Study on Functionally Gradient Proton Exchange Membrane fabricated by EB Irradiation with Heterogeneous Energy Deposition

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The revolutionary functionally gradient proton exchange membranes were fabricated by EB irradiation with heterogeneous energy deposition. These heterogeneous energy deposition profiles (Depth-Dose profiles) were simulated by Monte Carlo simulation code EGS5. In the process of EB-grafting method of styrene onto base fluorinated polymer, the energy depositions selected from the Depth-Dose profiles were used. The grafted membranes were sulfonated with chlorosulfonic acid in carbon tetrachloride. The DOGs in the direction of thickness showed that EB Depth-Dose profiles corresponded to the EB grafting reaction. The functionally gradient proton exchange membranes had a water uptake gradient in the direction of depth, and hence could be a promising solution to manage water behavior in Membrane Electrode Assembly (MEA) of Polymer Electrolyte Fuel Cell (PEFC).

Keywords: EB-grafting, EB, ULEB, PEFC, functionally gradient

1. Introduction

Polymer Electrolyte Fuel Cell (PEFC) has attracted much attention for many years mainly because of their high energy efficiency and portability. Water uptake condition in Membrane Electrode Assembly (MEA) is of interest for the fact that it has strongly influence on PEFC performance. PEFC operation under proper water uptake condition in MEA exhibits good performance and stability. In contrast, operation under excess or deficiency water uptake condition brings flooding phenomenon or Proton Exchange Membrane (PEM) dryness [1]. The revolutionary PEM which control itself water uptake condition would offer advantages for industry, such as Fuel Cell Vehicle (FCV). This is because the PEM doesn't need a humidifier which arise FCV cost. Some papers had reported how to observe water uptake condition in PEFC [2]. However, very few studies have been reported on the PEM which control itself water uptake condition.

In our previous study, PEMs for PEFCs were prepared by EB-grafting of styrene onto base fluorinated polymers and sulfonation [3]. EB-grafting is a widely used method for functional polymer fabrications [4]. This method takes advantage of heterogeneous energy deposition (Depth-Dose profiles), and these profiles were simulated by Monte Carlo simulation code EGS5 [5-7]. The soft (150 – 250 keV) and ultra low (40 – 100 keV) energy EB Depth-Dose profiles indicated that these energy depositions were dramatically graded within the EB-irradiated polymer thickness of 250 μm.

In a previous our work, using stack polymer films, the functionally gradient membranes based on 50 μm thickness partial-fluorinated polymer could be fabricated by the soft EB with heterogeneous energy deposition. Moreover, fuel cell performance was improved by functionally gradient PEM.
In Generally, PEFC performance depended on PEM thickness. The purpose of the present work is to fabricate functionally gradient membranes based on 25 μm thickness partial-fluorinated polymer membranes for more high performance. The PEMs with functionally gradients were expected to manage the water behavior in MEA, and make PEFC system simple.

2. Method
2.1. Materials and the heterogeneous energy deposition
Polytetrafluoroethylene-co-hexafluoropropylene (FEP, FLON INDUSTRY) films were used for the experiment.

The EB energy deposition profiles and electrons behaviors were simulated by Monte Carlo simulation code EGS5. EB energy deposition $D(z)$ per electron at depth $z$ was written as the following equation:

$$ D(z) = D_c(z) + D_b(z) $$

where $D_c(z)$ and $D_b(z)$ are the energy deposition by collision processes and the radiative (bremsstrahlung) processes, respectively [8]. In the used energy range (40 keV - 200 keV), the energy deposition processes were mainly collision process, which was given by following Bethe-Bloch equation [9].

2.2. Grafting and sulfonation
FEP films with 25 μm thickness were used to prepare for functionally gradient PEMs. To synthesize the two functionally gradient PEMs in consideration with soft energy EB Depth-Dose profile, two FEP film stacks were prepared. The stack of three 25 μm thickness FEP films was irradiated at 180 kV by low EB accelerator CURETRON® (NHV Corporation) and the bottom irradiated FEP film was used for the experiment through the grafting. On the other hand, the stack of 50μm and two 25μm thickness FEP films was irradiated at 160 kV and the bottom irradiated FEP film was used for the grafting.

The ultra low energy EB Depth-Dose profile indicated that these energy depositions were dramatically graded within thickness of 50 μm. From soft and ultra low EB Depth-Dose profiles, this energy deposition gradient was more dramatically than that of soft energy EB. To obtain more sharply functionally gradient PEM, FEP films with 25μm thickness were prepared. Each FEP film was irradiated at 40 kV, 60kV and 110 kV by ultra low EB accelerator EB-ENGINE® (HAMAMATSU PHOTONICS) respectively.

After EB irradiation at RT under N2, the irradiated films were grafted with styrene in liquid phase at 80 °C for 2 hours. The grafted films were sulfonated with chlorosulfonic acid in carbon tetrachloride (1:100, v/v) at RT for 24 hours. Subsequently, these sulfonated films were soaked in deionised water at RT and treated in 1 mol/l HCl for 24 hours to obtain acid form membranes.

2.3. Measurements of Functionally gradient
Ion Exchange Capacities (IEC) of the prepared PEMs were determined by an acid-base titration method with 716 DMS Titriono automatic titrator (Metrohm-herisau), and water uptakes were determined by the difference between wet and dry weight.

The functionally gradients were evaluated in terms of difference in chemical structures of electron-incident face and electron-transmit face with XPS JPS-9010 (JEOL) and FT-IR (JEOL).

2.4. Fabrication of MEAs and the cell performance
Carbon electrodes with 1 mg/cm² Pt loaded were purchased from Electro Chem. They were coated with Nafion®-dispersion 0.2 mg/cm² and subsequently dried at 80 °C for 2 hours to form binding layers on the electrodes. Gradient- and Flat-PEMs with an active area of 1cm² were stored in deionized water for 1 hour to obtain good adhesion between the PEM and electrodes. All these MEAs were prepared by hot pressing at 110 ºC under 8 MPa for 3 min.

Fuel cell tests were performed with humidified H2 and O2 supplied under 0.2 MPa, and both gas flow rates were 50 ml/min. The characterization of MEA was determined in terms of polarization performance and electrochemical impedance spectroscopy (EIS). FC operation was conducted at 60 ºC and controlled with a HZ-3000 Electrochemical analysis system (Hokuto Denko). EIS was measured in the frequency range from 100 kHz to 0.1 Hz at an AC current density of 500 mA/cm².

3. Results and Discussion
3.1. Heterogeneous energy deposition profiles
Figure 1 showed the soft EB with heterogeneous energy deposition profiles (Depth-Dose profiles) simulated by EGS5 code. The simulation model of CURETRON® was composed by 3 layers. The top layer was titanium window (thickness: 12.7 μm, p:
4.50 g/cm³). The middle layer was nitrogen atmosphere (thickness: 7.0 cm, ρ: 1.25 × 10⁻³ g/cm³). The bottom layer was FEP sample (thickness: 300 µm, ρ: 2.15 g/cm³). The simulation model of EB-ENGINE® was composed by 3 layers. The Simulated electron irradiated at 5000 times. These profiles were depended on accelerating voltages. A monotonic decrease of energy deposition with increasing depth was the observed in the soft EB (150 keV – 190 keV) energy deposition profiles. High accelerating voltage EB deposited itself energy at more deep regions. The soft EB Depth-Dose profiles would be explained by the collision energy deposition process. Because, less accelerating voltage EB was, higher probability of collision and energy deposition processes at near-surface regions.

Figure 2 showed the behavior of electrons in FEP simulated by EGS5 code. All 40 keV electrons couldn’t be transported to 25µm FEP electron transmit face, and penetrated at inside region. Some 60 keV electrons could be transported to electron-transmit face. On the other hand, most 110 keV electrons could be transported to electron transmit face. Although the window material of EB-ENGINE® is Beryllium, the information of thickness has not been disclosed. In this simulation, the thickness of top layer was 10.0 µm, ρ: 1.85 g/cm³. The middle layer was nitrogen atmosphere (thickness: 1.0 cm, ρ: 1.25 × 10⁻³ g/cm³). The bottom layer was FEP sample (thickness: 300 µm, ρ: 2.15 g/cm³). On the other hand, the ultra low energy EB (less than 110 keV) deposited much itself energy at near-surface regions. The deposition increased at near-surface regions, there was the energy deposition peak, and penetration depth was short. It resulted in a high probability of collision energy deposition process.

3.2. The soft energy EB

Table 1 showed the properties of functionally gradient PEMs properties. From XPS spectroscopy, the peak around 168 eV indicated the sulfonic acid group SO₃H. The peaks intensities at 168 eV of both electron incident-face and transmit-face were also summarized in Table 1. All properties of 75 – 100 µm regions (160keV) were lower than those of 50 – 75 µm ones (180keV). It would be explained by the integrated absorbed dose by the energy deposition in FEP were induced the free radicals, which were used for the EB grafting. The integrated dose of 50-75 µm (180 keV) was larger than 75-100 µm (160 keV). Therefore, it was thought that the amount of produced free radicals, grafted polystyrene and sulfonated acid group in 50-75 µm (180 keV) were also higher than those of 75-100 µm (160 keV). In case of 50 – 75 µm (180keV), the peak intensities of sulfonic acid group between both surfaces were almost same value. On the contrary, for 75 – 100 µm (160 keV), the peak intensity of electron incident face was about 2.5 times higher than that of electron transmit face. XPS results determined that different amount of sulfonated acid groups between faces could be formed in 75 - 100 µm (160 keV). It was clearly that the obtained 75 - 100 µm (160 keV)
would be formed functionally gradient sulfonated acid group, as compared with 50-75 µm (180 keV). Consequently, functionally gradient membranes based on 25 µm thickness FEP could be fabricated by using soft EB Depth-Dose profiles.

3.3. Fuel cell tests

Figure 3 showed polarization curves of MEA fabricated by 75 - 100 µm (160 keV). ‘Decrease’ and ‘Increase’ indicated water uptake gradient direction. Water uptake in Decrease-MEA decreased with proton transportation direction. On the other hand, water uptake in Increase-MEA increased with proton transportation direction. Decrease-MEA max current density was higher than that of Increase-MEA. However, Max power density and cell performance at low current density of Increase-MEA were higher than that of Decrease-MEA.

Figure 4 showed the results of EIS. The value of ohmic resistance ($R_{ohm}$) and charge transfer resistance ($R_{ct}$), which obtained by fitting the model parameters to the experimental data were listed in table 2. Rohm was intersection on the real axis at high frequency while $R_{ct}$ was the diameter of the semi-circle on the real axis. The ion conductivity (IC) was calculated from Rohm and membrane thickness. Rohm of Decrease-MEA and that of Decrease-MEA was almost same, but $R_{ct}$ of Increase-MEA was smaller than that of Decrease-MEA. The direction of water uptake gradient influenced fuel cell performance. The cell performance deterioration in the range of higher current density was caused by diffusion polarization. Hence, water uptake gradient of decrease direction might improve diffusion polarization. On the other hand, deterioration of voltage and power density in the range of lower current density was caused by activation polarization. Hence, water uptake gradient of increase direction might improve activation polarization. Fuel cell performances depended on water uptake condition in MEA. Water uptake gradient in functionally gradient membrane might be a promising solution to manage water behavior in MEA. To obtain more sharply functionally gradient, functionally gradient membrane fabricated by the ultra low EB irradiation.

### Table 1 Major property of PEMs and evaluation of functionally gradient

<table>
<thead>
<tr>
<th>Energy deposition region</th>
<th>DOG (%) (Ave.)</th>
<th>Thickness (µm) (Ave.)</th>
<th>IEC (meq/g) (Ave.)</th>
<th>Water uptake (%) (Ave.)</th>
<th>Peak intensity at 168 eV electron incident face</th>
<th>Electron transmit face</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 – 75 µm (180 keV)</td>
<td>47</td>
<td>39</td>
<td>2.3</td>
<td>65</td>
<td>126</td>
<td>108</td>
</tr>
<tr>
<td>75 – 100 µm (160 keV)</td>
<td>33</td>
<td>34</td>
<td>1.6</td>
<td>44</td>
<td>121</td>
<td>49</td>
</tr>
</tbody>
</table>

3.4. The ultra low energy EB

Figure 5 showed photographs of grafted FEPs fabricated by the ultra low energy EB irradiation. FEP-g-PSSA (40 keV) was grafted at only beam irradiated area (1 × 5 cm²), and near-surface regions. On the other hand, FEP-g-PSSAs (60 keV and 110 keV) were grafted at the whole of membranes. However, the shape of FEP-g-PSSA (60 keV) was quite different from FEP-g-PSSA (110 keV). FEP-g-PSSA (60 keV) was a curling shape. On the
### Table 2 Cell performance and electrochemical characterizations of Decrease-MEA and Increase-MEA.

<table>
<thead>
<tr>
<th>MEAs</th>
<th>$R_{th}$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>Ion Conductivity (S/cm)</th>
<th>OCV (V)</th>
<th>Max current Density (mA/cm²)</th>
<th>Power Density (mW/cm²) At 500 mA/cm²</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decrease-MEA</td>
<td>0.05</td>
<td>0.33</td>
<td>0.068</td>
<td>949</td>
<td>2458</td>
<td>339</td>
<td>465</td>
</tr>
<tr>
<td>Increase-MEA</td>
<td>0.05</td>
<td>0.28</td>
<td>0.069</td>
<td>933</td>
<td>2246</td>
<td>463</td>
<td>526</td>
</tr>
</tbody>
</table>

contrary, FEP-g-PSSA (110 keV) was a flat shape.

Figure 6 showed the ATR-F-IR spectra of each grafted membrane (electron incident face and electron transmit face). The absorbance peak around 2925 cm$^{-1}$ assigned -CH$_2$- stretch vibration, which was brought by grafted polystyrene. The absorbance peak of -CH$_2$- stretch vibration observed in FEP-g-PSSA (40 keV) electron incident face. On the contrary, doesn’t observed in electron transmit face. The absorbance peak intensity in FEP-g-PSSA (60 keV) in electron incident face was stronger than that of electron-transmit face. The absorbance peak intensities in FEP-g-PSSA (110 keV) electron-incident face and electron-transmit face were almost same.

The experimental results corresponded to the ultra low energy deposition profiles calculated by EGS5 code. As seen in Figure 1 and Figure 5, the electrons behaviors in FEP depended markedly on themselves accelerating energy. The differences in the energy deposition resulted in the differences in the electrons behaviors in FEP, and hence grated formed functionally gradient. In this experiment, 60 keV electrons irradiation was suitable for fabrication the functionally gradient PEMs.

### 5. Conclusion

The low and ultra low energy EB Depth-Dose profiles were calculated with EGS5. The Depth-Dose profile depended strongly markedly on EB of EB accelerating voltages. Because irradiated electrons behavior in FEP was depended on themselves energy. The FT-IR (ATR) and XPS spectra showed that the functionally gradient partial-fluorinated polymer membranes were fabricated by using the low and ultra low energy EB Depth-Dose profiles. The functionally gradient PEMs had water uptake gradient, and hence could be a promising solution to manage water behavior in MEA. Further study on management water behavior in MEA using the functionally gradient PEMs is being undertaken. The details of the water behavior management will be reported in our next paper.

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### References

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