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Characterization of Nafion/Pt/Polypyrrole Composite Membrane Prepared by Chemical In-situ Polymerization for DMFC

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Abstract : Nafion/Pt/Polypyrrole composite membranes were fabricated by chemical in-situ polymerization of pyrrole monomers with Pt precursors in Nafion matrix for DMFC. We demonstrated that positively charged pyrrolinium groups of polypyrrole particles were co-interacted with sulfonic groups of Nafion as verified by FT-IR results.

Mutual interaction between Nafion-SO₃⁻ (or negatively charged Pt precursors) and Polypyrrole -NH₂⁺ influenced the physical properties of pristine Nafion. Thermal property, proton conductivity, methanol permeability, and cell performance of pristine and modified Nafion were analyzed for an application of DMFC membrane. Thermal stabilities of sulfonic groups and side chains in Nafion/Pt/Polypyrrole composite membranes were higher than those of Nafion, due to mutual interaction between sulfonic groups of Nafion and pyrrolinium groups of polypyrrole. Methanol permeabilities of Nafion/Pt/Polypyrrole composite were reduced more than proton conductivities with the increase in the content of Pt particles. As a result of that, the enhancement of cell performance by Nafion/Pt/Polypyrrole O2 relative to Nafion was more pronounced under the specific experimental condition such as high temperature and more concentrated methanol solution.

1. Introduction

Recently, much attention has been focused on direct methanol fuel cell (DMFC) as an attractive energy generating system in the field of small and portable electrochemical or electronic devices such as cellular phones and laptop computers. Although DMFC has advantages over hydrogen-based fuel cells in terms of fuel handling and simple design owing to the use of methanol as safe fuel, there is a severe problem that the methanol crossover from

anode through membrane to cathode by electroosmotic drag and diffusion decreases the overall performance of the cell due to fuel loss and mixed potential. Among various polymer electrolyte membranes (PEMs) for proton conduction, Nafion is used as good proton conductor with reasonable chemical and thermal stability. Although Nafion obtains appropriate physical properties such thermal and mechanical properties owing to its pristine structure for an application of DMFC membrane, it is very difficult to reduce the methanol crossover with maintaining considerable proton conductivity,

because ionic clusters are the transport pathway of methanol as well as proton.

To overcome above trade-offs for DMFC, many strategies have been investigated to improve cell performance by reducing methanol crossover. Amongst them, Nafion/conducting polymer composites have been extensively studied to apply into electro dialysis and sensor as well as PEMs due to their extraordinary properties. Pickup and his coworkers demonstrated the chemical in-situ polymerization mechanism of pyrrole in the Nafion matrix and the enhancement of the performance in DMFC. We reported that the nano-sized polypyrrole particles were mainly present near the surface rather than the internal space by controlling the concentration and diffusion time of pyrrole monomers.⁽¹⁾ In addition, some researches indicated that pyrrole monomers were diffused into and in-situ polymerized at only one side of membrane by using diffusion method, thereby controlling the location of thin layer among two faces of Nafion matrix. In the case of electrochemical synthesis compared to chemically oxidative polymerization, the rate, extent, and location of polymerization could be controlled by electrochemical condition such as voltage or current as well as polymerization time and monomer concentration. However, few studies have been undertaken on the application of Nafion/conducting polymer/metal composite system into an electrolyte for fuel cells. Herein, we report the effective synthesis and surface characterization of Nafion-based composite membrane in connection with polypyrrole-Pt particles and its physical properties for an application of an electrolyte for DMFC.

2. Experimental Methods

2.1 Synthesis of Nafion/Pt/Polypyrrole Composite Membrane

Nafion membranes were prepared as follows.⁽²⁾ The pretreated Nafion membranes were dried at room temperature (25 °C) under vacuum for 24 h. Pyrrole monomers were dispersed in deionized water and controlled to the specific concentration at 0.1 M. The Pt precursors were mixed with an aqueous pyrrole solution, dispersed by sonification, and controlled to the wanted concentration ranged from 10^{-4} to 2×10^{-2} M.

The prepared Nafion membranes were immersed for 5 min in an aqueous pt-dispersed pyrrole

solution. To in-situ polymerize the pyrrole monomers in an aqueous solution via oxidative polymerization by an oxidant, they were immersed in 30 wt% H₂O₂ for 5 min at room temperature. After the in-situ polymerization, Pt precursors were reduced by 2 M NaBH₄ and washed by deionized water respectively for 1 h at 80 °C. The modified membranes were post-treated by 2 M methanol and washed by deionized water for 1 h at 80 °C respectively, in order to remove the unreacted pyrrole monomers. All samples were treated with nitric acid and sulfuric acid to change all the composite membranes into an H form. In order to prevent oxidative degradation of polypyrrole from acidic components, nitric and sulfuric acid were diluted into 1M and acid-treatment was performed for 1 hour at 80 °C, respectively. Each acid treatment was followed by washing step with deionized water. The obtained composite membranes are notated as Nafion/Pt/Polypyrrole 01 at 1×10^{-4} M, Nafion/Pt/Polypyrrole 02 at 5×10^{-3} M, Nafion/Pt/Polypyrrole 03 at 1×10^{-2} M and Nafion/Pt/Polypyrrole 04 at 2×10^{-2} M Pt precursor with 0.1 M pyrrole monomers.

2.2.1 Characterization

In order to prove mutual interaction between pyrrolinium groups of polypyrrole and sulfonic groups of Nafion in the composite membranes, we analyzed FT-IR spectroscopy. In addition, we used TGA, AC impedance spectroscopy, and refractometer to measure thermal and transport properties (i.e., proton conductivities and methanol permeabilities) of membranes. Cell performance was evaluated by using a DMFC unit cell and measured with a potentiostat (263A Power Booster) which recorded the cell potential from the circuit voltage under constant current conditions. Carbon papers (TORAY) were wet-proofed and coated with gas diffusion layers and subsequent electrocatalyst layers. Membrane Electrode Assembly (MEA) was manufactured as follows this literature.⁽¹⁾ The cathode electrode with Pt (unsupported Pt Black, Johnson-Matthey Inc.) loading of 2 mg/cm² and the anode one with Pt/Ru (unsupported Pt/Ru 50/50 (atom/atom) black, Johnson-Matthey Inc.) loading of 2 mg/cm² were prepared by blushing method. Its active area was 2cm×2cm. All electrodes were impregnated with NafionTM ionomer solution (Sigma-Aldrich). Two electrodes and polymer membrane were hot-pressed at 120 °C and 100 kgf/cm² for 2 min. The performances of all

samples were evaluated at room temperature under atmospheric conditions. 3 M or 6 M methanol solution was supplied to the anode side of the single cell at the rate of 3 cc/min, whereas oxygen gas was supplied to the cathode side of the single cell at the rate of 300 cc/min. Measurement range of current was from 0 to 1A.

3. Results and Discussion

FT-IR spectra show the symmetric SO_3^- stretching vibration bands of dried Nafion, hydrated Nafion, dried Nafion/Polypyrrole, and dried Nafion/Pt/Polypyrrole 02 and 04 around 1050 cm^{-1} . The shift of this peak was induced by the changes in polarization of the S-O dipole by means of the effect of chemical environment or surrounding. When sulfonic groups of Nafion were interacted with cations or positively charged functional groups, the location of symmetric SO_3^- stretching band was changed. Furthermore, the degree of hydration affects significantly the peaks of sulfonate groups which are the dissociation forms of sulfonic groups. Thus, the shift of SO_3^- peak in hydrated Nafion and dried composite membranes relative to dried Nafion, was associated with the changes in mutual interaction between sulfonic groups of Nafion and counterions of ionic surrounding. In a similar manner to Nafion/Polypyrrole system,⁽²⁾ positively charged pyrrolinium groups of polypyrrole were interacted with sulfonic groups of Nafion in Nafion/Pt/Polypyrrole composite, despite the simultaneous incorporation of pyrrole monomers and Pt precursor into Nafion matrix.

Figure 1 provides TGA curves and first derivative traces of Nafion, Nafion/Polypyrrole, and Nafion/Pt/Polypyrrole 02 and 04. The Nafion membrane was decomposed into three stages: the desulfonation process at the first stage from 250 to 400 °C, the side-chain decomposition at the second stage from 400 to 500 °C and PTFE backbone decomposition at the last stage from 500 to 600 °C. In line with previous report,⁽¹⁾ the peaks of the first stage in the first derivative curves of Nafion/Polypyrrole composites were shifted to a higher temperature due to the stabilization of the C-S bond with the formation of the Nafion- SO_3^- and $^+\text{NH}_2$ -polypyrrole ionic pairs. The degradation of side chain in the second stage was also obstructed by mutual interaction. In a similar manner to Nafion/

Polypyrrole, Nafion/Pt/Polypyrrole composite membranes also had higher thermal stabilities of sulfonic groups and side chains than Nafion, resulting from mutual interaction between Nafion- SO_3^- and Polypyrrole- NH_2^+ .

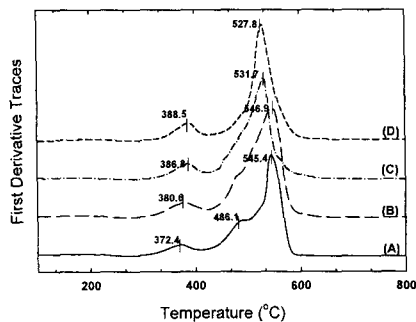


Figure 5. First derivative traces of TGA data of (A) Nafion, (B) Nafion/Polypyrrole, and (C) Nafion/Pt/Polypyrrole 02 and (D) 04.

Transport properties of Nafion such as proton conductivity and methanol permeability as well as thermal stability should be improved to apply the composite membranes to a solid electrolyte. In order to clarify the effect of Pt concentration on the transport properties, proton conductivities and methanol permeabilities of composite membranes relative to those of Nafion were measured by changing Pt concentration from 1×10^{-4} to 2×10^{-2} M with a constant pyrrole concentration at 0.1 M. As the content of Pt precursors increased, relative methanol permeability was decreased from 47.5 to 18.1 % and relative proton conductivity was reduced from 78.6 to 69.2 %. The slope of relative methanol permeability was sharper than that of relative proton conductivity in this measurement range. Typically, cell performance is proportional to proton conductivity and inversely proportional to methanol crossover, thereby suggesting that as the value of σ/P (σ is proton conductivity and P is methanol permeability) is enhanced, cell performance is improved. Taking into consideration that σ/P of Nafion/Pt/Polypyrrole 02 with the highest cell performance among Nafion/Pt/Polypyrrole series was 2.59, while that of Nafion/Polypyrrole is 1.86, the co-introduction of Pt particles with polypyrrole ameliorated more favorably transport properties as

well as thermal stabilities of Nafion.

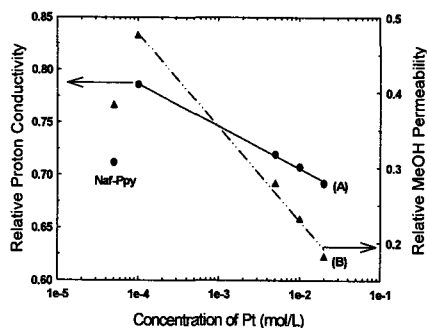
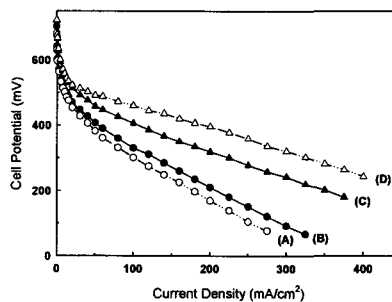


Figure 2. (A) Relative proton conductivity and (B) relative methanol permeability of Nafion/Pt/Polypyrrole as a function of H_2PtCl_6 concentration at pyrrole concentration of 0.1 M.

Figure 3 shows polarization curves of Nafion and Nafion/Pt/Polypyrrole 02 in DMFC operation. We chose Nafion/Pt/Polypyrrole 02 and compared its performance with that of Nafion. Although proton conductivity of Nafion/Pt/Polypyrrole 02 was lower than that of Nafion or 71.9% relatively, the former had higher performance than the latter due to the decreased methanol crossover or 27.8% relatively. In the case of OCV related to methanol crossover, Nafion/Pt/Polypyrrole 02 had higher OCV values than Nafion at both 303 and 343 K. As operational temperature increased from 303K to 343K and concentration of methanol from 3M to 6M, differences between cell performance of Nafion and Nafion/Pt/Polypyrrole 02 were enhanced. As the activity coefficient of methanol increased with its vaporization at high temperature and in more concentrated solution, the effect of methanol crossover was more prominent than that of proton conductivity in determining total cell performance. Therefore, cell performance of Nafion was improved by the reduction of methanol crossover after chemical in-situ polymerization of pyrrole monomers with Pt precursors around the surface.

Figure 3. IV curves of (A) and (C) Nafion, (B) and (D) Nafion/Pt/Polypyrrole 02 ((A) and (B): 303 K, 3 M MeOH, (C) and (D): 343 K, 6 M MeOH).



4. Conclusions

Nafion/Pt/Polypyrrole composite membranes were fabricated by chemical in-situ polymerization of pyrrole monomers with Pt precursors in Nafion matrix for an application of electrolyte for DMFC. Thermal stabilities of sulfonic groups and side chains in Nafion/Pt/Polypyrrole composite membranes were higher than those of Nafion and Nafion/Polypyrrole. Methanol permeabilities of Nafion/Pt/Polypyrrole composite were reduced more than proton conductivities with the increase in the content of Pt particles. As a result of that, the enhancement of cell performance by Nafion/Pt/Polypyrrole 02 relative to Nafion was more pronounced under the specific experimental.

Acknowledgements

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