PREPARATION OF SULFONATED SILICA NANOPARTICLES AND THEIR APPLICATIONS IN PROTON EXCHANGE MEMBRANES FOR DIRECT METHANOL FUEL CELLS

Ying-Ling Liu, Yu-Huei Su, Suryani and Juin-Yih Lai

R&D Center for Membrane Technology and Department of Chemical Engineering, Chung Yuan Christian University, Chungli, Taoyuan 32023, Taiwan

Introduction

Proton exchange membrane fuel cells (PEMFC) using hydrogen or methanol as fuels are one of the most studied systems for renewable energy. Since the perfluorinated sulfonated ionomers based PEMs, like Nafion® membranes, are not satisfied due to their high methanol permeability and high cost for using in direct methanol fuel cells (DMFCs), cheap and qualified alternatives of Nafion® are being sought for using as PEMs in DMFC.

Polymeric materials for uses in DMFCs must have critical proton conductivities. Since the proton conductivity of a polyelectrolyte usually is proportional its ion exchange capacity (IEC), i.e. the concentration of sulfonic acid groups, polyelectrolytes with high IEC values (high concentrations of sulfonic acid groups) are expected. However, the stability of these polyelectrolytes in methanol fuels is usually not as good as enough. Stabilization of PEMs is therefore critical to improve their performance. One workable method is formation of organic–inorganic nanocomposite membranes [1-4]. We study the effect of addition of sulfonated silica nanoparticles to polyelectrolytes on their properties and performances for PEMs in DMFCs. Nanocomposite polyelectrolyte membranes with un-modified silica nanoparticles are also prepared and studied to investigate the effect of sulfonic acid groups on silica nanoparticles in PEM modifications.

Experimental

Materials
Silica nanoparticle (SNP) with a size of 10–20 nm was purchased from Nissan Chemical Company. Sulfonated silica nanoparticles (SNP-SA) were prepared in the Lab. through surface modification on SNPs and sulfonation according to the methods reported in the literature [5]. Sulfonated poly(phthalazinone ether ketone) (SPPEK) with a degree of sulfonation of 1.23 (equivalent weight of sulfonated group = 514 g mol^{-1}) was obtained from direct sulfonation on poly(phthalazinone ether ketone) [2]. Sulfonated poly(arylene ether ether ketone ketone) (SPAEEKK) copolymer (degree of sulfonation = 0.67) was prepared according to the reported method [6]. Polybenzimidazole (PBI) was synthesized by polycondensation reaction according to methods described elsewhere [7].

Measurements
Proton conductivity of the membranes was measured with a Solartron 1255B frequency response analyzer equipped with a Solartron 1287 electrochemical interface with an oscillation amplitude of 10 mV and a frequency range of 0.1 Hz - 1 MHz. The measurements were taken at 20-80 $^{\circ}$C under a 95% relative humidity.

Results and Discussion

The chemical structures of silica nanoparticles and polyelectrolytes used in this work are shown in Figure 1. Both of the pristine SNP and SNP-SA form homogeneous solutions with the utilized polyelectrolytes and the corresponding polyelectrolyte/silica nanocomposite membranes. Addition of SNP to SPPEK and SPAEEKK significantly reduces their methanol crossovers and increases the PEM stability in methanol fuels. However, due to the lack of sulfonic acid groups of SNP, their nanocomposite membranes exhibit relatively low IEC values and proton conductivities comparing to the un-modified polyelectrolytes. To compensate the proton conductivity reduction, SNP-SA was used to replace SNP in preparation of nanocomposite membranes. The SPPEK/SNP-SA and SPAEEKK/SNP-SA nanocomposite

membranes show increases in proton conductivities comparing to the pristine polyelectrolyte membranes. The increases in proton conductivities could be contributed from the sulfonic acid groups in SNP-SA. However, due to the IEC values of the polyelectrolyte/SNP-SA membranes are still lower than those of the corresponding polyelectrolyte membrane, the high proton conductivities of the polyelectrolyte/SNP-SA membranes should not be only attributed to the increases in the IEC values but also to the morphology effect in the nanocomposite membranes.
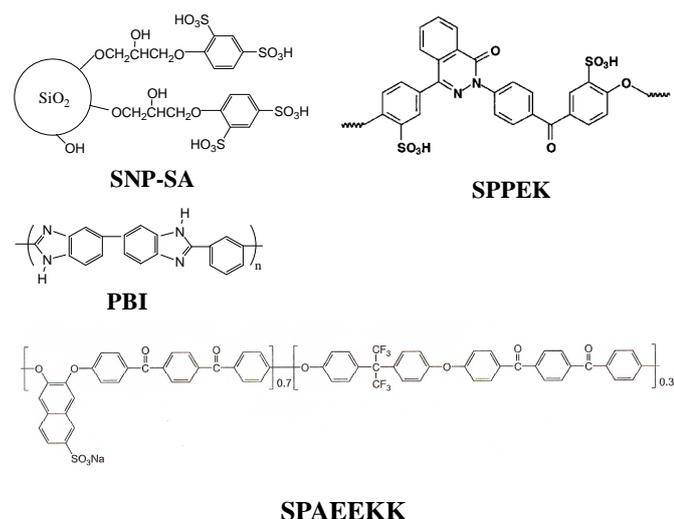

Fig. 1 The chemical structures of sulfonated silica nanoparticles (SNP-SA) and polyelectrolyte used in this work.

The presence of SNP-SA induces the formation of sulfonic acid–rich domains in the nanocomposite membranes through the strong interactions between the sulfonic acid groups of SNP-SA and polyelectrolyte. The microphase-separation forms channel-like pathways for proton transporting through the membranes (Figure 2). In addition, the formation of proton-conducting channels in the nanocomposite membranes could be further enhanced with using a relatively flexible polyelectrolyte chains. Therefore, the microphase-separation of sulfonic acid domains and formation of proton conducting channels are relatively obvious and significant in the SPAEEKK/SNP-SA nanocomposite membranes, even though they have relatively low IEC values. Besides, the nanocomposite membranes show relatively low methanol crossovers, so as to exhibit comparable selectivity and single cell performances.
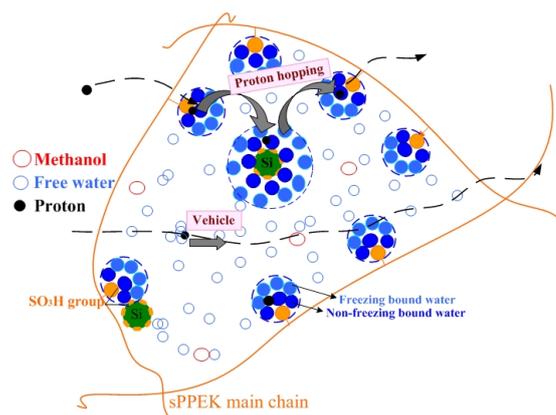

Fig. 2 The formation of sulfonic acid rich domains in SNP-SA based nanocomposite membranes.

SNP and SNP-SA are also suitable for modification of the base-type proton exchange membrane of PBI. Addition of silica nanoparticles alters the acid-doping behaviors and methanol resistance of PBI membranes. The sulfonic acid groups of SNP-SA also bring cross-linking effects to the PBI/SNP-SA nanocomposite membranes and stabilize the membranes. The proton conductivity of PBI/SA-SNP-10 (possessing 10 wt% SA-SNP) membrane is of about 3 folds of that observed with pristine PBI membrane. The selectivity (the ratio of proton conductivity to the methanol permeability) of PBI/SA-SNP-15 is of about 1.3 folds of that of the Nafion® 117 membrane.

Conclusions

Sulfonated silica nanoparticles are effective to modify polyelectrolytes in preparation of high performance proton exchange membranes which show low methanol crossovers, enhanced proton conductivity, and high selectivity.

References

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