**Fabrication and Characteristics of PSS / G-Ch Hybrid Membrane for DMFC**

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**Highlights**

* PSS / G-Ch hybrid membranes were prepared.
* The methanol permeability of membranes suppressed by GA cross-linked.
* Fabricated membrane have about equal methanol permeability with Nafion 117.

**1. Introduction**

The direct methanol fuel cell (DMFC) have attracted considerable attention in fuel cell technology owing to their stable operation, high energy efficiency, portable power source and low environmental burden for mobile electronic devices [1-3]. Protons transfers from anode to cathode are important components in a polyelectrolyte membrane (PEM) with a DMFC system. In addition, methanol crossover (MCO) is another important component. MCO is phenomenon that methanol is transported to the cathode, which decreases the fuel cell efficiency [4, 5]. Thus, both high proton conductivity and low methanol permeability are required for PEM of DMFC. However, these two factors are trade-off relationship. Because, though existence of water is indispensable for protons transfers so that water has methanol and high affinity. In our study, a glycol chitosan (G-Ch) and a sodium salt of polystyrene sulfonate (PSS) were selected as materials of membrane [6]. G-Ch, which is water-soluble derivative of chitosan, can prepare uniform aqueous solution without an acetic acid. This characteristic is used in a protonation of amino groups after mixture of anionic polymer. In addition, we expected to PSS having many sulfonate groups gives PEM the high proton conductivity. We investigated about preparation methods and characteristics in PSS/G-Ch hybrid membrane cross-linked with glutaraldehyde (GA). In addition, we estimated superiority of the hybrid membrane by comparison with Nafion 117.

**2. Methods**

The PSS powder and G-Ch powder of predetermined quantity were added to ion exchanged water, and it was stirred and was dissolved at 298 K for 24 hours. This PSS and G-Ch mixture solution was cast on the glass petri dish and placed at 298 K for three days. Subsequently, dry membrane was immersed by acetic acid/methanol aqueous solution (volumetric ratio, 5:80:15) for 24 hours to form polyionic complexes between the sulfonate group of PSS and the amino group of G-Ch , as shown in Scheme 1 (a). Furthermore, it was immersed by GA/methanol solution of predetermined concentrations for 24 hours to cross-linked between amino groups of G-Ch, as shown in Scheme 1 (b). Finally, the free-standing membrane was obtained by desorption from glass petri dish with immersing in ion-exchanged water for 24 hours. The obtained membrane was saved in ion-exchanged water. In this work, notation of a membrane sample is described as follows; PSS/G-Ch/GA. The number of notation stands for the gravimetric concentration of PSS in cast solution, the gravimetric concentration of G-Ch in cast solution, and the volumetric concentration of GA in methanol solution, respectively.



**Figure 1.** The scheme of the formation of polyionic complexes between PSS and G-Ch and the cross-linked G-Ch.

**3. Results and discussion**

In this study, we prepared PSS/G-Ch cross-linked by GA hybrid membrane for DMFC, and measured structure of hybrid membrane, water content, methanol permeability, and proton conductivity. From the values of proton conductivity and methanol permeability, we calculated the selectivity parameter. Higher selectivity parameter means that a performance of a hybrid membrane is superior. Table 1 shows the properties of PSS/G-Ch hybrid membranes and Nafion 117 membrane [7]. For the membrane cross-linked by GA, the swelling of PSS/G-Ch hybrid membrane controlled, the methanol permeability reduced, and the proton conductivity increased. The experimental results revealed that the 4/2/2 hybrid membrane exhibited high performance compared to the other composition membranes.

**Table 1.** The properties of PSS/G-Ch hybrid membranes and Nafion 117 membrane.



**4. Conclusions**

It reveals that the chitosan based hybrid membrane of polyionic complexes have higher proton conductivity value than that of the other polyionic complexes membranes, but lower than that of Nafion membrane, and have just about equal methanol permeability as compared with Nafion. From now on, we think of using the other cross-linking agent to decrease the water content and methanol permeability, more and more PSS to increase the proton conductivity.

**References**

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