

SILICA NANO-PARTICLE/POLYELECTROLYTE NANOCOMPOSITE MEMBRANES FOR DIRECT METHANOL FUEL CELLS

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Modification on PEMs to improve their thermal and chemical stability and to depress their methanol crossover is another approach to provide high performance PEMs. Organic-inorganic nanocomposites represent a useful approach to PEM modification.¹ Layered clays and silica nanoparticles are two major inorganic reinforcements in PEM modifications. Clay incorporation into PEMs introduces a winding pathway for a methanol molecule to reduce their methanol crossover. The presence of silica nanoparticles in PEMs keep their hydrophilicity to maintaining water and improve their thermal and mechanical stability. The methanol crossover of PEMs is also depressed with formation of polyelectrolyte-silica nanocomposites as reduction of their swelling degree in methanol fuel solutions.

Incorporation of nanosized inorganic reinforcements to proton exchange membranes, although brought about membrane stabilization, however would certainly lower their ion exchange capacity and proton conductivity. To overcome this problem, Lee et al² prepared sulfonated montmorillonite to modify Nafion. The prepared composite membranes showed dramatic decreases in methanol permeability and comparable proton conductivity to pristine Nafion membranes. Bébin et al³ also used sulfonated Laponite particles to prepare Nafion/clay-SO₃H composite membranes. The performance of the membrane-electrolyte assembly using the composite membrane is better than the one of a Nafion membrane. The above articles suggested that uses of sulfonated inorganic particles in preparation of polyelectrolytes nanocomposite membranes is an effective approach to improve the proton exchange membrane performances. Instead of clay, in this work silica nanoparticles and their sulfonated forms (silica-SO₃H) were utilized in preparation of polyelectrolyte/silica nanocomposite

membranes. Sulfonated poly(phthalazinone ether ketone) (sPPEK) with a high content of sulfonic acid groups is utilized as the proton conducting material.⁴ The properties of the prepared nanocomposite PEMs are examined and discussed.

The chemical structures of sPPEK polyelectrolyte and silica-SO₃H nanoparticles are shown in Figure 1. Mixing of these two substances in DMAc formed homogeneous and transparent solutions. sPPEK/silica-SO₃H nanocomposite membranes possessing various silica-SO₃H contents (NM-SA-X, X = silica-SO₃H (g)/100g of sPPEK in solutions) were prepared from solution casting on glass plates. All obtained membranes showed high transparency, indicating the silica particles did not aggregate during membrane preparation.

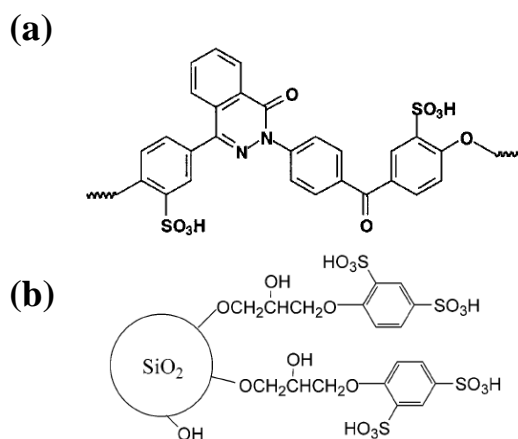


Fig. 1. The chemical structures of (a) sPPEK and (b) surface-functionalized silica nanoparticles.

The nanocomposite membrane possessing 5 phr un-modified silica nanoparticles (NM-silica-5) might move toward membrane surface during membrane preparation due to the relatively low surface energy of silica. However, this nanoparticles migration did not occur for silica-SO₃H particles in NM-SA-5 membrane. Surface elemental analysis on

nanocomposite membranes were done with an EDX. NM-silica-5 membrane showed a silicon content of about 5.4 % with addition of 5 phr un-modified silica nanoparticles. However, only about 0.8% silicon was detected on NM-SA-5 membrane surface. Un-modified silica nanoparticles could move toward membrane surface and sulfonated silica nanoparticles did not. The presence of sulfonic acid groups on silica surfaces restricts their motion in sPPEK matrix. The restriction might be due to the strong interaction between the sulfonic acid groups of silica-SO₃H and sPPEK, as un-modified silicon could not form such interactions. The -SO₃H/-SO₃H interaction might gather silica-SO₃H particles together. In addition, the gathered silica-SO₃H particles should tether to and be surrounded with sPPEK polymer chains. The sPPEK chains also served as separator to prevent from silica-SO₃H particle aggregation.

The strong interaction between silica-SO₃H and sPPEK might bring a physical-crosslinking structure to the nanocomposite membranes, so as to enhance the membrane stability in solvents. Figure 2 shows the water and methanol absorption properties of nanocomposite membranes. All nanocomposite membrane exhibited depressed water and methanol absorption. The absorption amounts of water and methanol leveled off for membranes possessing silica-SO₃H contents above 10 phr. Some water-absorption sites of sPPEK were blocked with addition of silica-SO₃H. This blocking effect could also be attributed to the presence of silica-SO₃H/sPPEK interaction, which reduce the swelling ability of sPPEK in water.

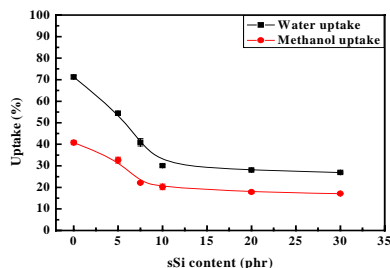


Fig. 2. Water and methanol uptake of sPPEK/sSi hybrid membranes with various sSi contents.

The proton conductivity of the nanocomposite membranes measured at different temperatures is shown in Figure 3. Addition of un-modified silica to sPPEK (NM-silica-5) caused a reduction on sulfonic acid group concentration so as to lower the membrane's proton conductivity. This proton

conductivity reduction can be compensated with using sulfonated silica-SO₃H. NM-SA-5 membrane exhibited higher proton conductivities than did NM-silica-5 membrane. It is also noteworthy that the proton conductivities measured with NM-SA-5 membranes at high temperatures are higher than the proton conductivities measured with sPPEK membrane. It is demonstrated that addition of the sulfonated silica nanoparticles to sPPEK can further enhance its proton conductivity with introduction of additional sulfonic acid groups. Increases in the silica-SO₃H contents of nanocomposites further increased their proton conductivities.

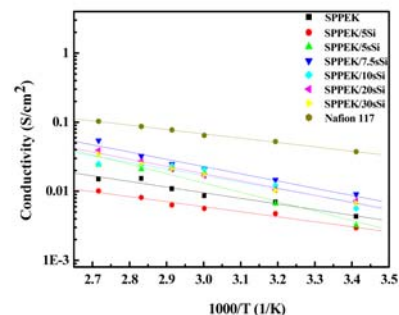


Fig. 3. Proton Conductivity of sPPEK/sSi hybrid membranes with various sSi contents.

The above results indicate that formation of silica-sPPEK nanocomposites is effective to simultaneously reduce their methanol crossover and to increase their proton conductivity. The single cell performances of MEAs with these nanocomposite membranes are under investigation.

References

- [1] Su Y.H., Liu, Y.L., Sun, Y.M. Lai J.Y. Lai, Guiver M.D. and Gao Y. "Using silica nanoparticles modifying sulfonated poly(phthalazinone ether ketone) membrane for direct methanol fuel cell: a significant improvement on cell performance", *J. Power Sources* **155**, 111, 2006.
- [2] Rhee C.H., Kim H.K., Chang H. and Lee J.S. Nafion/sulfonated montmorillonite composite: A new concept electrolyte membrane for direct methanol fuel cells, *Chem. Mater.* **17**, 169, 2001.
- [3] Bébin P., Caravanier M. and Galiano H. Nafion/clay-SO₃H membrane for proton exchange membrane fuel cell application, *J. Membr. Sci.* **278**, 35, 2006.
- [4] Gao Y., Roberston G.P., Guiver M.D. and Jian X. Synthesis and characterization of sulfonated poly(phthalazinone ether ketone) for proton exchange membrane materials, *J. Polym. Sci. Part A: Polym. Chem.* **41**, 497, 2003.