Mechanical Stress Effect on Ionic Conductivity of Perflurosulfonic Acid (PFSA) Film by Photolithography

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Direct Methanol Fuel Cell (DMFC) consists of a perflurosulfonic acid (PFSA) electrolyte as an attractive portable power source. It is possible to fabricate a DMFC array by dividing a PFSA film into micro pieces by photolithography. In this regard, it is known that photoresist film causes significant compressive and tensile stress generation in an underlying layer. Then it is needed to control preparation condition of photoresist film formed on a PFSA film. The effect of compressive load in a PFSA film is observed as enhancement of electro motive force. By applying compressive load to a PFSA film, proton ionic conductivity would be enhanced. On the other hand, a tensile load acts to decrease electro motive force. Therefore photoresist pattern shape should be design effectively in order to enhance proton ionic conductivity of PFSA film.

Keywords: stress, photoresist film, retention property, perflurosulfonic acid (PFSA), Direct Methanol Fuel Cell (DMFC)

1. Introduction
Recently, Direct Methanol Fuel Cell (DMFC) is recognized as a candidate of portable power source[1]. Many researchers have focused on minimization of DMFC[2-4]. In this case it is required to fabricate a micro DMFC array on a plane surface by dividing a PFSA film into micro pieces. In this regard, it is necessary to form a perflurosulfonic acid (PFSA) film into micro pieces by lithography technique. In this case, significant film stress generation in a photoresist film is well-known. Several studies have focused on film stress of photoresist[5-6]. By finite element method, compressive and tensile stress due to thermal treatment concentrate at an edge of photoresist pattern[5]. The peak stress was estimated around 20-25 MPa in a photoresist pattern. Moreover photoresist stress is strongly influenced by film preparation condition[6].

This paper focuses on enhancement of proton ionic conductivity of a PFSA film induced by photoresist preparation condition. The compressive load and tensile loads can be applied to a PFSA film. Our results raise the possibility that external compressive film stress enhances proton ionic conductivity of a PFSA film. However external tensile load decreases proton ionic conductivity. The design of photoresist pattern becomes important factor in order to control a PFSA film operation.

2. Experiment
2.1 Fabrication of Sheet type DMFC (S-DMFC)
A schematic of a S-DMFC structure is shown in Fig.1. This device is composed with two Pt electrodes and Nafion electrolyte (DE2020, DuPont). This device has an ability of electricity generation by applying a fuel.

The structure of S-DMFC was fabricated in the flowchart as shown in Fig.2.
(a): A PET film (Apica Co., Ltd) was cut by a cutter in a size of 15mm x 30mm.

(b): Slight amount of contamination on a PET film was removed by immersing in deionized water (DIW). Then a PET film was cleaned for 6min by an ultrasonic cleaning system (EC-4515, Twinbird Co., Ltd).

(c): A piece of glass of 0.9±0.1µm thick was prepared in size of 15mm x3mm, which was used as a mask of Pt film sputtering.

(d): A Pt film as a catalyst layer of approximately 100nm thick was sputtered at 250W for 150min by using a RF sputtering system (PDM-303, Samco Inc.). The purity of Pt sputtering target (JEOL Ltd.) was 99.99%. The purity of sputtering Ar gas was 99.9999% and flow rate was 4sccm.

(e): A glass plate on the PET film was removed, and then the Pt films for anode and cathode were formed.

(f): PFSA (Nafion®) solution of 0.03±0.01cc was dropped on a center of the PET film by using a dropper.

(g): PFSA solution is dried at 25±2°C for 1h. The films of 37±10µm thick for compressive test and 93±20µm thick for tensile test were formed.

2.2 Electric generation Measurement

The S-DMFC was operated in 25±2°C by applying 3wt% methanol aqueous solution of 0.2cc. The fuel was dropped on the anode Pt film. A certain amount of oxygen molecule was allowed to diffuse the cathode electrode from ambient air. The electro motive force E between two electrodes was measured by using an electric circuit as shown in Fig.3. The circuit was composed by a variable resister (TYPE 2786, Yokogawa Electric Works, Ltd.) and the S-DMFC. The load voltage $V_R$ was measured by using a digital multi-meter (DL-712, Kenwood).

The electric generation power $P$ of the S-DMFC is estimated by the following equations.

$$ P = \frac{R}{(R + R_0)^2} E^2 $$

$$ P_{\text{max}} = \frac{E_{\text{max}}^2}{4R_0}, $$

where $R$ is resistance of variable resister, $R_0$.
is internal resistance of the S-DMFC and $E$ is electro motive force of the S-DMFC. The values of $P_{\text{max}}$ and $E_{\text{max}}$ indicate maximum when $R = R_0$. In order to obtain the maximum electric generation power, the variable resister was adjusted from 100Ω to 100kΩ. The electric generation area of the S-DMFC was designed as the interface area between Pt electrode and the PFSA film to be 0.225cm².

2.3 Compressive load

External compressive load was applied to a part of PFSA film surface directly as shown in Fig.4. The loading experiments were carried out under (i) partially immersion and (ii) fully immersion conditions of the fuel on the PFSA film as shown in Fig.4.

2.4 Tensile load

As shown in Fig.5, the S-DMFC was easy to bend by human fingers. External tensile load was applied by wrapping the S-DMFC around a cylinder of 14mm diameter repeatedly in dry condition as shown in Fig.6. Therefore, tensile load was applied to the PFSA film directly in 0, 50, 100, 200, 300, 500, 700 and 1000 times. The electro motive force $E$ was measured after removing tensile load of each loading times.

3. Results

3.1 Compressive load effect

Figure 7 shows the typical electric generation properties of DMFC. The result shows that the S-DMFC indicates higher electric power density by immersing the PFSA film in the fuel fully, comparing with the partial one. Moreover time dependency of the electric power density under compressive load is shown in Fig.8. By immersing PFSA

![Fig.4 Schematic diagram of compressive load test. Compressive load was applied by adding a certain strain (20µm) to a center of the PFSA film with a load meter.](image)

![Fig.5 Photograph of bending of the S-DMFC by human fingers.](image)

![Fig.6 Schematic diagram of tensile load.](image)

![Fig.7 Typical electric generation of the S-DMFC.](image)

![Fig.8 Electric generation of S-DMFC by applying external compressive load.](image)
film with the fuel fully, it is clearly observed the retention property of the electric power density is enhanced by applying the compressive load.

3.2 Tensile load effect

Figure 9a shows an electric power density curve of applying times of tensile load. Figure 9b shows the maximum electric power density and internal resistance as a function of loading times increase. The maximum electric power density linearly decreases with increasing the applying load times. The internal resistance of the S-DMFC increases slightly with the tensile loads. The result shows that repetitive tensile load causes decrease of electric generation property.

4. Discussion

4.1 Improvement of electric power density under compressive load

The electric power density difference in Fig.7 reflects clearly the fuel supply volume difference. By immersing the PFSA film of fuel fully, it is supposed that the fuel can supply sufficient volume which causes the higher electric power density comparing with the partial one. The compressive load should act to compress the PFSA film. This phenomenon probably causes higher sorption of water molecule due to condensation of sulfonic acid groups[7]. Therefore the external compressive load would act to improve the retention property of the PFSA film.

4.2 Decrease of electric power density under tensile load

In this experiment, nano scale void would be formed and proton ionic conductivity would become low. In the literature, the peak stress of tensile load is localized at a water/PFSA film interface[8]. It can be supposed that bonding of sulfonic acid groups is expanded due to the stress concentration. Therefore it can be considered the internal resistance $R_0$ of the PFSA film increases and the electro motive force $E$ decreases under tensile load.

4.3 Stress effect of PFSA film by lithography process

Figure 10a shows a photograph of the
photoresist line patterns of 40µm formed on a PFSA film. The line patterns are smoothly formed. As shown in Fig.10b, a photoresist pattern is formed on the PFSA film in double layer structure. It can be considered that a photoresist film should act to generate both compressive and tensile film stress in the PFSA film[5]. Our results raise the possibility that compressive film stress induced by photoresist film act to enhance a proton ionic conductivity of the PFSA film. However, tensile film stress of photoresist film would decrease a proton ionic conductivity of the PFSA film. Then it is needed to design the photoresist pattern to generate effective compressive stress in the PFSA film.

5. Conclusion
On the point of micro DMFC fabrication by lithography, the relationship between mechanical stress and electric generation property of a PFSA film is discussed. External compressive stress acts to enhance electric generation property and tensile stress acts to decrease. Therefore it is needed to design the photoresist pattern effectively in order to enhance the PFSA film property.

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