

Preparation and characterization of matrix retaining electrolyte for a phosphoric acid fuel cell by non-volatile solvent, NMP

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Abstract

A novel process for preparing a matrix using non-volatile *n*-methyl-2-pyrrolidone (NMP) solvent was developed to increase its productivity and reproductivity, while maintaining high porosity and high phosphoric acid absorbency which supply the advantages of silicon carbide (SiC) whisker-polyethersulfone (PES) binder matrix system. The effect of the change from the volatile solvent to the non-volatile one on the properties of matrix and the performance of fuel cell was investigated. The change from the volatile solvent to the non-volatile one decreased the porosity and increased the bubble pressure of matrix. The electrolyte resistance under the same thickness increased due to the decrease of phosphoric acid absorbency, and the fuel cell performance slightly decreased. When the thickness of the matrix was reduced to the 170 μm , the electrolyte resistance decreased and the performance of single cell increased.

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Keywords: Matrix retaining electrolyte; Non-volatile solvent; *n*-Methyl-2-pyrrolidone (NMP); Phosphoric acid fuel cell

1. Introduction

The matrix containing phosphoric acid is one of the most important components of the phosphoric acid fuel cell (PAFC) because of its effect on the ionic conductivity, the crossover of reactant gases, and the triple phase reaction zone [1,2]. Therefore, the matrix must be wet enough to reserve sufficient amount of acid under operational condition and have sufficient mechanical strength within stack structure. Commonly used matrix is composed of silicon carbide (SiC) tied with a small amount of binder like polytetrafluoroethylene (PTFE) [3]. It was reported that the matrix used polyethersulfone (PES) as a hydrophobic binder, instead of PTFE improved wettability, and the matrix used mixtures of SiC whisker and polyethersulfone binder increased porosity [4,5].

The volatile solvent, dichloromethane (CH_2Cl_2) used for PES binder has the advantages to dry temperature and high porosity [6]. It has difficulty of controlling viscosity due to strong volatility. In this study, the matrix was prepared by *n*-methyl-2-pyrrolidone (NMP), a non-volatile solvent and the effect of the change from the volatile solvent to the non-volatile one on the properties of matrix, and the performance of fuel cell was investigated.

2. Experimental

The matrices were prepared by tape-casting method according to the procedures described schematically in Fig. 1. SiC whisker (TWS-100, Tokai Carbon) was used to increase porosity, and hydrophilic PES was used as a binder. SiC slurries were prepared by mixing of the solutions in which PES was dissolved by NMP and dichloromethane, respectively, and SiC whisker was dispersed. The weight ratio of PES:SiC was 0.17:1. The measurement of pore size distribution was done using a mercury porosimeter (Autopore II, Micromeritics), and Bubble pressure was measured while nitrogen gas was effused to the matrix containing phosphoric acid. The amounts of acid in the cathode layer, matrix and the anode layer from the cell were analyzed using an ion chromatographic analyzer (model Dionex 4500i) to investigate the distributional change of electrolyte in single cell. The eluant was solution mixed 0.0018 M Na_2CO_3 with 0.0017 M NaHCO_3 . The performance characteristics of matrix layers in single cells were carried out using the electrodes with a Pt catalyst loading of 0.25 and 0.5 mg/cm^2 for anode and the cathode, respectively. The electrodes were obtained from the Fuel Cell Research Center of the Korea Institute of Energy Research, Korea [7]. The geometric area of electrode was 1 cm^2 . Electrochemical interface (Solatron SI1287) and impedance/grain-phase analyzer (Solatron SI1260) were used to measure ac impedance.

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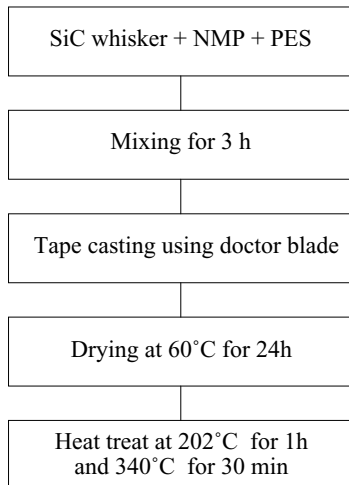


Fig. 1. Procedure for preparation of matrix using NMP solvent.

3. Results and discussion

NMP, which is nontoxic, has the advantage of improving productivity, compared with dichloromethane, a toxic solvent. In addition, it is vapor pressure that most highly affects the properties of matrix. When the matrix dries, the degree of shrink is in proportion to the constant rate period in which most of shrink is made [8]. And evaporating speed of solvent in constant rate period is in proportion with the vapor pressure of solvent [8]. While the vapor pressure of dichloromethane is 350 mm H₂O at room temperature, that of NMP is so low as 4 mm H₂O at 60 °C which is dry temperature. Therefore, drying speed is slow, the constant rate period that matrix shrinks becomes long and matrix gets dried more compactly. Fig. 2 shows different microstructures

and the surfaces of matrix prepared by NMP (matrix 1) and by dichloromethane (matrix 2). Matrix 1 had smaller sized pores and smoother surface than matrix 2, because the former shrank more than the latter due to different vapor pressure. The change of pore size had an effect on the porosity and bubble pressure of matrices. Fig. 3 shows the pore size distribution of matrices prepared by NMP and dichloromethane. The mean pore size and porosity of matrix 1 were 2.83 μm and 79.1%, respectively, while those of matrix 2 were 3.50 μm and 89%. The matrix 1 prepared by NMP had slightly lower porosity than the matrix 2, however, its bubble pressure was 2700 mm H₂O. This is not only higher than 1480 mm H₂O of matrix 2, but also more than twice as high as the value of vapor pressure required for the use in fuel cells. During the operation of fuel cell, as the cross over of fuel gas degrades the efficiency of cells and deteriorates stability of cell, the value of bubble pressure has to be high enough [9].

Fig. 4 shows the distributional change of electrolyte before and after assembling in single cells using matrices 1 and 2, which was measured by ion chromatography. Before assembling in a single cell, the matrix layer was saturated enough with phosphoric acid at 150 °C for 24 h, and the single cell was operated at 190 °C for 1 h with operating voltage of 0.7 V, which was frozen using liquid nitrogen, and separated into matrix, anode and cathode. The sample solution for an ion chromatographic analyzer was prepared by extracting phosphoric acid from each component and it was assumed that electrolyte was distributed 100% in matrix before the configuration of single cells. In both cases of matrices 1 and 2, phosphoric acid was contained more in anode than in cathode, which coincided with the result already reported in the literature [10]. The phosphoric acid in both anode and cathode of the cell which matrix 1 was used

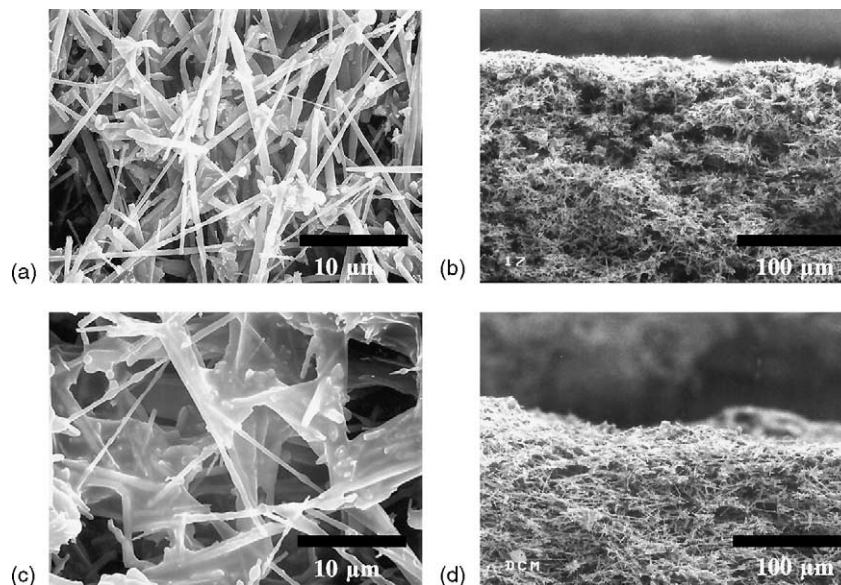


Fig. 2. SEM microstructures and surface images of matrices prepared by different solvent: (a), (b) matrix 1 and (c), (d) matrix 2.

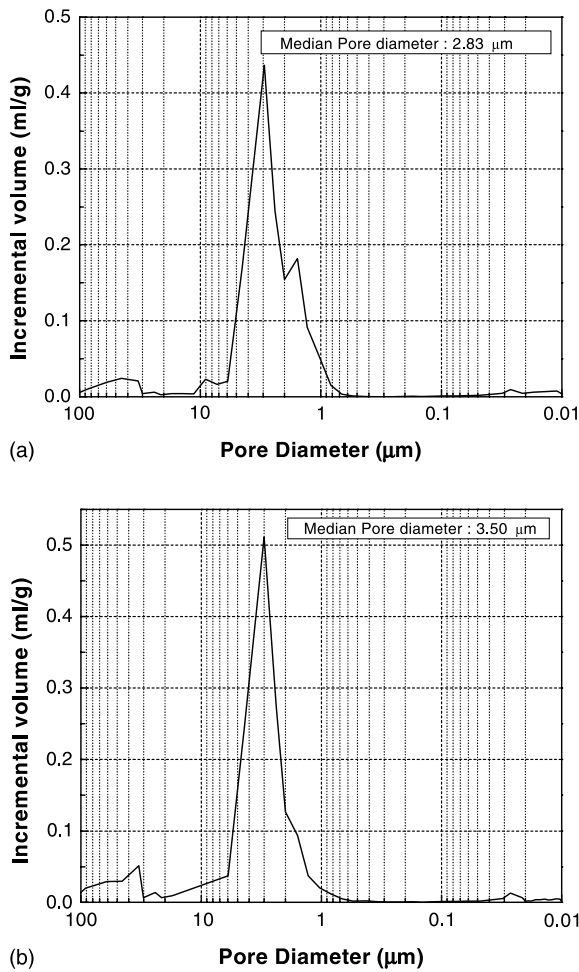


Fig. 3. Pore size distribution of matrices prepared by (a) NMP and (b) dichloromethane.

was more absorbed than the one matrix 2 was used. Mori et al. [11] reported that in order to get a good performance of cells in long-term operation, more absorption of phosphoric acid in anode than cathode is favored, and to reduce polarization in cathode, less absorption of phosphoric acid in cathode is preferable. Therefore, it was expected that the cell using matrix 1 exerts more stable performance than the one using matrix 2 in long-term operation.

In order to investigate the effect of preparation variables on performance of cell, impedance spectra and current–voltage characteristics were examined. To measure the difference, under the same condition, made by the structural change of matrix, the thickness of matrix was made 250 μm in both matrices 1 and 2. The working temperature of the cells was 190 °C, at a flow rate of 50 cm³/min with oxygen and hydrogen as an oxidant and a fuel gas, respectively. In Fig. 5, Nyquist plot displayed the result of impedance spectra of single cells using matrices 1 and 2 at 0.7 V which was near the potential of the operation of cells. While electrolyte resistance was 0.22 Ω cm² in case matrix 2 was used, it was 0.33 Ω cm² in matrix 1. As mentioned above, under the same thickness of matrices, the overall porosity of the

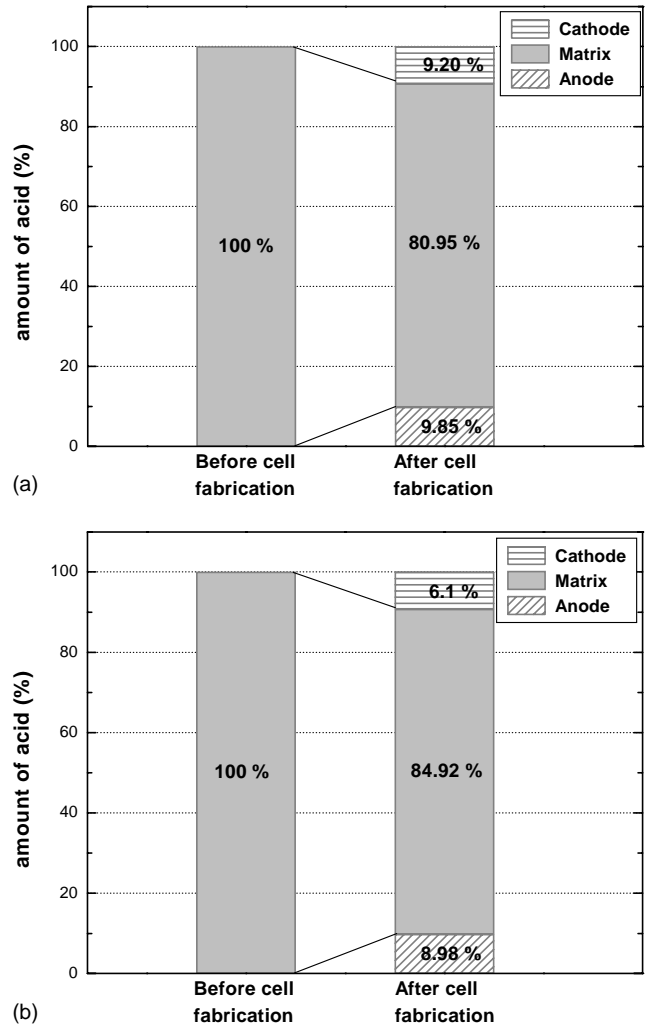


Fig. 4. Change in acid distribution of single cells with matrices prepared by (a) NMP and (b) dichloromethane.

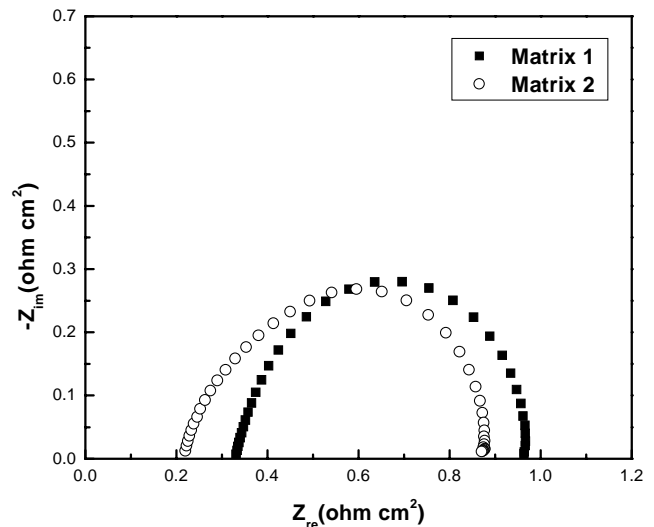


Fig. 5. Impedance spectra of single cells with matrices prepared by (■) NMP and (○) dichloromethane (thickness of matrices: 250 μm).

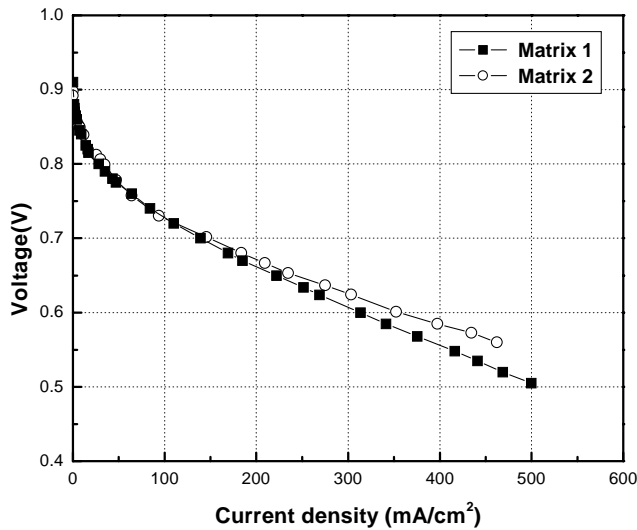


Fig. 6. Performance of single cells with matrices prepared by (■) NMP and (○) dichloromethane (thickness of matrices: 250 μm).

matrix using NMP, non-volatile solvent decreased, which brought the lowering of phosphoric acid absorbency. And it caused the decrease of ionic conductivity of electrolyte, so the resistance of electrolyte grew [5]. To the contrary, polarization resistance was the same, $0.65 \Omega \text{ cm}^2$ in matrix 2 and $0.65 \Omega \text{ cm}^2$ in matrix 1.

Fig. 6 shows the current–voltage characteristics of single cells using matrices 1 and 2. In the single cell using matrix 1, current density was 139 mA/cm^2 at 0.7 V , but in case of matrix 2, it was 147 mA/cm^2 . And current density was 313 mA/cm^2 in matrix 1 and 352 mA/cm^2 in matrix 2 at 0.6 V . The single cell using matrix 1 of which open circuit voltage (OCV) 0.91 V was similar to 0.90 V of the single cell using matrix 2. But it had bad current–voltage characteristic because of large voltage drop. As observed in the result of impedance spectra, large voltage drop of matrix 1 was assumed to be ascribed to the increase of electrolyte resistance.

Because matrix 1 prepared by non-volatile solvent has bubble pressure more than twice as high as the one required for the use in fuel cell, it gets less thick than matrix 2. This brings the decrease of electrolyte resistance, expecting enhancement of performance of single cells. The thickness of matrix 1 was reduced to $170 \mu\text{m}$ (bubble pressure was above $2000 \text{ mm H}_2\text{O}$), then the impedance and current–voltage characteristic of single cell were measured. Fig. 7 shows the impedance spectra of matrix 1 with $170 \mu\text{m}$ thick and matrix 2 with $250 \mu\text{m}$. As the thickness of matrix 1 was reduced from 250 to $170 \mu\text{m}$, electrolyte resistance was decreased from 0.33 to $0.25 \Omega \text{ cm}^2$. This value was similar to $0.22 \Omega \text{ cm}^2$ of matrix 2 prepared by volatile solvent. This result was attributed to a reduction the thickness of matrix, electrolyte resistance decreased in inverse proportion to thickness.

Fig. 8 indicates the current–voltage characteristics of single cells using matrix 1 with $170 \mu\text{m}$ and matrix 2 with

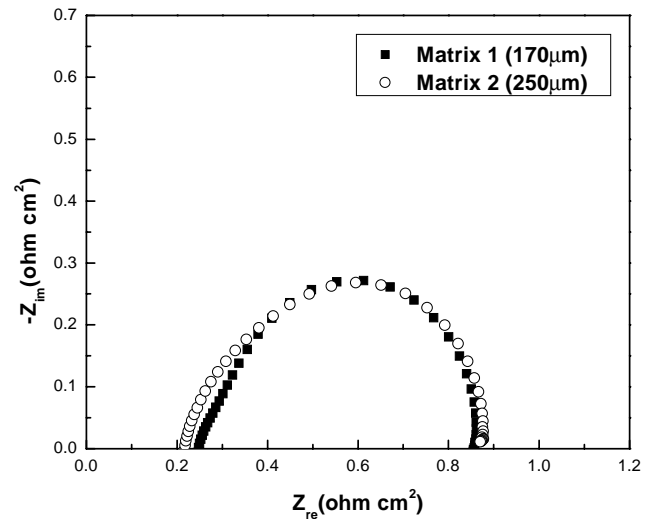


Fig. 7. Impedance spectra of single cells with matrices prepared by (■) NMP (thickness: $170 \mu\text{m}$) and (○) dichloromethane (thickness: $250 \mu\text{m}$).

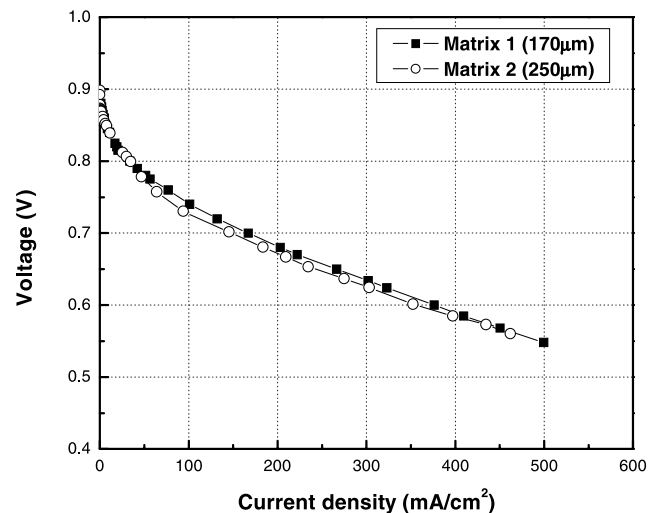


Fig. 8. Performance of single cells with matrices prepared by (■) NMP (thickness: $170 \mu\text{m}$) and (○) dichloromethane (thickness: $250 \mu\text{m}$).

$250 \mu\text{m}$. The current densities (167 mA/cm^2 at 0.7 V and 376 mA/cm^2 at 0.6 V) of the single cell using matrix 1 were higher than those (147 and 352 mA/cm^2) of the matrix 2. In accordance with the assumption on the results of Figs. 4 and 5, this result showed that matrix 1 had the worse current–voltage characteristic than matrix 2 under the same thickness of $250 \mu\text{m}$ because of the increase of electrolyte resistance ascribed to relatively low porosity.

4. Conclusions

The effect of change from the volatile solvent to the non-volatile one on the matrix retaining electrolyte and the performance of single cell was investigated. The matrix prepared by the non-volatile solvent had smaller pore size and

higher bubble pressure than that prepared by the volatile solvent. The electrolyte resistance in the condition of the same thickness increased due to the decrease of phosphoric acid absorbency. The current–voltage characteristics of single cells indicated large voltage drop of matrix using NMP, which was ascribed to the increase of electrolyte resistance. As the thickness of the matrix was reduced from 250 to 170 μm , the electrolyte resistance decreased from 0.33 to 0.25 $\Omega\text{ cm}^2$ and the performance of single cell increased.

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