Low-cost non-fluorinated membranes for fuel cells

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INTRODUCTION

Energy is one of the most important factors that will influence the shape of society in the 21st century. Fuel cells are electrochemical energy converters, transforming chemical energy directly into electricity. Fuel cells are the main zero emission energy converters fed with hydrogen or renewable fuels like methanol and ethanol to power vehicles, portable devices or to supply electricity to buildings. Fuel cell technology will forever change our concept of alternative energy systems and will become the driver of the next growth wave of the world's economy.

A proton conductive membrane is the core of the polymer electrolyte membrane fuel cell (PEMFC). Presently, Nafion® membranes are widely used in PEMFC. However, the high cost, low operation temperature (<80°C), propensity for dehydration, high methanol crossover, and environmental recycling uncertainties of Nafion® and other similar fluorinated membranes are limiting their widespread commercial application in PEMFC and DMFC [1-3]. Therefore, developing cheaper membranes with low methanol crossover have become an active area of research

We developed low-cost proton conductive membranes based on non-fluorinated polymer. The membranes are thermally and chemically stable, mechanically strong, highly proton conductive and have low fuel crossover.

EXPERIMENTAL

The starting material, sulfonated-sulfinated poly (oxa-p-phenylene-3,3-phthalido-p-phenylene-oxa-p-phenylene-oxy-phenylene) (SsPEEK) was prepared by reducing sulfonated-chlorosulfonated PEEK-WC (SCPEEK-WC).

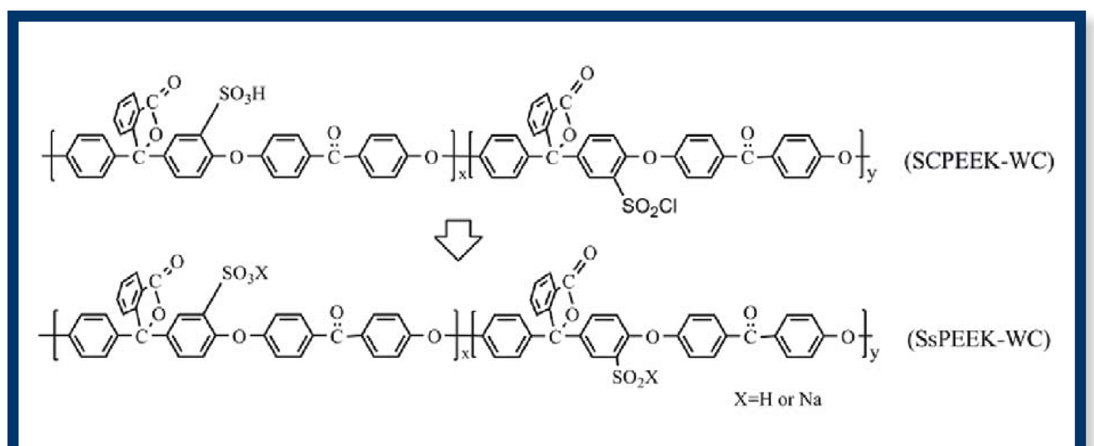

Figure 1: SCPEEK-WC and SsPEEK-WC

Covalently cross-linked membrane: The cross-linker was added to the SsPEEK-WC solution in NMP with magnetic stir. The solution was cast on a glass Petri dish.

Covalent-ionically cross-linked membrane: The diiodomethane for covalently cross-linking and polybenzimidazole solution for ionically cross-linking was added to the SsPEEK-WC solution in NMP. After homogenisation of the solution by stirring, the polymer solution was cast on a glass Petri dish. The solvent was then removed in a vacuum oven. The membranes were peeled off from the Petri dish. An uncross-linked membrane was also prepared, but was water soluble.

Results and discussion

After cross-linking, the membranes became water insoluble. The water uptake of the covalently cross-linked PEEK-WC membrane was 44% at room temperature and reached 110% at 80°C. Although, the value of water uptake at 80°C was tolerant to reduce the value of water uptake is indispensable for the membrane used in DMFC at higher temperature such at 80°C. The covalent-ionically cross-linked PEEK-WC membrane exhibits a reduced increasing trend of water uptake with increasing temperature (**Figure 2**). The water uptake was reduced to 43% at 80°C.

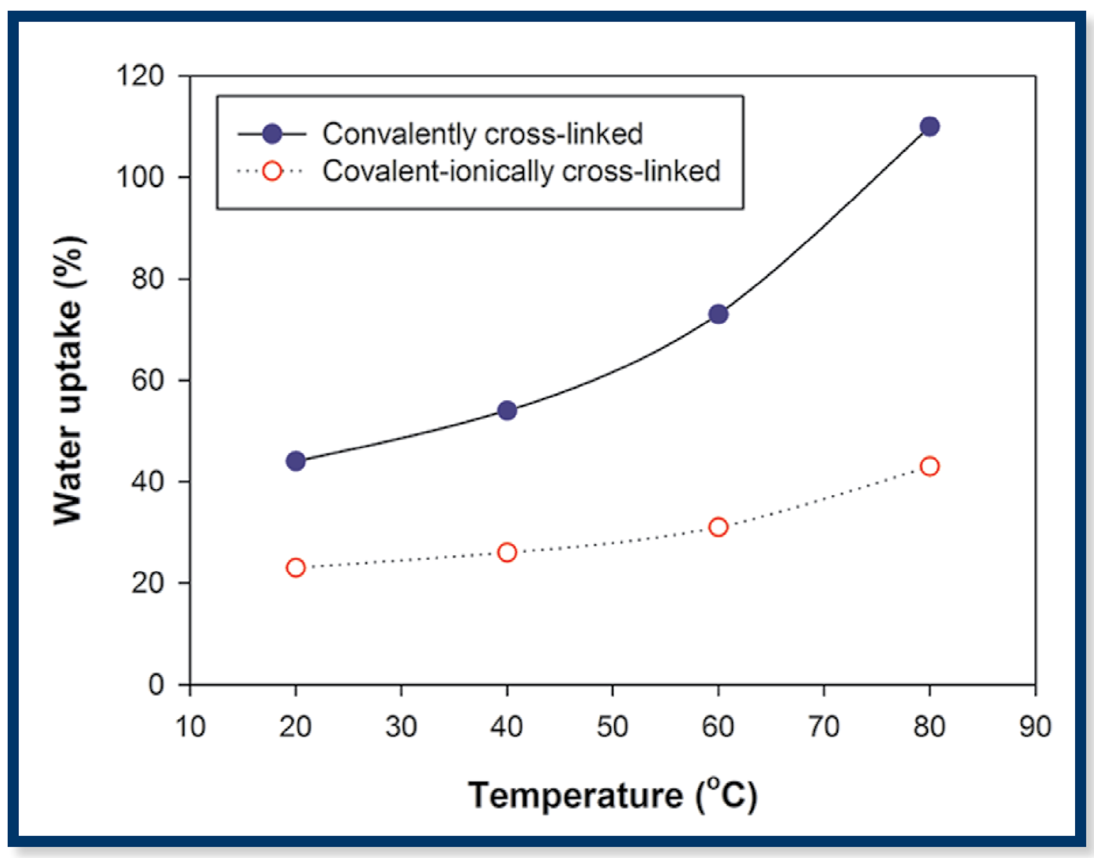

Figure 2: Water uptake as a function of temperature

The proton conductivities of the cross-linked membranes were determined from 20°C to 80°C. **Figure 3** shows that the proton conductivity of the cross-linked membranes as a function of temperature.

It was found that the proton conductivity of the cross-linked membranes increases continuously with increasing temperature. The covalent-ionically cross-linked PEEK-WC membrane shows slightly-reduced proton conductivity compared with that of covalently cross-linked PEEK-WC.

The proton conductivity of covalent-ionically cross-linked PEEK-WC membrane was 2.1×10^{-2}°S cm^{-1} at 20°C and reached to 4.1×10^{-2}°S cm^{-1} at 80°C. The proton conductivity of the cross-linked membrane is lower than that of Nafion® 117 which was measured at the same condition, however, the resistance of the cross-linked membrane can be reduced by reducing the thickness due to its extremely low methanol permeability.

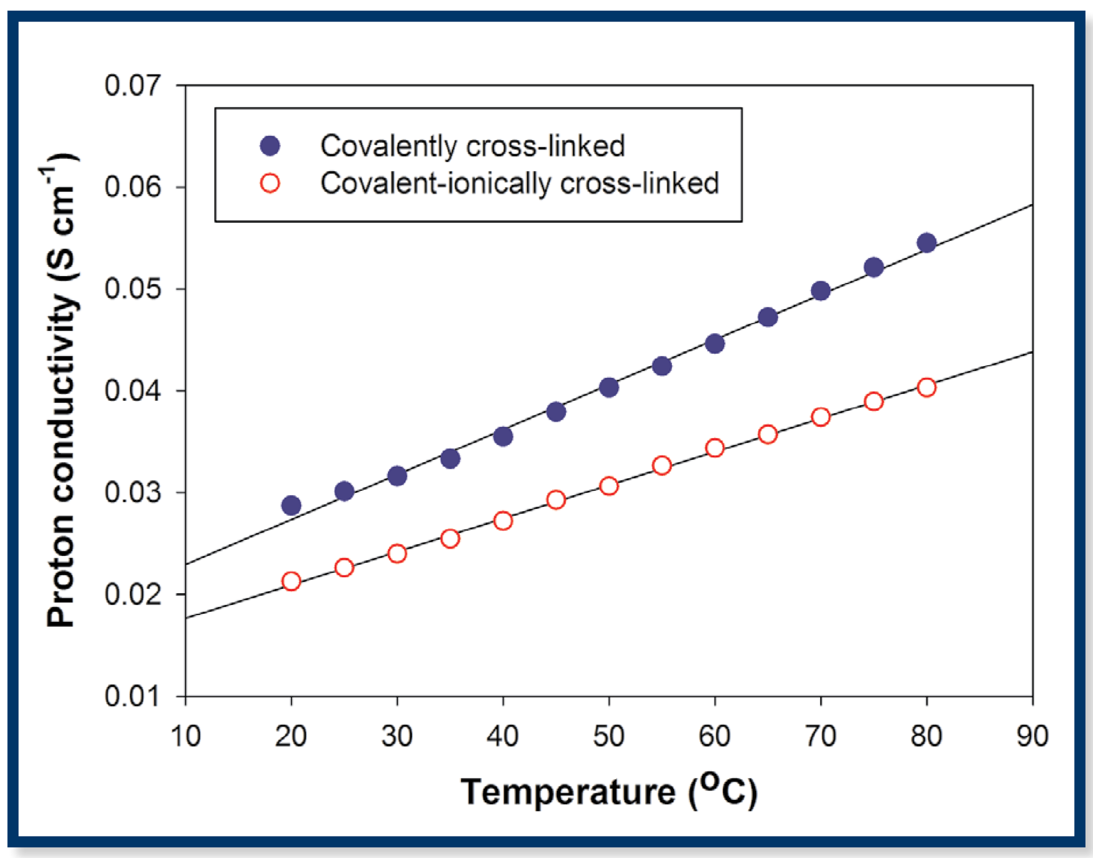

Figure 3: Proton conductivity as a function of temperature

The cross-linkages between the polymer chains in the membrane form a three-dimensional network as illustrated in **Figure 4** and prevent the polymer from swelling to infinity, in other words from dissolving. This is due to the elastic retraction forces of the network which decreases the entropy of the chains as they become denser after cross-linking. The covalent-ionically cross-linked membrane shows reduced water uptake and slightly-reduced proton conductivity compared with that of the covalently cross-linked membrane.

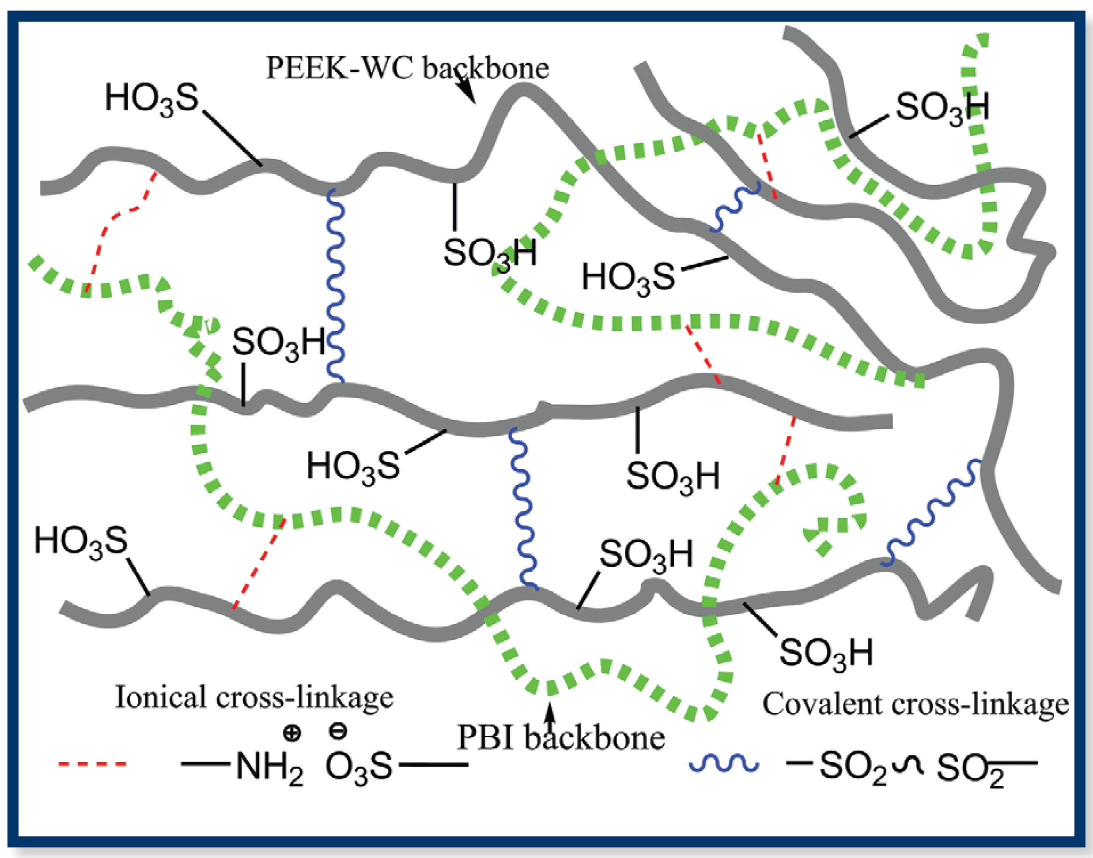

Figure 4: Network structure of covalent-ionically cross-linked membrane

It was found that the methanol permeability of the covalent-ionically cross-linked PEEK-WC membrane was reduced from $1.6\times10^{-7} cm^2 s^{-1}$ to $1.3\times10^{-7} cm^2 s^{-1}$ compared with that of covalent cross-linked PEEK-WC $1.6\times10^{-7} cm^2 s^{-1}$, much lower than that of Nafion® 117 membrane. The comparative properties of the prepared membranes are listed in **Table 1**.

Table 1: The comparative properties of the cross-linked membranes

Membrane	Water uptake 20°C (%)	Water uptake 80°C	Conductivity 20 °C (S cm-1)	Conductivity 80°C (S cm-1)	Methanol permeability 20°C (cm2 s-1)
Covalently cross-linked	44	110	2.9×10-2	5.5×10-2	1.6×10-7
Covalent-ionically cross-linked	23	43	2.1×10-2	4.1×10-2	1.3×10-7

CONCLUSIONS

The low-cost covalent-ionically cross-linked PEEK-WC membrane shows reduced water uptake, reduced methanol permeability and enhanced thermal stability, but slightly-reduced proton conductivity comparing with covalently cross-linked PEEK-WC membrane. The result recommended that the covalent-ionically cross-linked membrane is a promising candidate for fuel cell application.

REFERENCES

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Developing novel proton exchange membrane as an alternative to Nafion for fuel cell application that is low cost and environmental friendly.