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The effect of a modified Nafion binder on the performance of a unitized regenerative fuel cell (URFC)

Ho-Young Jung · Jong-Ho Choi

Abstract A modified Nafion binder using a different dispersion solvent, dimethylacetamide (DMAc), was applied to an electrode for a unitized regenerative fuel cell (URFC). The properties of the new Nafion binder, such as dissolution rate, proton conductivity, water uptake, and I–V curves, were characterized in the study. The new Nafion binder showed less brittleness, leading to good structural integrity in the electrode and improvement of stability in the URFC performance. SEM images showed that the interfacial adhesion between the membrane and the electrode was improved by using the new Nafion binder. Therefore, the new Nafion binder was suggested as a promising candidate for a binding material in the electrode of the URFC.

Keywords Dispersion solvent · Dimethylacetamide · Interfacial stability · Nafion binder · Unitized regenerative fuel cell (URFC)

Introduction

A unitized regenerative fuel cell (URFC) could become a primary future renewable energy source due to its high energy density system based on small volumetric dimensions, a long-term energy storage system, and high utilization efficiency of hydrogen energy [1–3]. The URFC technology is composed of two operation modes: the fuel cell mode and the electrolyzer mode [4, 5]. During fuel cell operation, the URFC can generate electricity and water through oxidation of hydrogen at the anode and reduction of oxygen at the cathode, typically in a similar fashion to a conventional polymer electrolyte membrane fuel cell. During electrolyzer operation, the URFC can regenerate hydrogen and oxygen through the oxidation of the water generated in the fuel cell mode. In this process, the operation of the electrolyzer mode needs an additional power source, such as solar cells or wind power, for applying electricity to the cell. The regenerated hydrogen and oxygen can be supplied for the fuel cell operation, which can generate electricity and water again. Therefore, the membrane/electrode assembly (MEA) goes through a fatal dimensional change during the operation of the URFC because gas phase fuel is supplied for fuel cell operation, when liquid phase fuel is supplied for electrolyzer operation. This phenomenon can cause interfacial stability issues for the long-term operation of the URFC.

Interfacial unstability can be caused by the degradation of interfacial adhesion according to the significant dimensional change of membrane, degradation of membrane, dissolution of catalyst, and dissolution of Nafion binder in the electrode of the polymer electrolyte-based fuel cell [6–9]. To reduce interfacial resistance, various methodologies such as a modified membrane with high dimensional stability [10, 11], preparation of a new electrode binder [12, 13], and thermal heat treatment of MEA [14] were suggested for the polymer electrolyte-based fuel cell. Among these approaches, modification of the commercial Nafion binder using thermal heat treatment significantly improved the long-term stability of the fuel cell owing to the enhanced interfacial stability.

H.-Y. Jung (✉)
Department of Chemical Engineering,
Kangwon National University,
1, Joongang-ro, Samcheok,
Kangwon-do 245-711, Republic of Korea
e-mail: jungho@kangwon.ac.kr

J.-H. Choi
Department of New and Renewable Energy, Kyungil University,
33 Buhori, Hayangup, Gyeongsan,
Gyeongbuk 712-701, Republic of Korea

Nafion is typically used as a catalyst-binding material in the electrode of a polymer electrolyte-based fuel cell [15]. It plays critical roles in the structural integration of the catalyst layer, the dispersion of catalyst particles, the interfacial adhesion between the membrane and the electrode, and also in the creation of the proton conduction pathway from the electrode to the membrane [15, 16]. Nafion binder is known to increase the electrochemically active surface area in the catalyst layer and the interfacial adhesion between the membrane and the electrode, thus decreasing cell resistance [17]. These factors bring enhanced performance in the fuel cells. However, the commercial Nafion binder has several problems, such as brittleness, high dissolution rate in an alcoholic solution, and low proton conductivity [9, 14, 18]. These issues can directly cause poor cell performance and affect the long-term stability of the URFC. To overcome these issues and improve the interfacial stability for long-term operation of the URFC, Nafion binder should be modified and applied to the electrodes. Nafion binder should have high chain flexibility for improved interfacial stability due to the interpenetration of polymer chain. To create these properties of a new Nafion binder, a commercial Nafion solution was modified in this study by using a different solvent, dimethylacetamide (DMAc). DMAc is well known as a good dispersion solvent [19]. Nevertheless, there are few studies about the specific modification of Nafion binder for its use in the fuel cells. Therefore, the new Nafion binder using a different dispersion solvent is applied to an electrode for the URFC in order to improve its interfacial stability in this study. The objective of this study is to modify the Nafion binder and investigate the effects of this new Nafion binder on the URFC performance.

Experimental

Preparation of the homemade Nafion binder solution

The commercial Nafion solution with the concentration of 5 wt.% was purchased from DuPont™. The commercial Nafion solution was cast onto a Pyrex petri dish and evaporated at 50 °C, then at 80 °C, to remove the solvent. During the drying process, recast Nafion showed some brittleness. The recast Nafion was soaked in de-ionized (DI) water and the film was peeled off. After removing the water on the surface of recast Nafion, it was left in a vacuum oven at 80 °C overnight. The dried recast Nafion was redissolved in DMAc. The concentration of Nafion in DMAc solvent was 5 wt.%.

Characterization of the Nafion films

For all characterization in the Nafion films, three specimens were prepared on each test and the data were averaged in the study. The volumetric change of the commercial Nafion 112 membrane was calculated by measuring the change of membrane size (volume = length × width × thickness) before and after hydration in deionized water at 20 °C for 24 h. For the measurement of volumetric change at an elevated temperature, the commercial Nafion 112 membrane was incubated for 2 h at 70 °C.

Typically, the conventional recast Nafion showed brittleness after evaporation of the solvent at 80 °C overnight. To obtain an uncracked Nafion binder, the temperature of the drying process was carefully controlled from 50 to 80 °C with increments of 10 °C for 3 h at each step. For the measurements of proton conductivity and water uptake of the conventional recast Nafion, thermal heat treatment was applied to the uncracked part of the recast Nafion at 110 °C for 3 h after the drying process. For the homemade recast Nafion, the homemade Nafion solution was cast onto a clean glass plate. The homemade Nafion solution was dried at 50 °C, then at 80 °C, for 3 h at each step. To remove the solvent from the homemade Nafion binder, it was kept in the vacuum oven at 110 °C overnight, soaked in DI water, and detached by peeling off. After removing the water from the surface of the recast Nafion, it was acidified using sulfuric acid solution (1 M). The homemade Nafion binder was then washed with DI water several times.

Dissolution of the Nafion binder was performed in accordance to the procedures reported previously [14, 18]. Briefly, dried recast Nafion was weighed and stirred in 2 M methanol solution for 24 h and then sonicated for 12 h. Residual Nafion was then filtered and dried in a vacuum oven overnight. The dissolution ratio was calculated from the weight difference before and after the dissolution test.

The proton conductivity of Nafion binder was measured by electrochemical impedance spectroscopy. The electrochemical impedance spectra were recorded over a frequency ranging from 1 Hz to 1 MHz. The amplitude of the sinusoidal modulation voltage was 10 mV. Nafion 112 membrane was used for reference.

For determination of the water uptake, all Nafion films were dried in a vacuum oven at 80 °C for 24 h before the measurements were taken. Then, the films were immersed in deionized water for 24 h at RT to attain equilibrium water uptake. The water uptake measurement was determined with the weight difference before and after the test. Commercial Nafion 112 membrane was used for the reference data in the test of dissolution, proton conductivity, and water uptake with the same experimental condition of Nafion binder.

Preparation of membrane electrode assembly

The active material of the cathode was unsupported PtIr black catalyst and the active material of the anode was Pt black

catalyst. Catalyst inks were prepared by dispersing the catalyst and two types (commercial and homemade) of Nafion binder. To control the viscosity of the catalyst slurry ink, a small amount of isopropyl alcohol and DMAc were added to the ink dispersed in the commercial and homemade Nafion solution, respectively. In this study, the Nafion content for the anode and the cathode was 20 wt.% for the URFC.

The catalyst ink was brushed onto the electrodes. The amount of catalyst loaded in the electrode was 4 mg cm^{-2}. The MEAs were prepared by hot-pressing the electrodes onto Nafion membranes at 130 °C for 3 min with a pressure of 800 psi.

Unit cell operation

The MEAs were characterized using a 25-cm^2 single cell after installation in the URFC test fixtures and connection to a test station equipped with an electric load. The cell temperatures for the URFC were 75 and 90 °C, and hydrogen/oxygen humidified with 100% RH was supplied to the anode/cathode, respectively, in the fuel cell mode. For the electrolyzer mode, DI water (70 °C) was supplied to the bifunctional oxygen electrode.

Morphology characterization

The cross-sectional images of the MEAs were produced using a Phillips scanning electron microscope at an accelerating voltage of 15 kV.

Results and discussion

In the fuel cell mode of the URFC, humidified gas is supplied to the cell. In the electrolyzer mode of the URFC, hot water is supplied to the cell. Because of the application of these fluids, the interfacial adhesion between the membrane and the electrode in the MEA can be seriously deteriorated due to the dimensional change of membrane during the URFC operation. Thus, the polymer electrolyte membrane should have high dimensional stability when used in the URFC. Figure 1 shows the volumetric change of the Nafion 112 membrane at a fully hydrated state in DI water chamber of 20 and 70 °C. The volumetric change of the Nafion 112 membrane was about 35% at 20 °C. The Nafion 112 membrane exhibited a volumetric change approximately two times higher at 70 °C (about 65%), which is the typical temperature for the fuel cell operation. Thus, profound difference in the volumetric change of the Nafion membrane can cause the interfacial delamination between the membrane and the electrode during the URFC operation due to the small difference (≤1.0%) in the volumetric change of the electrode.
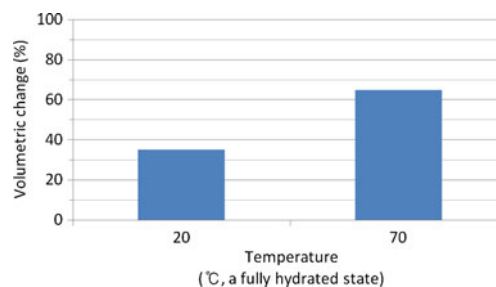

Fig. 1 The volumetric change (%) of Nafion 112 membrane in a DI water chamber at 20 and 70 °C

Because the dissolution of Nafion binder in the catalyst layer is an important factor for the interfacial adhesion of the MEA and the structural integration of the electrode, the dissolution of Nafion binder should be suppressed efficiently during the URFC operation. Therefore, it is highly necessary that the dissolution of Nafion binder should be confirmed for an estimation of the interfacial stability. In this study, the dissolution of Nafion binder was determined by an accelerated test with 2 M methanol solution of 20 °C. Figure 2 shows the dissolution data of the Nafion 112 membrane, the commercial Nafion binder, and the homemade Nafion binder. The commercial Nafion binder showed higher dissolution rate than the others. This phenomenon may lead to interfacial delamination in the MEA during the long-term operation of the URFC. On the other hand, the homemade Nafion binder showed much lower dissolution than that of the commercial Nafion binder. This observation indicates that the homemade Nafion binder is applicable for long-term operation of the URFC. Therefore, the dimensional change of the membrane and the dissolution of binder can be critical factors in determining the interfacial stability of the MEA in the URFC.

Figure 3 shows the proton conductivity of different Nafion films at RT. The homemade Nafion binder exhibited
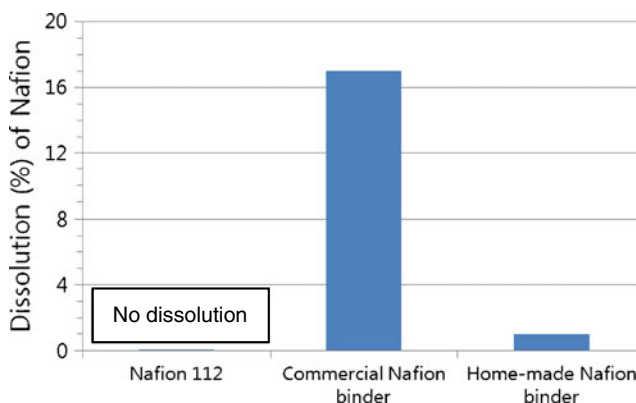

Fig. 2 The dissolution (%) of Nafion membrane casted with different solvents in methanol solution (2 M) stabilized at 20 °C
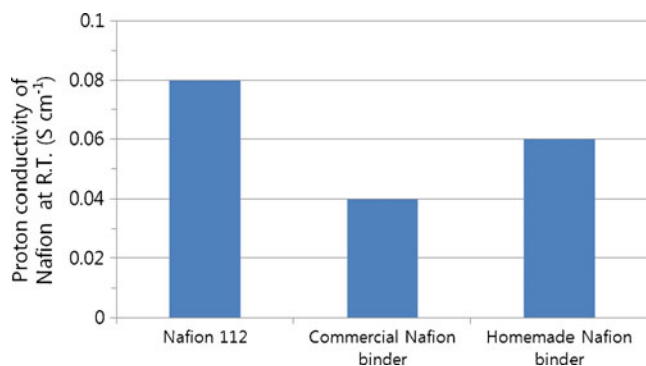
Fig. 3 The proton conductivity of different Nafion membranes at RT

higher proton conductivity than the commercial Nafion binder. For reference, the proton conductivity of the Nafion 112 membrane was about 0.08 S cm^{-1}. Proton conductivity is normally influenced by water uptake of the membrane when the proton sources are the same. As shown in Fig. 4, the homemade Nafion binder showed higher water uptake than the commercial Nafion binder, which was consistent with the proton conduction behavior.

In addition, when the Nafion binder solution was cast on the surface of the glass plate, the commercial Nafion binder showed a cracked morphology after the evaporation of solvent. On the other hand, the homemade Nafion binder showed a free-standing state, most likely due to the good entanglement of polymer chain. Additionally, the enhanced mechanical strength of homemade Nafion binder can affect the structural integration in the catalyst layer and the interfacial stability between the membrane and the electrode for the operation of the URFC.

In order to confirm that the homemade Nafion binder has a positive effect on the interfacial stability in the URFC, the homemade Nafion binder was applied to the MEA for the URFC in this study. After the activation of the cell, the polarization curves in the fuel cell mode and the electrolyzer mode were separately obtained at 75 and 70 °C, respectively. Then, the cell temperature was increased to 90 °C when supplied with hot water. In order to confirm the effect of the new Nafion binder on the interfacial stability
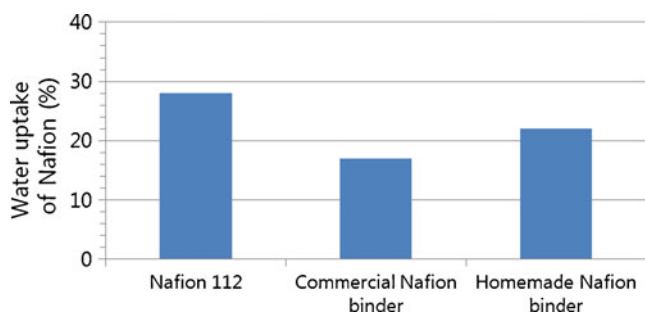
as soon as possible, hot water of 90 °C was supplied to the cell. It was expected that the dissolution of Nafion binder and the dimensional change of the membrane might be accelerated and the interfacial adhesion between the membrane and the electrode might be degraded due to hot water. Finally, the cell temperature was cooled down to room temperature. This procedure was repeated every day during the URFC operation.

The polarization curves obtained in the fuel cell mode are shown in Fig. 5. Each curve shows the performance of MEAs with electrodes prepared with different Nafion binders, both commercial and homemade. As shown in Fig. 5a, the performance of the MEA with the commercial Nafion binder was highly degraded with the operation time of the fuel cell. On the other hand, the MEA with the homemade Nafion binder showed a slightly more stable performance during the operation of the fuel cell, as shown in Fig. 5b. To compare the degradation rates of performance in the fuel cell mode, the change in voltage at 2.0 A cm^{-2} is shown in Fig. 6. The MEA with the commercial Nafion binder showed a higher degradation rate of voltage (1.3 mV h^{-1}). The MEA with the homemade Nafion binder showed a lower degradation rate

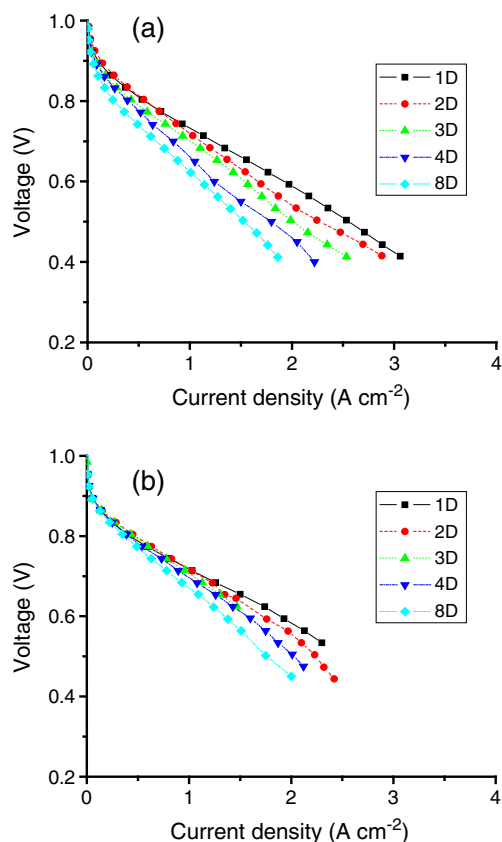Fig. 4 Water uptake for different Nafion membranes

Fig. 5 The polarization curves obtained in fuel cell mode with **a** commercial Nafion binder and **b** homemade Nafion binder (*1D* represents the cell performance after a 1-day operation in fuel cell mode)
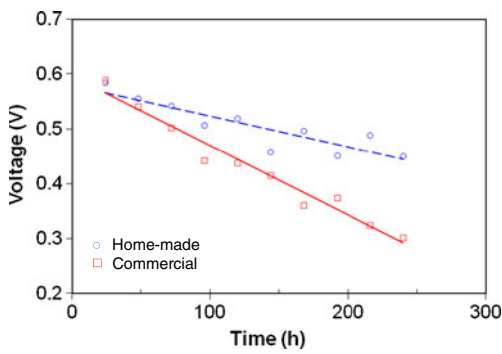
Fig. 6 The degradation rate of performance in fuel cell mode with operation time at 2 A cm^{-2} of current density

Fig. 8 The degradation rate of performance in electrolyzer mode with operation time at 0.3 A cm^{-2} of current density

of voltage (0.6 mV h^{-1}). These results indicate that the homemade Nafion binder can significantly improve the interfacial adhesion for the MEA in the fuel cell mode.

Figure 7 shows the performance of each MEA with two different Nafion binders in the electrolyzer mode. The performance of the MEA with the commercial Nafion binder rapidly decreased with operation time of the water
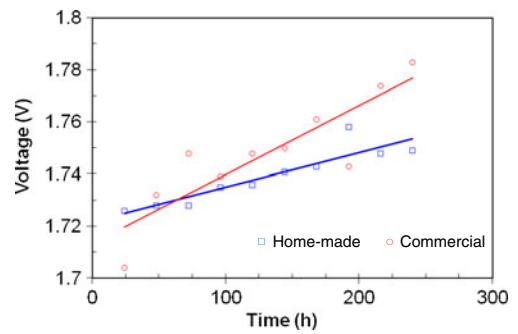
electrolyzer. However, the performance of the MEA with the homemade Nafion binder slowly decreased with the operation time. In order to compare the degradation rate of each MEA in the electrolyzer mode, the change of voltage at the current density of 0.3 A cm^{-2} against the cell operation time is shown in Fig. 8. The MEA with the commercial Nafion binder showed a higher degradation rate
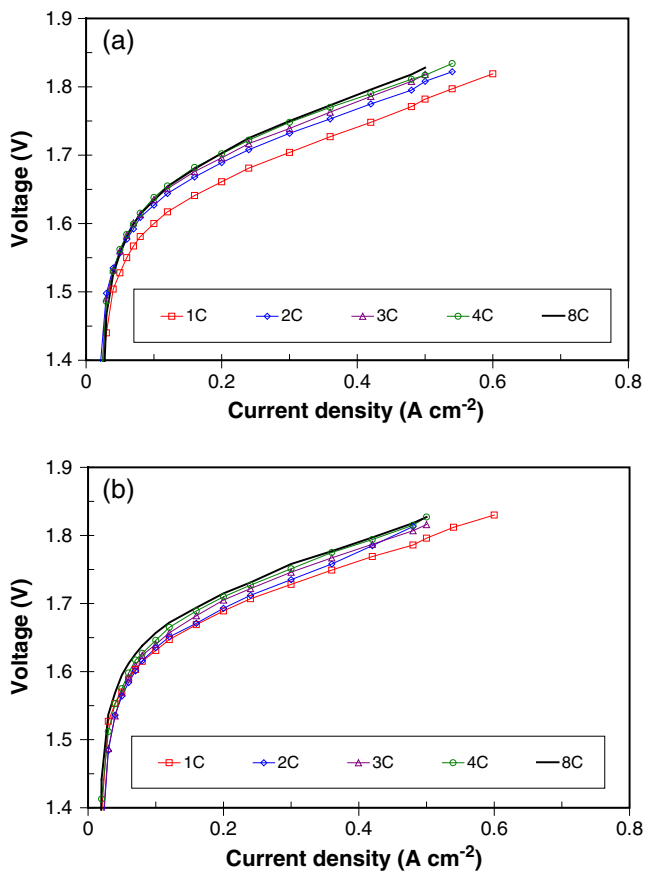

Fig. 7 The performance of each MEA in electrolyzer mode with two different Nafion binders: **a** commercial Nafion binder and **b** homemade Nafion binder (*1C* represents the cell performance after a 1-day operation in electrolyzer mode)
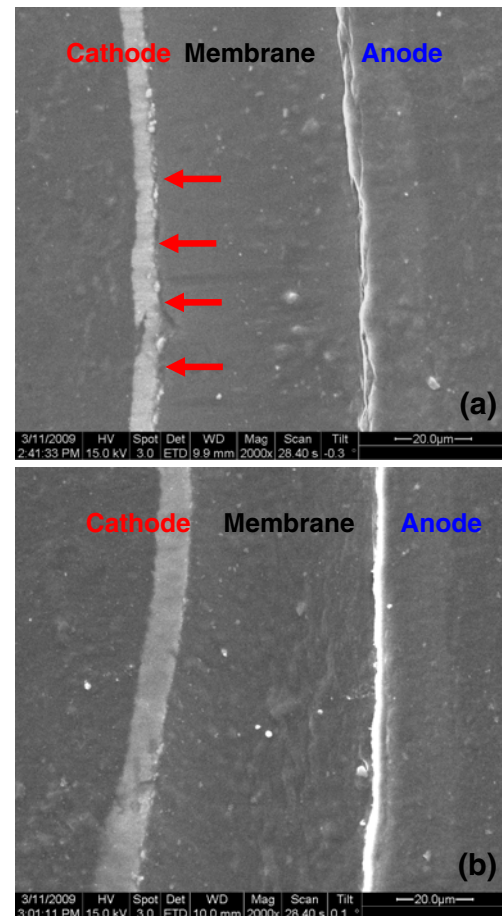

Fig. 9 The cross-sectional images of two MEAs with **a** commercial Nafion binder and **b** home-made Nafion binder after the accelerated test of 240 h

of voltage (270 $\mu V\ h^{-1}$). The MEA with the homemade Nafion binder showed a lower degradation rate of voltage (130 $\mu V\ h^{-1}$). Therefore, the homemade Nafion binder has shown a positive effect on the interfacial adhesion for the MEA in the water electrolyzer mode.

In order to confirm the interfacial adhesion between the membrane and the electrode, the cross-sectional images of two MEAs were investigated by SEM after the accelerated test of 240 h, as shown in Fig. 9. The catalyst layer in the MEA prepared using homemade Nafion binder showed a stronger persistence than the MEA prepared with the commercial Nafion binder. Hence, the homemade Nafion binder was proved to be more effective for the interfacial adhesion between the membrane and the electrode.

Conclusion

To improve the interfacial stability in the URFC, the new Nafion binder solution was prepared and applied to the electrode. The homemade Nafion binder using DMAc as a solvent showed less solubility and higher proton conductivity than the commercial Nafion binder.

For use in the URFC, the performance of MEA with a commercial Nafion binder was highly degraded as the operation time of the fuel cell increased. Meanwhile, the MEA with a homemade Nafion binder showed a slightly more stable performance during the operation time of the fuel cell. Therefore, the homemade Nafion binder is able to provide a positive effect on the interfacial stability in the MEA for the URFC.

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