

Self-Assembly Modification of Perfluorosulfonic Acid Membranes for the Application to Direct Methanol Fuel Cells

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Abstract: The mitigation or elimination of methanol crossover for perfluorosulfonic acid fuel cell membranes has been investigated extensively for direct methanol fuel cell applications with the aim of increasing the electrochemical performance and enhancing the utilization rate of methanol. Self-assembly modifications by applying an oppositely charged polyelectrolyte to Nafion membranes were attempted in order to block or reduce methanol crossover while maintaining the other advantageous properties of Nafion membranes. It was reported that anionic polyallylamine hydrochloride (PAH) was the most efficient polyelectrolyte in reducing methanol crossover, and considerable cell performance was obtained even at a methanol feed concentration of 10 M.

Keywords: direct methanol fuel cell, nafion, methanol crossover, self assembly, surface modification.

Introduction

Fuel cell has been studied and developed extensively throughout the world as one of the most feasible next generation clean energy source for the future. The automobile industry has been the major driver for the development. There are many different types of fuel cells, among them proton exchange membrane fuel cell which utilize hydrogen as a fuel seek its major applications in automobile, residential fuel cell, and the portable fuel cell. However, PEMFC in the portable applications faces several hurdles such as the expensive and complicated fuel reformer and bulky hydrogen storage, so that the high cost and space limitation are inevitable considering the mobile environment. Direct methanol fuel cell (DMFC) has been illuminated as an alternative for the battery although it has several disadvantages such as low kinetic response time, high cost as a result of high precious metal ($\approx 8 \text{ mg/cm}^2$) catalyst loading, and methanol crossover etc.

There are a number of applications where the direct methanol fuel cell can provide real benefit based on its high energy density and instantaneous refueling time with the simple exchange of the fuel cartridge.

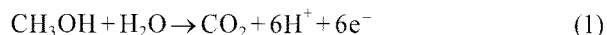
For examples, the next generation of high bandwidth mobile devices, battery charger and military applications

are good niche markets for DMFC since these applications require the supply of higher power density than existing batteries can provide. Consequently, the need for a better battery with a longer operating time is a top priority to the portable electronic device industries and drives the development of micro DMFC among various technologies. There have been prevailing safety concerns on methanol usages in public transportation like airplanes since it is categorized into toxic chemical. However recent International Civil Aviation Organization meeting in 2005 allowed the passengers to carryover methanol cartridges properly packaged into the cabin from 2007 although more permissions from each governments and airlines should be granted.

In spite of the broad debates, the development of efficient DMFC is still of prime interest to many energy storage developers and advanced prototypes have been announced. In the fundamental side among the development efforts, there are two main research streams to overcome its low performance. One is to develop novel anode and cathode catalysts to reduce the kinetic loss. The other is to develop novel membranes having low methanol crossover.

Methanol crossover is the problem that anode fuel, the mixture of methanol and water, diffuses through the ion exchange membrane, typically Nafion of Dupont and reacts with the cathode catalysts as shown below in eq. (1) under the electrochemical operating condition so that it causes voltage loss and reduced fuel efficiency.

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Nafion, developed in 1960s, has been a standard membrane in fuel cell area as well as chloro-alkali industry. Its fuel cell performance, ionic conductivity, longevity, physical and chemical properties became a sole benchmark to the membrane researchers. However, its successful adoption in proton exchange membrane fuel cell was hesitated in direct methanol fuel cell because of the methanol crossover. Now there are numerous research activities in fuel cell arena developing novel membranes satisfying the operating condition of the direct methanol fuel cell at low expense.

Driving forces for methanol crossover are the methanol concentration gradient through the membrane involving the higher fuel concentration, the larger crossover and the electro-osmotic drag related to the proton transport from anode to cathode which becomes substantial at high current densities.¹

Methanol reacting with the cathode catalyst not only reduces the oxygen reduction efficiency but also creates the water flooding which results in the poor mass transport of the air within the gas diffusion layer structure.

In practice, the effects of methanol crossover can be reduced to a large extent by careful design of the MEA structure or by the application of novel membrane materials or cathode catalysts² as well as by optimizing the cell operating conditions such as the cathode hydraulic pressure, the temperature and concentration of the feed fuel, methanol.

Since current study is part of our efforts to mitigate the methanol crossover by means of Nafion modifications, we review the previous efforts related to the Nafion modifications although there have been significant amounts of reports exploiting novel DMFC membranes other than Nafion. Materials investigated for DMFC application are polyaryl-blend-membranes,³ PVA/PSSA blend membranes,^{4,24} PES/sulfonated PSf or sulfonated PEEK membranes,^{5,23} sulfonated SEBS⁶ copolymer and hydrophilic 2-acrylamido-2-methylpropanesulfonic acid and hydrophobic 2-hydroxyethyl methacrylate⁷ copolymer, inorganic modification of sulfonated PEK and PEEK with SiO₂, TiO₂ or ZrO₂.⁸

However, a trade off phenomena between the methanol crossover and ionic conductivity is unavoidable in most of above studies, so practical applications of those membranes are limited. Scott *et al.*'s work¹³ obtained the promising MEA performances based on the PSSA-graft-ETFE or -LDPE membranes although the de-lamination of catalyst layer was a major issue. Other than the efforts to find inexpensive alternatives among hydrocarbon based materials, porous silica inorganic base membranes filled with ionomers were proposed by Yamaguchi *et al.*¹⁶

Since Nafion has been known to be widely adopted commercial fuel cell membrane currently, significant efforts to endow enhanced barrier properties to Nafion while keeping its high ionic conductivity by means of the modification

have been widely executed, e.g., deposition of hydrocarbon or fluoro polymer barrier film onto Nafion by plasma polymerization^{9,10} and coating of PVA barrier layer on both sides of Nafion,¹¹ incorporation of inorganic powders in Nafion matrix, which resulting in the retention of more water due to hydrophilic nature of fillers and the better exclusion of methanol,^{12,17} electroless plating of Pd,¹⁸ and sputtering of Pd on the plasma etched Nafion.¹⁹ Although most of the modification efforts were successful in reducing the methanol crossover, it is very common to find out the results sacrificing the ionic conductivity. It is interesting to note that study of Dimitrova *et al.*¹² showed the enhancement of the conductivity with the sacrifice of methanol permeation rate in spite of the higher crystallinities of the inorganic modified membranes with SiO₂ and molybdophosphoric acid. Yang *et al.*¹⁴ have shown that the Nafion impregnated with zirconium phosphate is capable of the promising performance at high temperature up to 150 °C without the cathode humidification, which is attributed to the improved water retention characteristics of the composite membrane. Similar approach¹⁵ impregnating Nafion's pores with 1-methylpyrrole to reduce the size of the diffusion channel in the matrix of Nafion achieved the reduction of methanol crossover while maintaining the competitive ionic conductivity.

Most of approaches mentioned above were bulk modifications which could be costly and time consuming.

Self assembly layers can be assembled on anionically charged Nafion membrane by alternating exposure to solutions of polyanions and polycations. A reproducible amount of polyelectrolyte is deposited on the oppositely charged reaction sites. Upon exposure in reversely charged polyelectrolyte surface charge of the film can be continuously alternated as wished. Repetitive deposition steps provide a precise control over the total thickness and allow building up films from several Å to mm range. It was revealed that layer-by-layer deposition of linear poly(ethylene imine) (LPEI) on Nafion membrane resulted in lower ionic conductivity that that of commercial Nafion since the crosslinking of sulfonic acid sites limited ionic mobility.²⁰

The interfacial properties of each assembly layers can be modified by the choice of polyelectrolyte types in the film. That is, the hydrophobic portion of the polyelectrolyte endows the new surface properties to the membrane against the methanol molecules in direct methanol fuel cell application. Self assembly methods to reduce the methanol crossover are adopted in several works. Methanol blocking barriers were self assembled nanoparticles of Pd²¹ and Au²² on Nafion 112.

In this study, ionic surfactants and polyelectrolytes were utilized as self assembly layers. We aimed to endow Nafion with the barrier properties against MeOH molecules while maintaining its high ionic conductivity and durability by the method of monolayered and multilayered self assembly methods.

Experimental

Materials. Nafion 115 membranes and 5% solution were obtained from Dupont. Catalysts were from E-Tek, Pt/Ru black and Pt black, for anode and cathode, respectively. Catalyst inks were prepared by combining the appropriate amount of catalyst and Nafion ionomer in alcohol/water solvent mixture. Polystyrene sulfonic acid (M_w 125,000) and polyallylamine hydrochloride (PAH, M_w 70,000) were obtained from Aldrich. FS62 is the anionic fluorosurfactant from Dupont.

Self Assembly Process. Polyelectrolyte solutions for the self assembly process were prepared in the forms of aqueous solutions with appropriate concentrations. Cationic PAH was prepared in the concentration of 0.1 M. Polystyrene sulfonic acid solution was 1.5 wt%. Anionic fluorosurfactant, FS 62 were dissolved in the water at the concentration of 0.2 wt%. Figure 2 shows the manufacturing steps of self assembled Nafion membranes. First Nafion 115 membranes were immersed in the cationic solutions for 2 min followed by thorough washing in DI water in order to remove the excessive unassembled molecules. Further self assembly process was conducted in anionic solutions by similar method. In case of PSSA where the solution is relatively viscous, self assembly was conducted in the environment of sonication which is expected to provide more collisions between the two oppositely charged substances.

Methanol Crossover and Ionic Conductivity. Methanol permeability was measured by the diffusion cell connected to the automatic refractive index meter under the non-current situation at 22 °C.

Proton conductivities of Nafion and surface modified Nafion membranes were measured by ac impedance spectroscopy using a Solatron over a frequency range of 1-10 MHz. Rectangular shaped membrane samples were fully hydrated and placed in four probe conductivity cell.

It is well known that the ionic conductivity strongly depends on the saturation level in the membrane and the temperature. Thus, the measuring cell was kept in a bath at room temperature. The conductivity was calculated from the membrane resistivity according to $\sigma = \kappa^* L/A$, where κ is the resistivity, L is the membrane thickness in cm and A is the surface area of the membrane in cm^2 .

MEA Fabrication. The membrane electrode assembly (MEA) for a single cell operation was fabricated as follows. The electrodes consisted of uncatalyzed carbon papers; in other words, gas diffusion layers and catalyst layers were directly coated on the membrane. Gas diffusion layers were hydrophobized by soaking in liquid PTFE solution before coating the carbon layer. 50% Pt/50% Ru black catalyst was used for the anode catalyst layer, Pt black for the cathode catalyst layer. The catalyst solution was composed of polar solvents, water, catalyst and 30 wt% Nafion solution, which acts as a binder and an electron conductor in MEA geome-

try. It is widely accepted that Nafion binder is located on the electrode catalyst particles as a bridge among the active catalyst sites, as well as between the catalysts and the membranes in the interface. All components were mixed and thoroughly sonicated to ensure the complete dispersion of nanosized catalyst particles. The carbon and catalyst layers were deposited on the carbon paper and on the membrane, respectively, using the spraying method. The five-layer MEA was obtained by hot pressing the gas diffusion layers on both sides of Nafion 112 membrane at 120 °C. Catalyst was deposited at 4 mg cm^{-2} for the anode and 4 mg cm^{-2} for the cathode.

Results and Discussion

Surface modification of anionic polymer, that is, Nafion, is undertaken by immersing it into the solution of the oppositely charged polyelectrolytes. Polyallylamine hydrochloride (PAH) was adopted as a cationic polyelectrolyte due to its high reactivity, and polystyrene sulfonic acid (PSSA) and fluoro surfactant having sulfonate end group, FS 62 from Dupont have been utilized as anionic polyelectrolytes. Structures of them are shown in Figure 1. Self assembly modification was carried out by dipping the membranes into the oppositely charged polyelectrolytes during definite duration, and then un-reacted surface polyelectrolytes were rinsed out by immersing the membranes into the DI water. Similar steps were performed consecutively for the preparation of multilayered self assembly as illustrated by Figure 2.

First of all, the effects of membrane dipping time and concentration of polyelectrolyte solution were illuminated for the case of PAH adsorption on Nafion in Figure 3. Nafion membranes were dipped into the 0.01 M solution of PAH for 5 to 30 sec in order to clarify the effects of self assembly

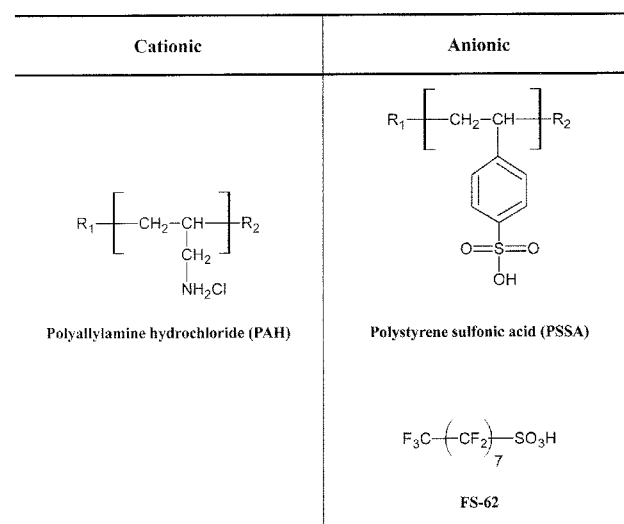


Figure 1. Surfactants and polyelectrolyte utilized for the surface modification of Nafion.

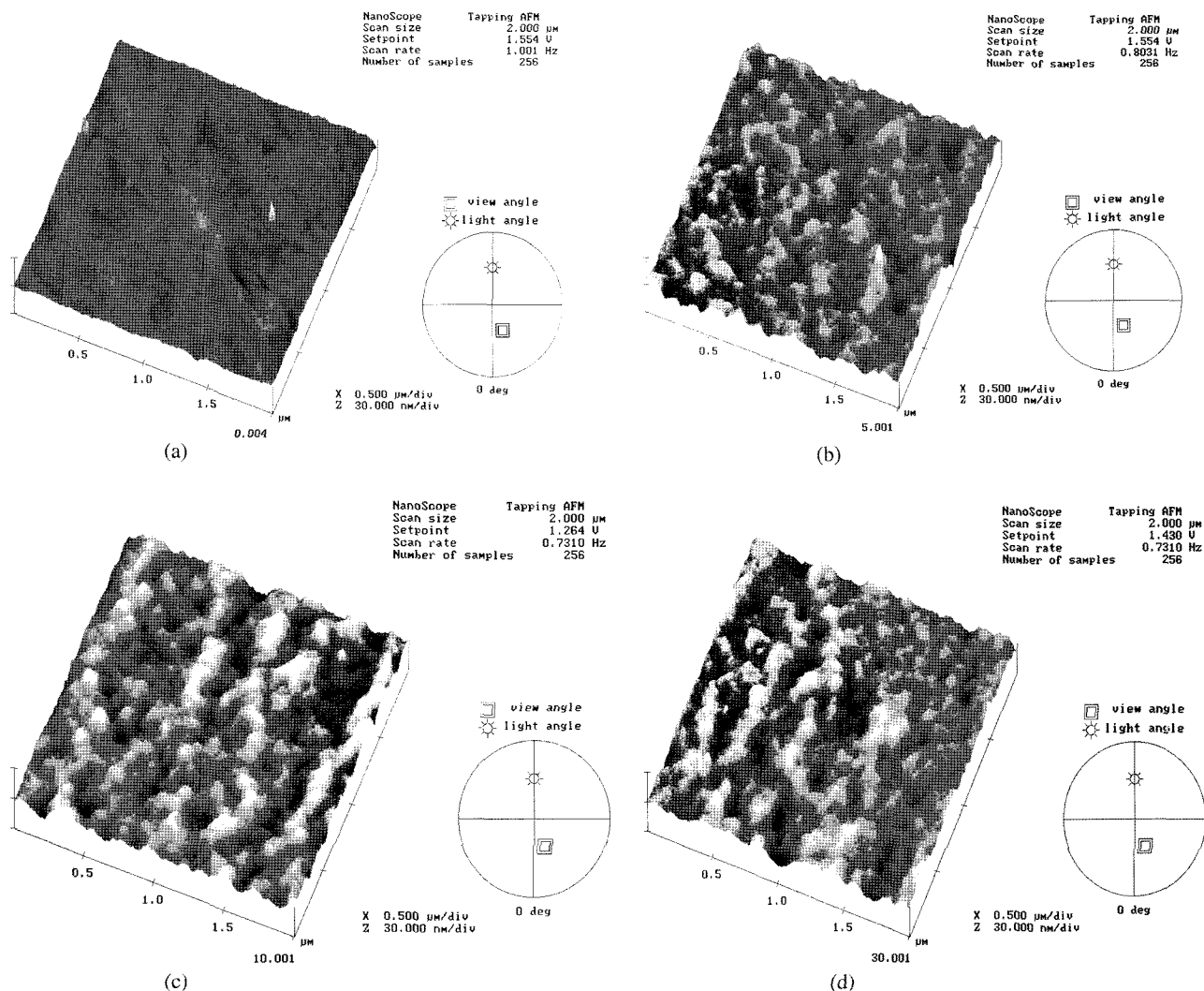


Figure 4. AFM pictures of surfaces of PAH assembled Nafion membranes according to the dipping time; (a) intact Nafion 0 sec, (b) 5 sec, (c) 10 sec, and (d) 30 sec.

It was observed from AFM study that roughness increased more than 2 times with the introduction of first layer of PAH molecules and further increased more than 3 times for PAH+FS-62 double layer membrane compared to that of intact Nafion membrane. It is believed that double layer self assembly structure was successfully formed by alternative exposure to PAH and FS-62 solutions. Membrane resistance was measured for mono layer and double layer self-assembled membranes as shown in Figure 6. It was obvious that resistance of PAH assembled membrane increased due to the introduction of thin cationic polymer electrolyte layer. However it is interesting to note that resistance of double layer membrane is lower than that of mono layer membrane even though the roughness of double layer membrane is larger than that of mono layer membrane which is induced by presumably thicker layer. It can be rationalized that more water molecules trapped in the thicker double layer structure contributed to reduced resistance.

Effects of self-assembly layers on electrochemical performance were investigated for the membrane electrode assemblies fabricated from intact Nafion, PAH assembled Nafion, PAH and FS-62 assembled Nafion membranes. From Figure 7, it was found that MEA of PAH assembled membrane obtains the highest cell performance among three membranes for 2 to 10 M methanol feed concentrations. Benefit of self-assembly layer is significantly announced for extremely high feed concentration. Especially at 10 M feed concentration, MEAs fabricated with mono layered and double layered membranes obtain approximately 90 mA/cm² of current density at 0.4 V meanwhile intact Nafion based MEA shows negligible current density due to the mixed potential originated from high methanol crossover. This phenomenon proves that self-assembled layers block or reduce the methanol crossover by modifying the membrane surface properties. However for 2 and 5 M feed concentrations, MEA of double layered membrane shows lower cur-

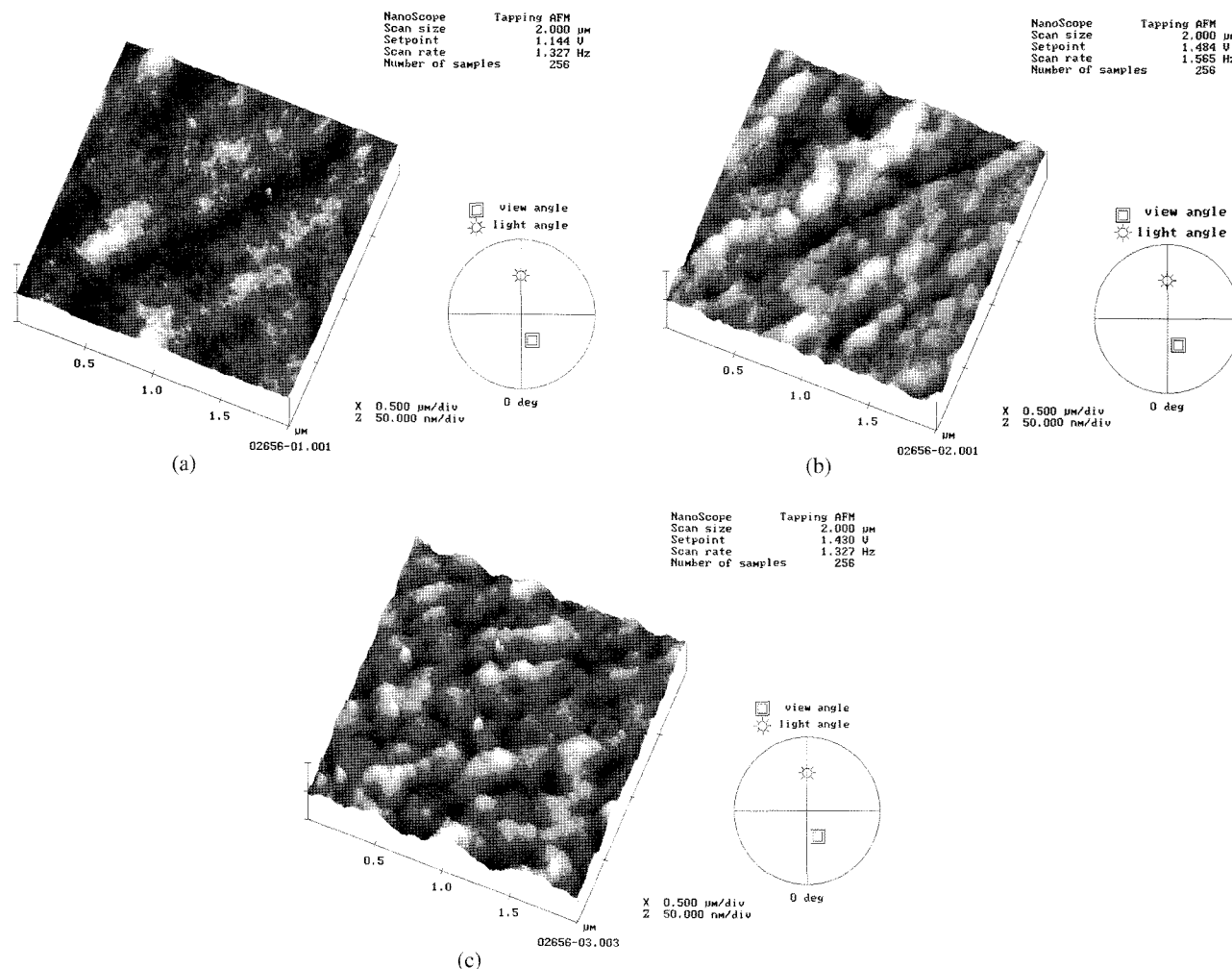


Figure 5. AFM pictures of surfaces of self assembled Nafion membranes; (a) intact Nafion, (b) Nafion+PAH assembled surface, and (c) Nafion+PAH-FS62 double assembled surface.

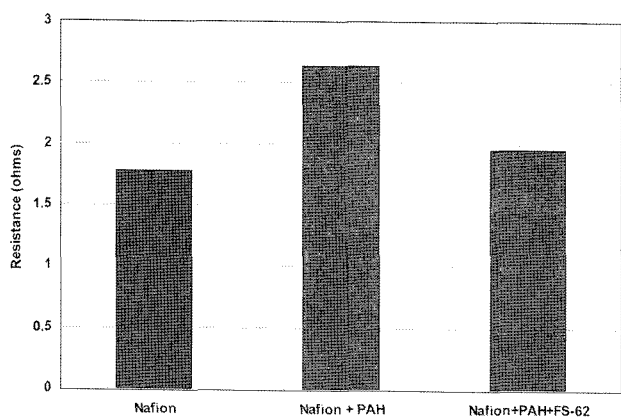


Figure 6. Effect of self assembly layer on the membrane resistance.

rent density than that of MEA of intact Nafion. Increased ionic resistance induced by the assembly layer resulted in reduced electrochemical performance. Thus, it can be inferred that there are the optimum conditions of self-assembly

materials and layers according to the feed concentration of methanol fuel. The electrochemical performance of MEA is largely affected by not only methanol crossover but also ionic conductivity of membrane, in this study, the surface ionic conductivity which resulted in the degree of ionic channel in the interface during MEA fabrication.

Overall it was believed that PAH mono layer on the membrane acts as a adequate barrier for methanol fuel without limiting ionic contact significantly between the electrode catalyst and perfluoro sulfonic acid membrane during MEA fabrication. In order to clarify the effect of the triple self-assembly layer on Nafion membrane, polystyrene sulfonic acid (PSSA) was newly adopted as an alternative anionic polyelectrolyte since FS-62 with single reaction end group cannot accept consecutive opposite reaction group. It is shown that ionic conductivity and methanol permeability are decreasing according to adding more self-assembly layers alternatively on Nafion membrane in Figure 8. It is reasonably understood that the thicker self assembly layer the less ionic conductivity and methanol permeability. In Figure

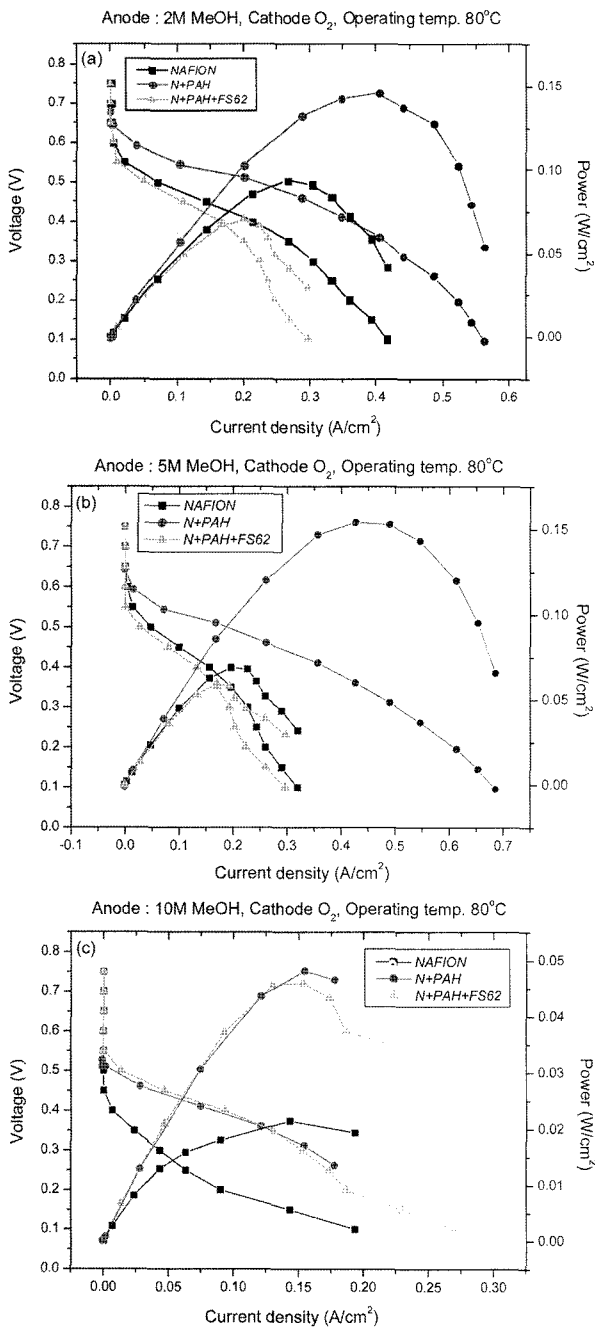


Figure 7. Polarization curves according to the change of feed concentrations of (a) 2 M, (b) 5 M, and (c) 10 M MeOH at O₂ 1000 cc, operating temperature 80 °C.

9 the effects of double- and triple-layer on Nafion membranes in terms of the electrochemical performance of MEA are similar to that found in Figure 7(b). That is, protonic transport through the interface of MEA is substantially hindered due to the reduced free sulfonic acid groups in Nafion and ionic barrier layer of PAH in self-assembly.

In summary, effects of self-assembly modification of Nafion membranes were demonstrated positively for the

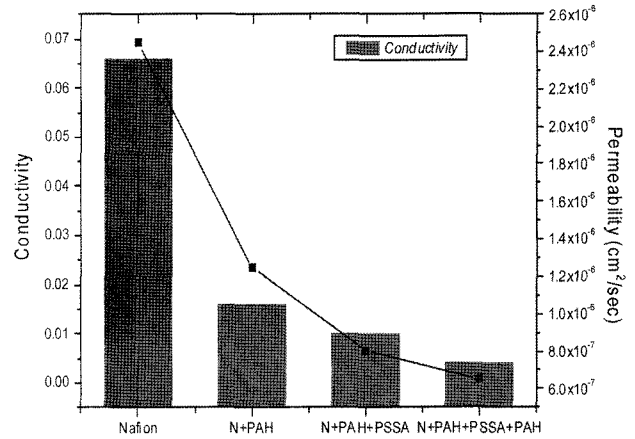


Figure 8. Permeability and conductivity of Nafion 115 and PAH, PSSA self assembled multi layer membranes.

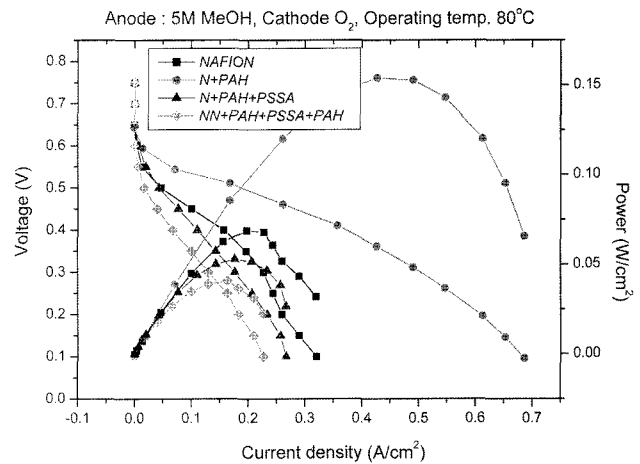


Figure 9. Electrochemical performances of Nafion and PAH and PSSA assembled Nafion.

reduction of methanol crossover and considerable IV performance especially at high concentration of feed methanol. Reduced methanol crossover while maintaining high ionic conductivity and durability of perfluorosulfonic acid membranes by optimizing the type of polyelectrolyte, the number of layer and the assembly process will result in enhanced cell performance and increased fuel cell operating time for the given volume of fuel cartridge in direct methanol fuel cells.

Conclusions

Surface modification of perfluorosulfonic acid membrane was carried out by the introduction of oppositely charged molecules on anionic Nafion membranes in order to reduce the methanol crossover. It was found that methanol crossover properties were significantly affected according to the change of reaction time, concentration and type of self-assembly molecule as well as the number of self-assembly layer.

In consequence, the electrochemical performances of membrane electrode assemblies made from PAH self-assembly modified membranes were moderately enhanced presumably due to the reduction of methanol crossover especially in high feed concentration of 10 M while that of intact Nafion membrane based MEA was negligible.

It was revealed that the type of self-assembly molecule and the number of self-assembly layer should be optimized since ionic conducting channel in the electrode is highly critical for the electrochemical performance.

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