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Using a novel sulfonated silica nanoparticles for Nafion® membrane for direct methanol fuel cell

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1. Introduction

Perfluorinated sulfonated ionomers like Nafion® membranes show excellent mechanical properties, chemical stability and high proton conductivity for using in direct methanol fuel cell (DMFC). However, high fuel crossover encountered with Nafion®, especially for using at high temperatures. To improve the stability of Nafion® in methanol, many efforts have been done on formation of Nafion®–silica hybrid membranes [1–2]. Incorporation of silica into Nafion® would certainly decrease its concentration of sulfonic acid groups and lower its proton conductivity. Rhee et al. used a sulfonated layer clay to form polyelectrolyte–clay nanocomposites [3]. The sulfonated clay would simultaneously stabilize the polyelectrolytes and increase the proton conductivity. Basing on the above concepts, in this work we modify Nafion® with a sulfonated silica nanoparticles. The membrane properties and cell performance were examined and discussed.

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2. Results and discussion

Sulfonated silica nanoparticles (S-SNP) were obtained from a two-step modification on commercially available silica nanoparticles, as shown in Fig. 1 [4]. The modified silica nanoparticles could be well dispersed in N′ N-dimethylacetamide (DMAc) to form a clear solution. Direct mixing the solutions S-SNP and of Nafion® in DMAc in various ratios resulted in Nafion®–silica solutions. These solutions were ready for casting to form Nafion®–silica nanocomposite membranes. In this work, Nafion®–silica nanocomposite membranes (NSN membranes) possessing 3–10 phr (parts per resin) of S-SNP were prepared.

The NSN membranes were not soluble in DMAc at room temperature to indicate their improved stability in organic solvents. This stabilization was due to the formation of physical cross-linked structures in NSN membranes with the strong interaction between the sulfonic acid groups of Nafion® and S-SNP. Under heating, NSN membranes readily dissolved in DMAc to demonstrate their physical cross-linked structure. Thermogravimetric analysis (TGA) on

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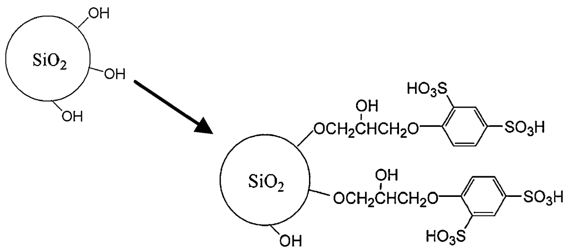

Fig. 1. Chemical structure of sulfonated silica nanoparticles.

NSN membranes exhibited that incorporation of S-SNP into Nafion® did not alter its thermal stability and degradation pattern. The TGA results further supported that no chemical linkages formed between Nafion® and silica. The homogeneity of NSN membranes was observed with their appearances and SEM micrographs. All of NSN membranes showed good transparency to indicate that the silica particles did not aggregate in the Nafion® matrix and no microphase separation existed in NSN membranes, which were also demonstrated with the SEM micrographs of NSN membranes. The homogeneity of the NSN membranes was also examined with energy-dispersive X-ray (EDX) Si-mapping. Homogeneous dispersion of silicon in the membranes was observed with all samples.

Fig. 2 showed the proton conductivity of the NSN membranes measured at various temperatures. It was found the NSN membranes showed higher proton conductivity than did the pristine Nafion® membrane. It is demonstrated that using sulfonated nanoparticles to modify Nafion® membrane could compensate the proton conductivities of the membranes.

3. Conclusions

From the preliminary results, it was concluded that using sulfonated silica nanoparticles to modify Nafion® could result in Nafion®–silica nanocomposite membranes. These nanocomposite membranes exhibited improved stability, reduced methanol crossover and comparable proton conductivity for comparing with pristine Nafion® membrane. Single-cell performance in DMFC with using the Nafion®–silica nanocomposite membranes are under studies.

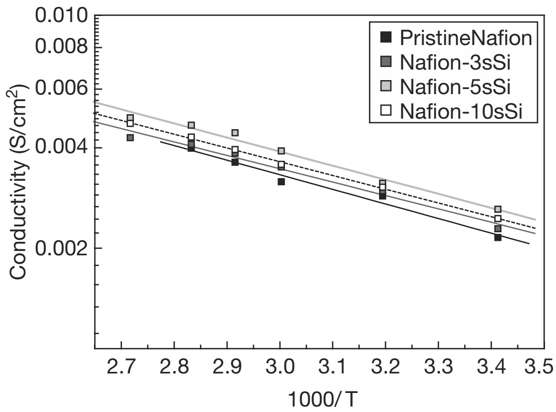

Fig. 2. Proton conductivity measured on the prepared membranes.

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