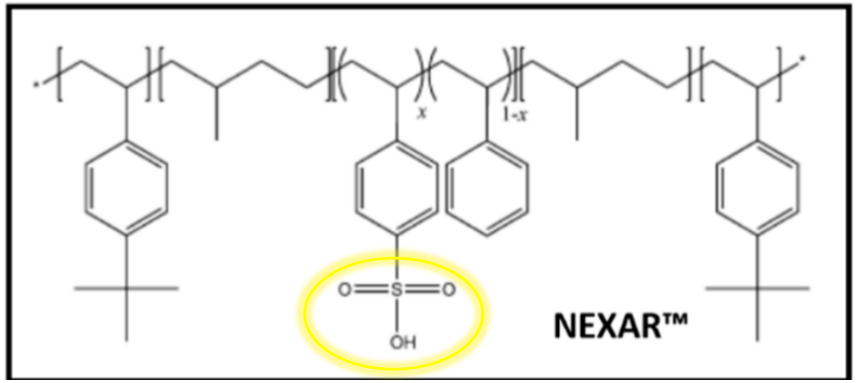
- Fuel cells: Chemical energy → Electricity
- Polymer electrolyte facilitates transport of ionic charges
- PEM=Proton Exchange Membrane

Nexar/ PBC membrane

- ✓ Sulfonated pentablock copolymer (PBC) : tert-butyl styrene, hydrogenated isoprene, sulfonated styrene : styrene, hydrogenated isoprene, tert-butyl styrene (tBS–HI–sS : S–HI– tBS)
- ✓ Pure materials cannot embody all the physical, chemical, and mechanical properties required for future and current applications

Inorganic –Organic nanocomposites: SiO_2-TiO_2-PBC



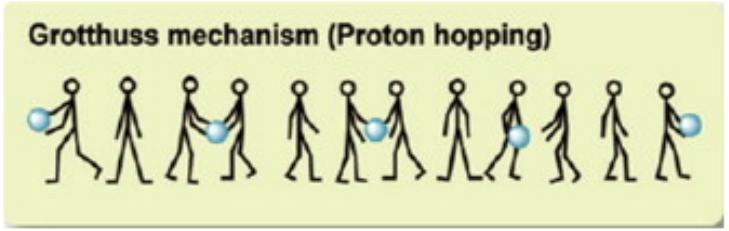


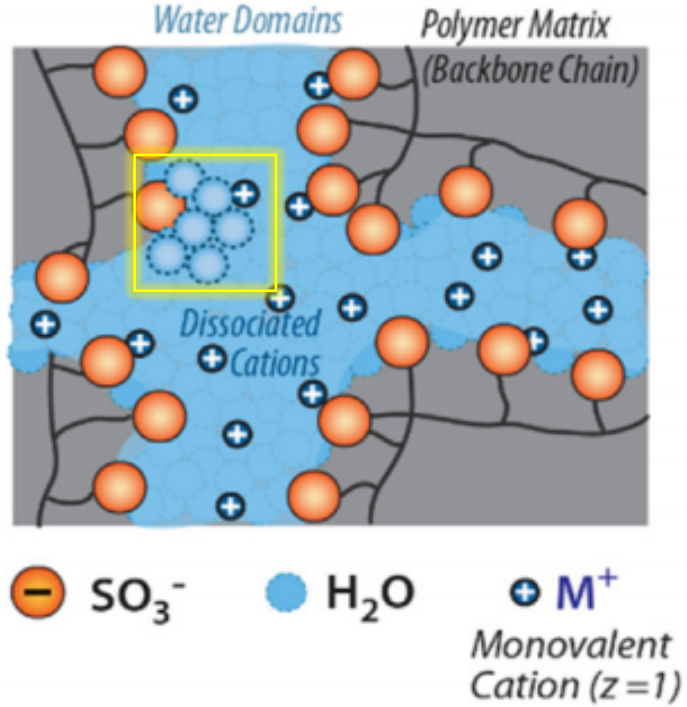
Wang, Y., Chen, K. S., Mishler, J., Cho, S. C. & Adroher, X. C. A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Appl. Energy* **88**, 981–1007 (2011).

Shi, S., Weber, A. Z. & Kusoglu, A. Structure-Transport Relationship of Perfluorosulfonic-Acid Membranes in Different Cationic Forms. *Electrochim. Acta* **220**, 517–528 (2016).

Motivation

- Transport properties are associated with the cation/water interaction
- Transport Properties are investigated in H+ forms and have not been explored for other cations
- Size and charge of cations ,alter the strength of interactions with the sulfonate groups
- Cation contamination and membrane stability in fuel cells





The focus of the study is to investigate the effect of cation on the cell performance and durability of SiO_2-TiO_2-PBC nanocomposite membrane

Borup, R. *et al.* Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chem. Rev.* **107**, 3904–3951 (2007).

Ping, Z. H., Nguyen, Q. T., Chen, S. M., Zhou, J. Q., & Ding, Y. D. (2001). States of water different hydrophilic polymers - DSC and FTIR studies. Polymer, 42(20), 8461–8467. https://doi.org/10.1016/S0032-3861(01)00358-5

Objectives

1) Design homogenous inorganic-organic membrane based on PBC with different compositions and weight% of SiO_2-TiO_2 nanocomposites

2) Modify the membranes with cations by exchanging ions with the respective salt

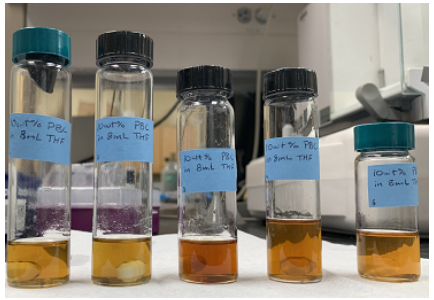
3) Investigate the effect of cations on the membrane : Water Uptake and Thermal Stability

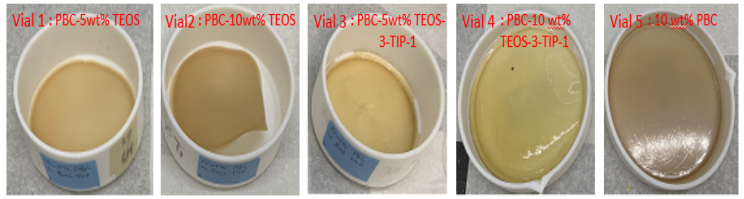
Experimental Method

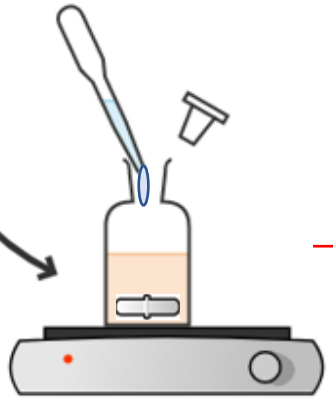
Step 1: Design homogeneous PBC membranes based on different compositions and wt% of TEOS-x-TIP-y

Tetraethyl orthosilicate (TEOS)
Titanium isopropoxide (TIP)

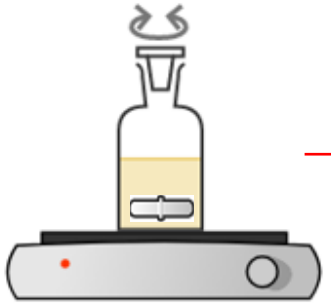
1) Homogenous Mixture of TEOS-x-TIP-y in isopropanol



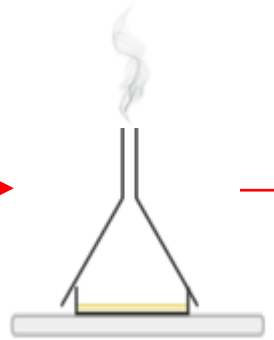




2) Desired wt% of TEOS-x-TIP-y is slowly added to homogenous solution of PBC in Tetrahydrofuran



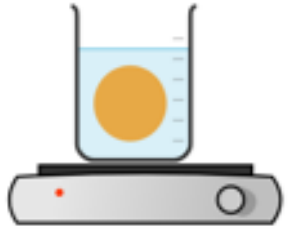
3) The PBC and TEOS-x-TIP-y is continuously stirred at room temperature for 3 days



4) The mixture is casted on a Teflon mold and the solvent is allowed to slowly evaporate at room temperature for 3 days

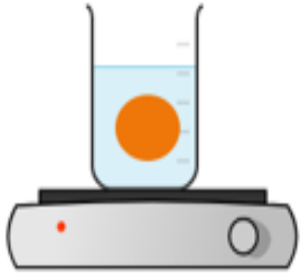
5) The membrane is dried in vacuum oven at 35 °C for 1 day

Step 2: Incorporating cations in the membrane



1) Boil the membrane in 0.5M H_2SO_4 for 5 hours

2) Rinse it thoroughly in DI water



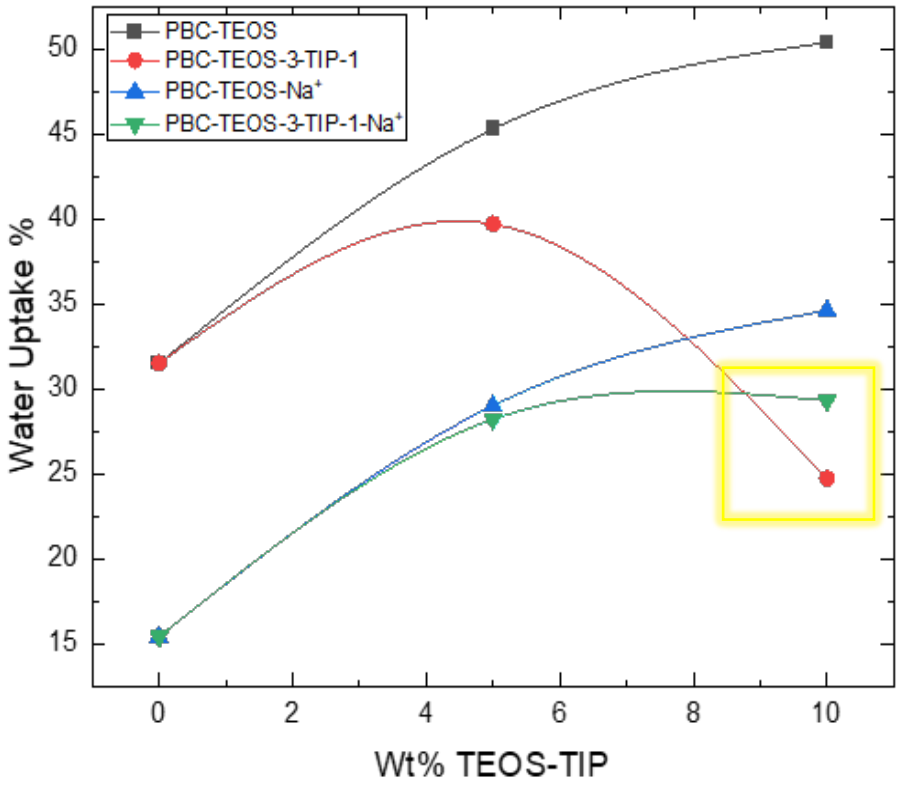
3) Boil the membrane in 1 M NaCl for 5 hours , rinse it thoroughly in DI water and dry the membrane

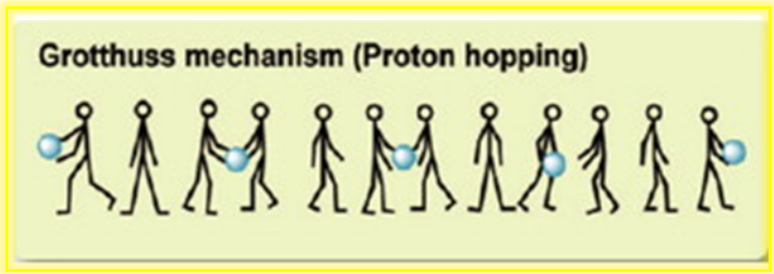
Results and Discussion

1) Water Uptake

- W_{wet} → immersing the membranes in deionized water at room temperature for 48 h
- W_{dry} → membranes were then dried at 50 °C under vacuum for 24 h
- Water uptake of all the unmodified membranes are higher than the those with Na^+
- In all cases, the water uptake increases increasing TEOS-TIP wt% except 10wt% PBC-TEOS-3-TIP-1 (modified and unmodified)
- Attributed to morphological transitions between the micro-phase separations of nanocomposites, sulfonate groups disruptions and ionic interactions

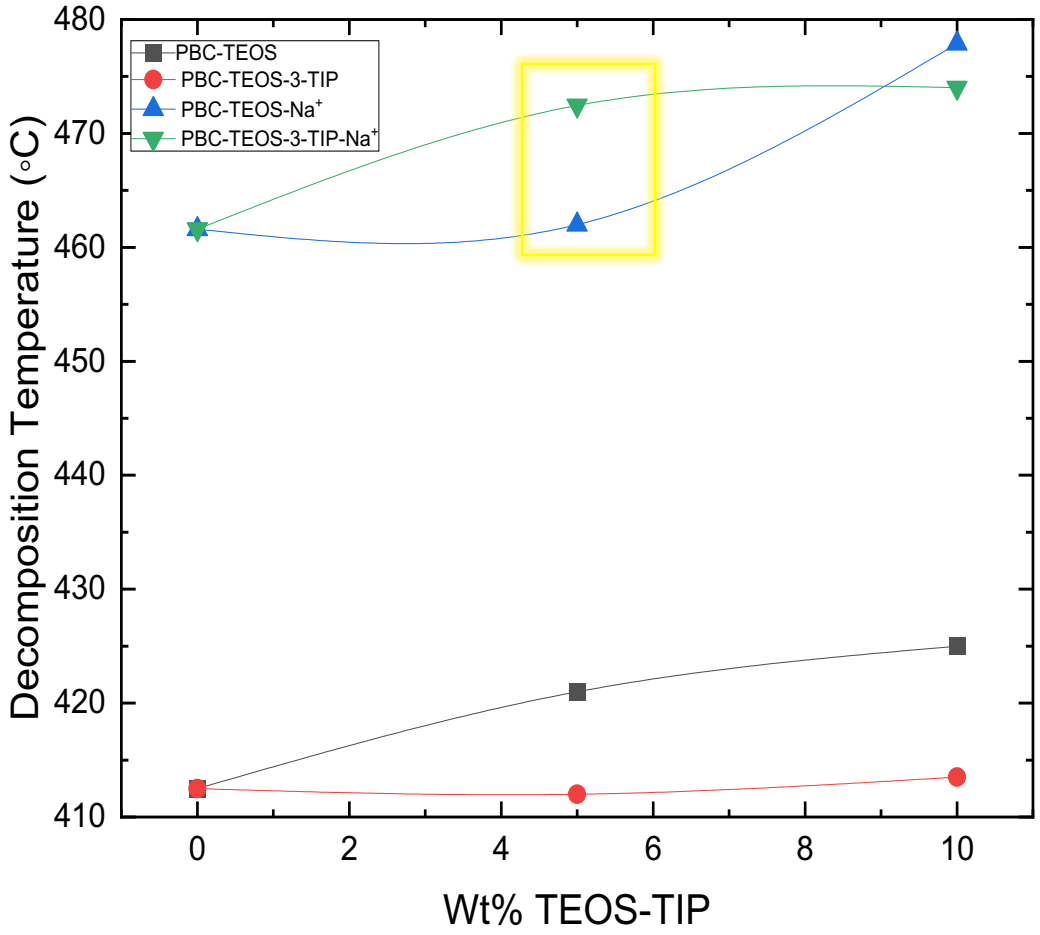
$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$





2) Thermal Stability

- Thermal Gravimetric Analysis
- Decomposition temperature of all the Na^+ exchanged membranes are higher than that of unmodified membranes
- Exchanging membranes with Na^+ improves the thermal stability
- Introducing TIP reduces the decomposition temperature except 5wt% PBC-TEOS-3-TIP-1
- TIP is a lewis acid which can increase the decomposition reaction rate as a kind of catalyst



Conclusions

Incorporating SiO_2-TiO_2 nanocomposites into pure PBC membrane improves the properties of the membrane

Exchanging the membranes with cation (Na^+) alters the properties significantly: Improved thermal stability and reduced water uptake

Attributed to morphological transitions due to ionic interactions

Role of cations in polymer electrolyte membrane must be considered to fully understand the cell performance and its durability

Future studies will be focused on proton conductivity and morphological changes exhibited by the membrane

Acknowledgement

UNIVERSITY OF Nebraska Lincoln | NEBRASKA CENTER FOR ENERGY SCIENCES RESEARCH

Thank You!