Modification of Sulfonated Poly Ether Ether Ketone (SPEEK) Proton Exchange Membrane with Sodium Chloride for Fuel Cell Application

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Outline

Introduction

1. Direct methanol fuel cell is a class of fuel cell under PEMFC where the fuel used is methanol.
2. At room temperature, methanol is liquid which makes it easy to transport and store.
3. Main components that make up a fuel cell are electrodes, reactant, oxidant and electrolyte that separate the reactant and oxidant.

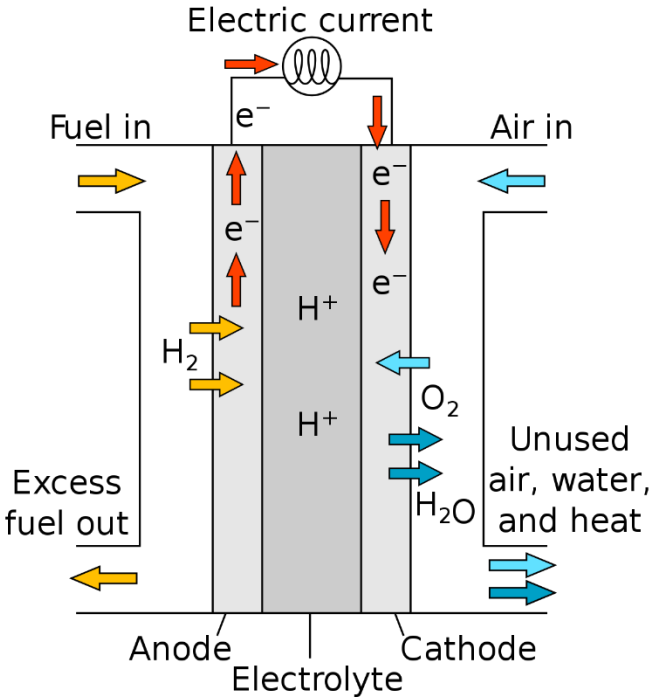

Figure 1: Process Diagram of PEM Fuel Cell Device

Introduction

4. Proton Exchange Membrane (PEM) was the epicenter of the fuel cell where the membrane facilitates the conduction of proton and at the same time, separates the fuel components.
5. There are a variety of PEM available in the market and most notably is the commercially successful and widely available Nafion manufactured by DuPont Company.
6. However, Nafion membrane does have its weakness such as high methanol permeability, low operation temperature, difficulty in synthesizing and processing and high cost (Charradi *et al.*, 2019).

Introduction

6. SPEEK is a sulfonated form of poly (ether ether) ketone (PEEK) functionalized by electrophilic substitution with sulfuric acid
7. This material has a big potential in fuel cells owing to its good film forming ability, high thermal and mechanical stabilities, and easier processability (Ranjani *et al.*, 2020).
8. **Figure 2** show a SPEEK membrane structure.

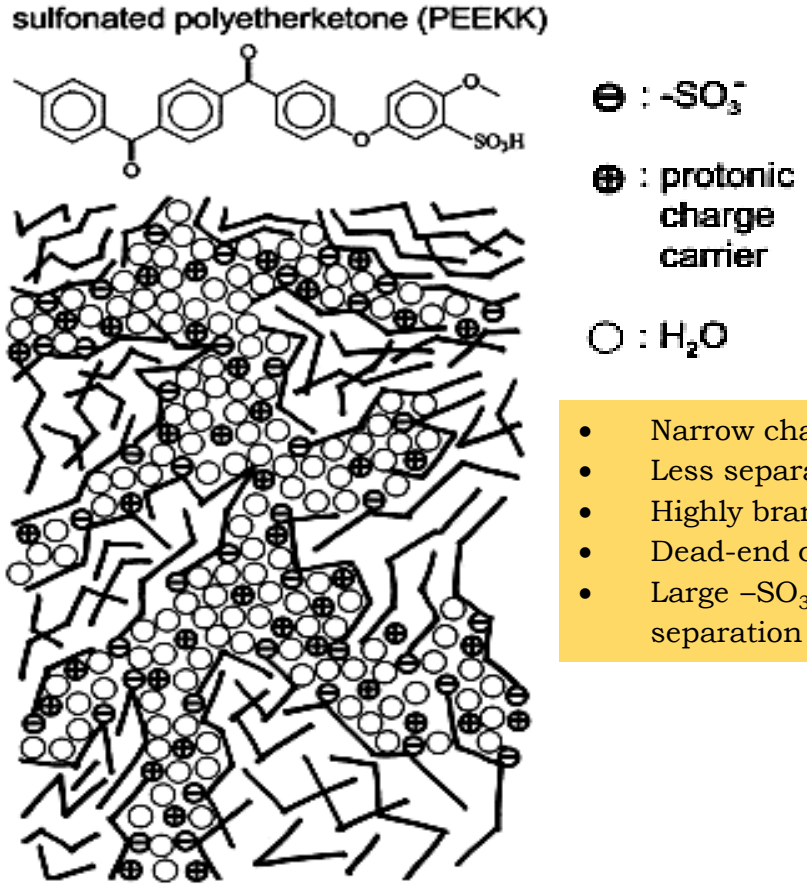

Figure 2: SPEEK membrane structure

Introduction

6. SPEEK, is characterize according to the degree of sulfonation (DS) where the amount of DS were controlled through reaction time and temperature.
7. The DS is defined as ratio of sulfonate group containing SPEEK over the total amount of SPEEK.
8. According to Wan Mohd Noral Azman *et al.* (2020), DS governs the properties of SPEEK membranes in term of water uptake and proton conductivity (Wan Mohd Noral Azman *et al.*, 2020).
9. However, the mechanical properties and methanol permeability of SPEEK membranes display a gradual declining trend as the DS increase (Wan Mohd Noral Azman *et al.*, 2020).

Introduction

9. Modifying existing SPEEK with inorganic filler is an effective and cheap way to improve desired properties of a PEM.
10. Sodium chloride (NaCl) is an inorganic compound that have a different charge. They are attracted to each other and create an ionic bond between them.

Methodology

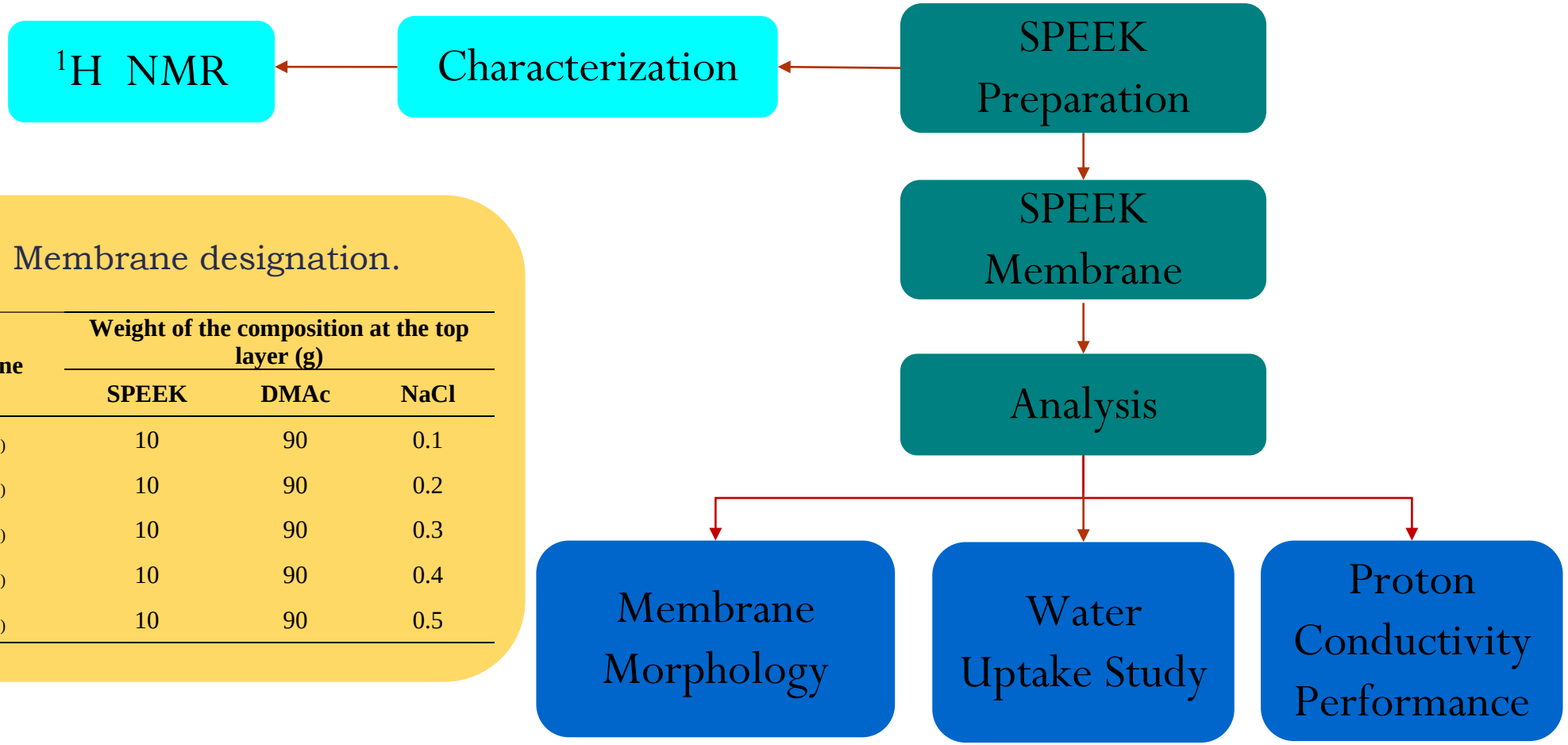

Table 1. Membrane designation.

Membrane	Weight of the composition at the top layer (g)		
	SPEEK	DMAc	NaCl
$SP_{NC(0.1)}$	10	90	0.1
$SP_{NC(0.2)}$	10	90	0.2
$SP_{NC(0.3)}$	10	90	0.3
$SP_{NC(0.4)}$	10	90	0.4
$SP_{NC(0.5)}$	10	90	0.5

Result & Discussion

Hydrogen Nuclear Magnetic Resonance (H^1 NMR)

1. In the **Figure 3(B)**, three characteristic peaks were observed to occur at 7.53ppm, 7.22ppm and 7.12ppm.
2. These peaks represent the resonance signals of H_E, H_C and H_D as shown in **Figure 3(A)**.
3. To identify DS within the sample, it is estimated from the area under the peak of H_E to that of all other peak area within the aromatic ring's hydrogen.
4. DS of the prepared SPEEK was approximately 0.61 (61.7 %)

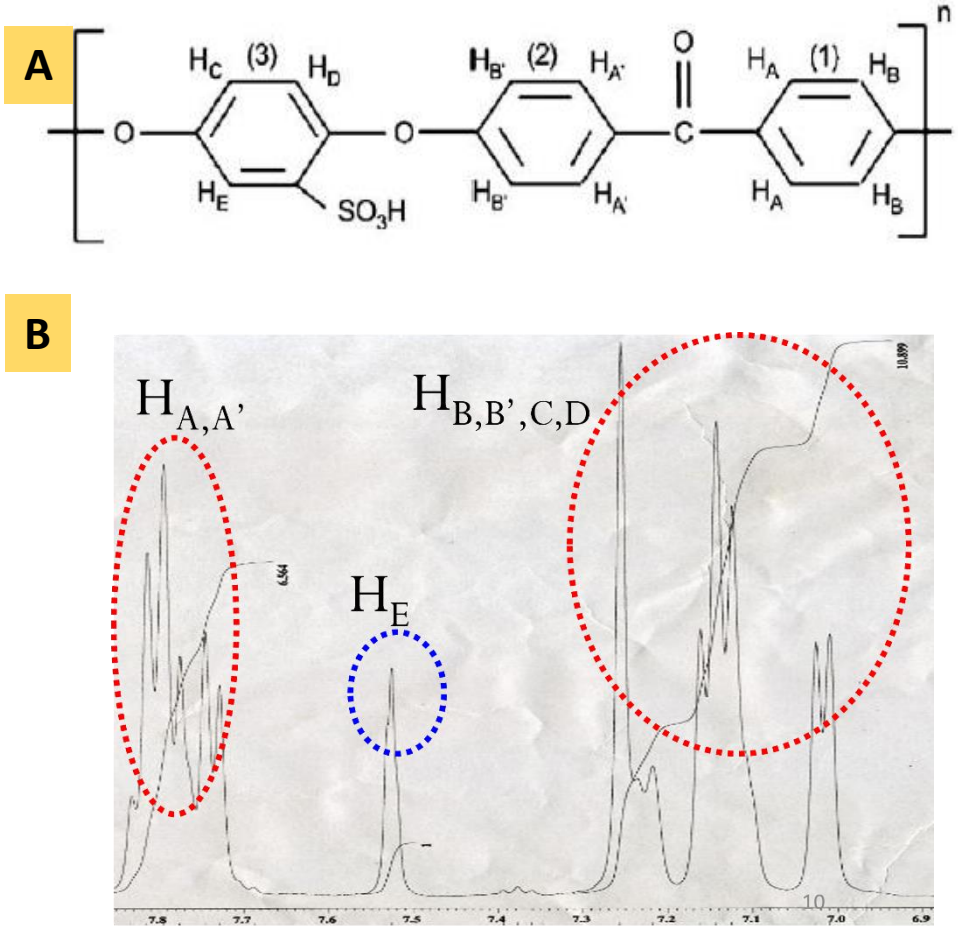

Figure 3: A) SPEEK chemical structure B) NMR trend for solid SPEEK

Membrane Morphology

1. In **Figure 4(A)**, the increasing amount of NaCl, leading to a more porous membrane structure (several crystalize NaCl were noticed scattering across the membrane surface).
2. In **Figure 4(B)**, no apparent phase separation for $SP_{NC(0.1)}$ and $SP_{NC(0.2)}$, which indicated that both layers were attached seamlessly.
3. $SP_{NC(0.3)}$ has a slightly different structure between the layers where the rough layer was identified as a pure SPEEK membrane, and the smooth layer is SPEEK with NaCl.
4. The pores were noticeable for $SP_{NC(0.5)}$ due to the high amount of salt content in the membrane

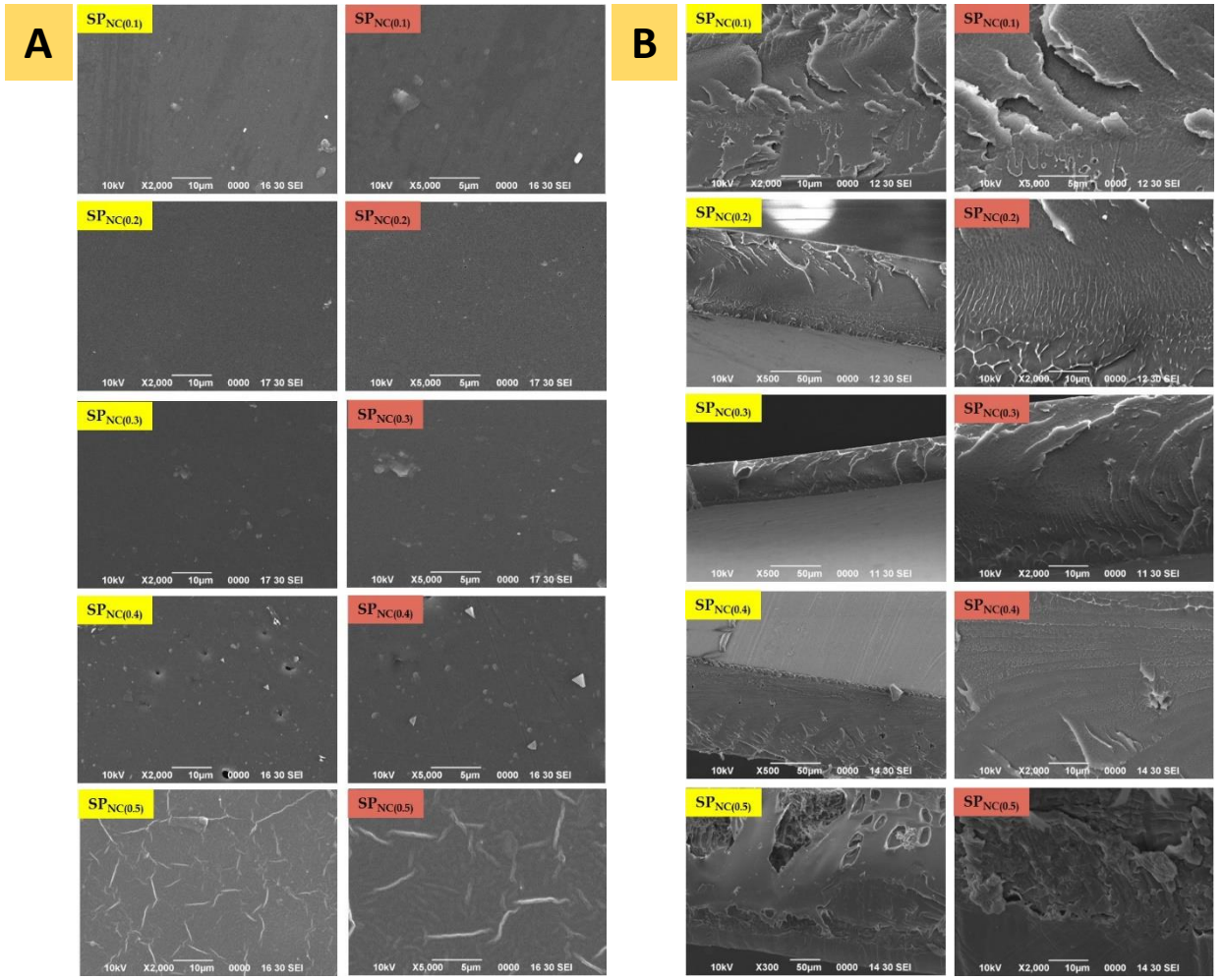

Figure 4: SPEEK Membrane morphology at low and high magnifications A) top surface B) cross section

Water Uptake

1. Based on **Figure 5**, as the NaCl loading in the SPEEK polymer matrix increases, the water uptake also increase.
2. This might be due to the ability of NaCl itself that can absorb the water (hygroscopic).
3. Hygroscopy is the ability of a substance to attract and hold water molecules from the surrounding environment.
4. Ions are free to move -The water content in the membrane helps to transfer the ion through the electrolyte.

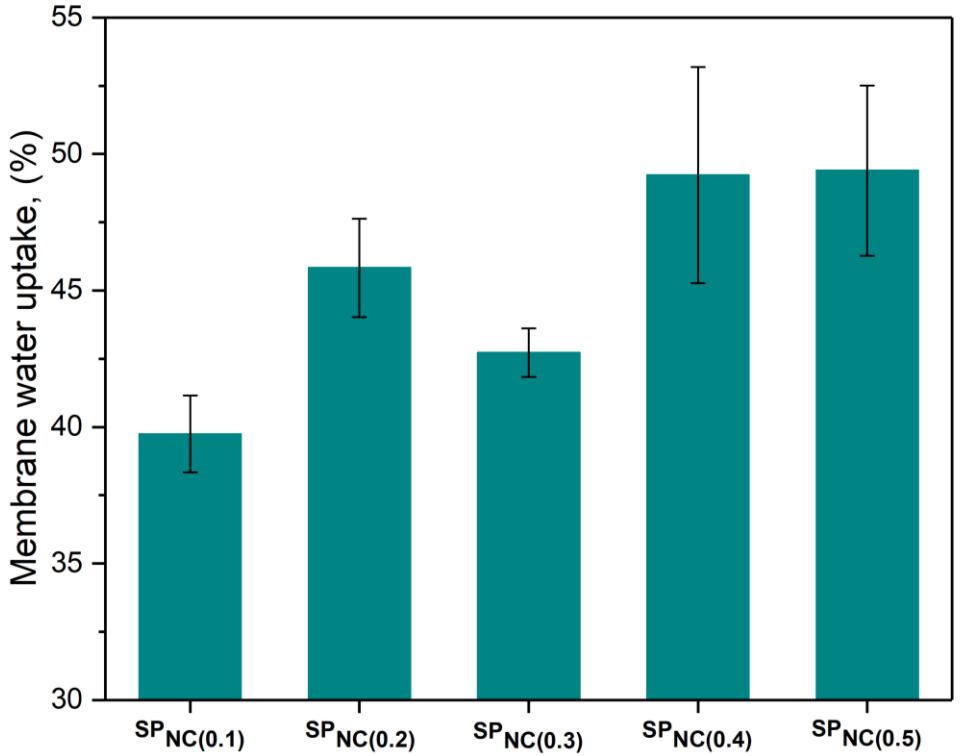

Figure 5: Water Uptake of a prepared membrane at different loading of NaCl

Proton Conductivity Test

1. Conducted using Impedance test instrument
2. The formula is:

$$\textbf{Proton Conductivity}, \boldsymbol{\sigma} = \frac{d}{R \times S}$$

Where:

R= resistivity

d = thickness of membrane, m

S = Surface area, m^2

3. From **Figure 6**, as NaCl incorporated in the membrane increased the proton conductivity increased by 2 to 4 fold.
4. According to Wan Mohd Noral Azman *et al.* (2020), A threshold of matrix water is needed to uphold proton conductivity wherein high-water uptake leads to high proton conductivity.

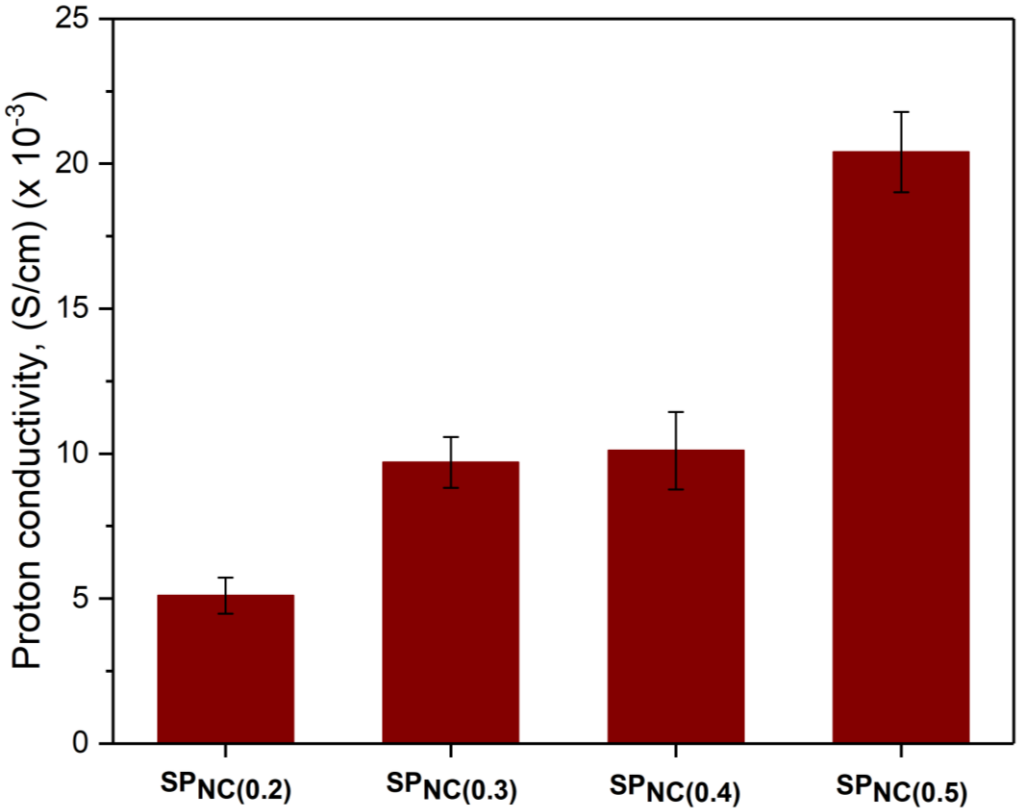

Figure 6: Membrane conductivity at of a prepared membrane at different loading of NaCl

Performance Comparison

1. Table 2 shows, a comparison of prepared membrane in this study with pure SPEEK membrane and Nafion 117 in other recent studies.

Table 2: Comparison performance of prepared membrane, unmodified SPEEK membrane and Nafion 117

Membrane Designation	Water Uptake (%)	Proton Conductivity (x 10^{-3}) (S/cm)
S/$S_{0.1NaCl}$	34.03	-
S/$S_{0.2NaCl}$	39.54	6.7
S/$S_{0.3NaCl}$	42.17	9.0
S/$S_{0.4NaCl}$	47.7	9.1
S/$S_{0.5NaCl}$	52.17	19.6
S_{pure} (Wan Mohd Noral Azam *et al.* 2020)	45	6.4
PBI/ZrP (Kamaroddin *et al.* 2019)	41.7	5.67
Nafion 117 (Kamaroddin *et al.* 2019)	13	10.1

Conclusion

1. A multilayer SPEEK/SPEEK-NaCl membrane was fully fabricated.
2. The result obtained from prepared membrane shows an improvement in term of proton conductivity by 2 to 4 folds as compare to unmodified membrane.
3. Compared to pure SPEEK membrane and Nafion 117, the prepared membrane ($SP_{NC(0.5)}$) show higher proton conductivity and water uptake.
4. Thus, the incorporation of NaCl into multilayer SPEEK membrane play a significant role in enhancing the proton conductivity.

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Thank You