

In-Situ Cross-linked Polymer Electrolyte Membranes from Thermally Reactive Oligomers for Direct Methanol Fuel Cells

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Introduction

The direct methanol fuel cell (DMFC) is an attractive candidate for a mobile energy source because of its advantageous properties such as easy fuel storage, low operating temperature, and simple design applicability. However, DMFC does not show enough performance for application in small electronics. Methanol cross-over through membrane which results in mixed potential at cathode, decreases the performance and fuel efficiency, and produces the undesired heat generation.¹ Hydrocarbon based polymer electrolyte membrane (PEM) have been studied due to their rigid backbone and lower solvent permeability to apply in DMFC. Polymer electrolyte based on sulfonated polysulfone, modified perfluorinated polymer or other kinds of PEM are reported to have high electrochemical properties and polymeric properties.²⁻⁴ The membranes showed that higher IEC higher swelling to methanol. To overcome excess swelling accompanied by high ionic contents, pore-filling structure, cross-linked PEM, or PEM with proton conductive inorganic materials have been also proposed.⁵⁻⁶ In the present study, we demonstrated novel hydrocarbon based membranes showing low methanol permeability and high ionic conductivity at the same time. Unprecedented reduction of methanol cross-over (<5% of Nafion-115) and high ionic conductivity (~80% of Nafion-115) has been achieved through in-situ thermal polymerization and cross-linking of telechelic sulfonated sulfone oligomers during a membrane preparation.

Experimental

Two step simple synthetic methods were accomplished for producing thermally reactive oligomers for PEM. 4,4'-dichlorodiphenyl sulfone (DCDPS), sulfonated 4,4'-dichlorodiphenyl sulfone (s-DCDPS) and 4,4'-Isopropylidenediphenol (BPA) were reacted in N,N-Dimethylacetamide (DMAc) to get OH terminated sulfonated sulfone (OH-s-OSfx). Molecular weight of synthesized sulfonated oligomers were 6000~8000 g/mol and equivalent weight of OH-s-OSfx were achieved 92~96% of targeted ones. OH-s-OSfx was functionalized with Allyl Chloride to convert thermally reactive oligomers, Al-s-OSfs. PEMs were fabricated from Al-s-OSfs 3wt% solution in DMSO. After removing most of DMSO for 12 hours at 80 °C, in-situ thermal polymerization and cross-linking reaction was carried out over 200 °C of temperature under Nitrogen atmosphere. Membranes (expressed as X-Al-s-OSfs) obtained by thermal polymerization and cross-linking were treated for conversion to proton form PEM with the same method in perfluorinated PEM, such as Nafion® from DuPont.

Results and discussion

Ionic conductivity and methanol cross-over of X-Al-s-OSfs membranes were measured at room temperature and shown in Figure 1. Ionic conductivity of membranes was increased with sulfonation degree as expected. The method ① for post treatment showed very low ionic conductivity in the membranes X-s-OSf 55, X-s-OSf 64, and X-s-OSf 73 even though those membranes had sulfonation degree over 50%. After post treatment with method ②, ionic conductivity of X-Al-s-OSf 73, X-Al-s-OSf 64, and X-Al-s-OSf 55 membranes was dramatically increased by twice or three times. X-Al-s-OSf 73 showed ionic conductivity as high as 0.07 S cm⁻¹ of.

X-Al-s-OSf 55, X-Al-s-OSf 64, and X-Al-s-OSf 73, which show high ionic conductivities, were tested for methanol cross-over. Measured methanol permeability of X-Al-s-OSfs membranes, 5*10⁽⁻⁸⁾ cm²/sec was just 2~3% of that of Nafion 112, and one order less than that of reported rigid rod polymer membranes for DMFC.⁷ Network structure due to cross-linking is considered to be a key-feature which

decreases methanol cross-over very much even though higher IEC. X-Al-s-OSf 73 membrane showed high ionic conductivity of 0.07 S/cm. Moreover, despite much higher IEC of X-Al-s-OSf 73 of 2.2 mmol/g than Nafion (0.9 mmol/g) it had very low methanol cross-over compared with Nafion membrane. Such unprecedented properties (high ionic conductivity and low methanol cross-over) also verify that a cross-linked network effectively suppressed a swelling behavior of the membrane with high sulfonation degree.

Conclusions

In conclusion, thermally reactive cooligomers were synthesized and fabricated for getting polymer electrolyte membrane followed by thermal cross-linking. Membrane XL-PES-70-H showed 0.07 S cm⁻¹ of ionic conductivity and 5.5 * 10⁽⁻⁸⁾ cm²/s of methanol cross-over. Those values correspond to a methanol permeability over 95% lower than Nafion membrane while ionic conductivity is comparable (~80%) to that of Nafion membranes. Thermally reactive cooligomer with higher ionic groups made it possible that ionic groups were distributed homogeneously in PEM and insoluble despite of high IEC. Ionic conductivity was increased with sulfonation degree but methanol cross-over was not increased with high IEC. Therefore, cross-linked network structure of our membrane by thermal cross-linking of allyl oligomers is the most important technological feature which achieved high ionic conductivity and low methanol cross-over for DMFC applications.

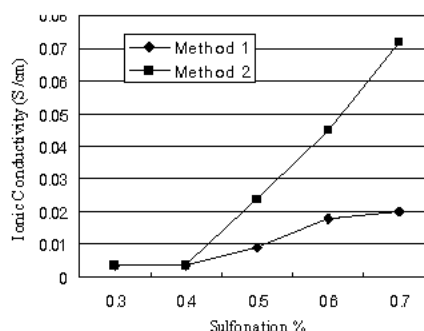


Figure 1. Ionic Conductivity of X-Al-OSfx

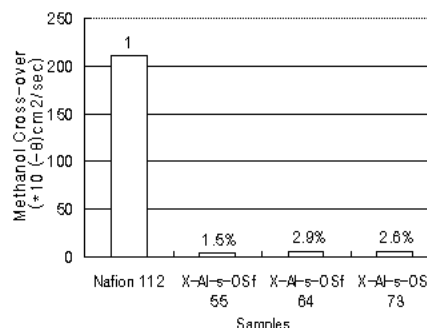


Figure 2. Methanol Cross-over of X-Al-OSfx

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