Composite polymer electrolyte membrane for high temperature operation of DMFC

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The fuel cell technology has been considered as a promising alternative for future energy needs and cleaner environment. The fuel cell is the electric chemical reaction device which converts the chemical energy of the fuel to direct electrical energy. Among the several kinds of fuel cells, direct methanol fuel cells (DMFCs) is one of the most attractive power sources for a variety of wide applications from vehicles to portable electrical equipment.

Recently, the operation of DMFC at temperature above 100°C is receiving worldwide attention in order to decrease the complexity and increase the efficiency. In high temperature, the methanol crossover could be decreased and the catalytic reaction could be enhanced. Unfortunately, however, currently used perfluorosulfonic membranes do not sustain the prolonged operation at temperatures higher than 90°C. It is due to dehydration phenomena occurring at high temperatures, with consequent lower conductivity and performance losses. For the overcome of this drawback, non-fluorinated electrolyte membrane have been considered. Sulfonated polysulfone are primarily chosen because of their high chemical and thermal stability, and also because of the convenient sulfonation procedures. In this study, we prepared sulfonated polysulfone-based composite membranes. Various polymers including soluble polyimide and poly(vinylidene) were blended with sulfonated polysulfone to enhance the thermal stability of sulfonated polysulfone. And, high temperature operations of DMFC were performed with the composite membranes.

For the sulfonation of polysulfone, the polysulfone was dissolved in dimethylformamide at 0°C, then treated with chlorosulfonic acid. The fine yellow polymer was then separated by filtration and vigorously washed with dichloroethane. Finally, the sulfonated polysulfone polymer was dried in an oven for at least 24h at 80°C for complete removal of solvents. The membranes of sulfonated polysulfone were cast on a glass petri dish. Thermal analysis of the sulfonated polysulfone reveals high thermal stability and good proton conductivity. The proton conductivity was increased with operating temperature. The proton conducting mechanism generally involves an activation barrier and thus the relationship between the ionic conductivity and temperature can be expressed by the Arrhenius law.

$$\sigma = A \exp \left( - \frac{E_a}{RT} \right)$$

where $\sigma$, $A$, $E_a$, $R$, and $T$ denote the proton conductivity, frequency factor, activation energy for conduction, gas constant and temperature, respectively. The proton conductivity of sulfonated polysulfone membranes were well correlated with the temperature. As increasing the temperature, the proton conductivity of sulfonated polysulfone membrane was enhanced.

The methanol crossover rate is the crucial factor in direct methanol fuel cell. In general, the transport of methanol and water through conducting polymer membrane is a complex process. At a whole experimental temperature, the methanol crossover of sulfonated polysulfone membrane was quite lower than that of Nafion® membrane. The hydrocarbon chain in polysulfone membrane could efficiently block the methanol crossover.

The performance of the single cell was measured at various cell temperature (40, 80, 120, 160, 200 °C). The power output was increased with the cell temperature up to 160 °C. The highest cell current density of sulfonated polysulfone at 0.3V was 200mA/cm² at 160°C. The improved performance at high temperature should be increased by the enhanced proton conductivity and reduction of the methanol crossover.

Figure 1. Proton conductivity of sulfonated polysulfone membrane with temperature

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Reference
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