EFFECT OF LOADING CONDITIONS ON MECHANICAL BEHAVIOR OF NAFION MEMBRANE

Keisuke Kawanishi¹, Isamu Riku² and Koji Mimura³

Department of Mechanical Engineering, Osaka Prefecture University,
1-1, Gakuen-cho, Naka-ku, Sakai City 599-8231, Japan
¹swb03038@edu.osakafu-u.ac.jp, ²riku@me.osakafu-u.ac.jp, ³mimura@me.osakafu-u.ac.jp

Keywords: Nafion membrane, Mechanical Behavior, Molecular Dynamic Simulation

ABSTRACT

To clarify the effect of loading conditions on mechanical behavior of Nafion membrane, we at first employ molecular dynamic (MD) method to constitute the computational models for Nafion membranes under periodic loading condition and for Nafion membrane under LJ flat wall loading condition. And then, a series of MD simulations are performed for Nafion membrane under different relative humidity (RH) circumstance. It is found that the computational results of the model under LJ flat wall loading condition gives a good agreement with the experimental result and is useful for the discussion on the localization of molecular chains at microscopic region.

1 INTRODUCTION

Because of the high power density, high efficiency, fast start-up and zero emission at the point of use, polymer electrolyte fuel cells (PEFCs) are the most promising candidates for replacing internal combustion engines in automobiles, and are also being developed for portable and distributed stationary power generation applications. However, the life of PEFCs is currently limited by the mechanical endurance of polymer electrolyte membrane (PEM) [1].

The failure of PEM is believed to be the result of a combined chemical and mechanical effect acting together [2]. While chemical degradation of the membrane has been investigated and reported extensively in literature, there is little work published on mechanical degradation of the membrane. Recently, it is found that cyclic hydration of the membrane during the operation cycles (start/shut down) of the fuel cell may cause mechanical degradation of the membrane [3]. To investigate such mechanical degradation of the membrane subjected to fuel cell cycles, some microstructure analyses have been done for the membrane made from the sulfonated tetrafluoroethylene copolymer with the trade name Nafion® [4]. Nafion® consists of a hydrophobic polytetrafluoroethylene (PTFE)-like backbone and pendant chains with sulfonated (SO3−) end groups. Under humidified conditions, the hydrophilic end groups segregate into nano-sized clusters, which imbibe water and cause the swelling of the ionomer [5]. To account for the effect of such change of the microstructure of the membrane on the mechanical response, Benziger et al. [6] proposed that membrane swelling and relaxation processes work as an interfacial contact switch between the membrane and the catalyst layer. Moreover, a viscoelastic model has been developed by Lai et al. and the mechanical response predictions upon implementing the model using the data for Nafion® NR111 have been validated with stress measurements from a relaxation test performed at small initial strain (3%) in the linear elastic region [3]. However, in these studies, the computational models are mainly performed for Nafion membrane under simple tension, the effect of loading conditions on the mechanical behavior of Nafion membrane has not been accounted for explicitly.

Therefore, in this paper, to clarify the effect of loading conditions on mechanical behavior of
Nafion membrane, we at first employ MD method to constitute the computational models for Nafion membranes under periodic loading condition and for Nafion membrane under LJ flat wall loading condition. And then, a series of MD simulations are performed for Nafion membrane under different RH circumstance.

2 MD SIMULATION MODEL

Figure 1 shows the structure formula of Nafion®. In this paper, molecular chains of Nafion membrane are represented by coarse-grained model, in which each bead corresponds to a group of atoms such as CF, CF$_2$ and CF$_3$.

![Structure formula of Nafion](image)

Figure 1: Structure formula of Nafion.

2.1 Calculation parameters

The number of the group of monomers shown in Figure 1 is prescribed as $m = 7$, $x = 30$. The number of the beads of Nafion membrane is 300,000 and the number of molecular chains is 370. The equation of motion is solved using the velocity Verlet algorithm with time step 2fs. The simulation is performed under constant temperature of 300K and under constant density conditions (NVT-Nose Hoover ensemble). All the simulations are done using the coarse-grained molecular dynamics program OCTA/COGNAC [7].

2.2 RH

To realize the different RH circumstance, in this paper, water molecules are added to the computational model and the number of water molecules is increased together with the increase of the value of RH [8]. Furthermore, due to the expansion of the Nafion membrane at wet condition, the unit cell size increases together with the increase of the value of RH, which leads to the decrease of the density of the unit cell. Table 1 lists the corresponding parameters under each RH circumstance.

<table>
<thead>
<tr>
<th>RH(%)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell size(nm)</td>
<td>22.4</td>
<td>22.8</td>
<td>23.2</td>
<td>23.5</td>
</tr>
<tr>
<td>Number of water molecules</td>
<td>17,797</td>
<td>36,531</td>
<td>50,582</td>
<td>57,139</td>
</tr>
<tr>
<td>Number of particles</td>
<td>353,092</td>
<td>409,294</td>
<td>451,446</td>
<td>471,117</td>
</tr>
<tr>
<td>Density(g/cm$^3$)</td>
<td>1.92</td>
<td>1.87</td>
<td>1.81</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Table 1: Parameters of computational model.
2.3 Potential energy

The total potential function of the molecular chain of Nafion membrane are given by

\[ U_{\text{total}} = U_{\text{bond}}(r) + U_{\text{angle}}(\theta) + U_{\text{torsion}}(\phi) + U_{\text{nonbond}}(\bar{r}) + U_{\text{coulomb}}(\bar{r}) + U_{\text{external}}(\bar{r}) \]

where \( U_{\text{bond}}(r) \), \( U_{\text{angle}}(\theta) \), \( U_{\text{torsion}}(\phi) \), \( U_{\text{nonbond}}(\bar{r}) \), \( U_{\text{coulomb}}(\bar{r}) \) and \( U_{\text{external}}(\bar{r}) \) represents bond stretching energy, bending energy of successive bonds, torsion energy, van der Waals potential, Coulomb potential and external potential coming from the LJ flat wall, respectively. These potential functions are defined as below:

\[ U_{\text{bond}}(r) = \frac{1}{2} k_r (r - r_0)^2 \]
\[ U_{\text{angle}}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \]
\[ U_{\text{torsion}}(\phi) = \sum_{n=1}^{4} \frac{1}{2} V_n \left[ 1 - (-1)^n \cos(n\phi) \right] \]
\[ U_{\text{nonbond}}(\bar{r}) = D_0 \left[ \left( \frac{\sigma_b}{\bar{r}} \right)^{12} - \left( \frac{\sigma_b}{\bar{r}} \right)^6 \right] \]
\[ U_{\text{coulomb}}(\bar{r}) = \frac{q_i q_j}{4\pi\varepsilon_0 \bar{r}^2} \]
\[ U_{\text{external}}(\bar{r}) = D_w \left[ \frac{1}{5} \left( \frac{\sigma_w}{\bar{r}} \right)^{10} - \frac{1}{2} \left( \frac{\sigma_w}{\bar{r}} \right)^4 \right] \]

where \( k_r \), \( k_\theta \), \( V_n \), \( D_0 \), \( D_w \) are constants, \( r_0 \) is equilibrium bond length, \( \sigma_0 \), \( \sigma_w \) are Lennard-Jones diameters, \( \theta_0 \) is equilibrium angle, \( q_i \), \( q_j \) are the electric charge held by \( i \)th and \( j \)th bead, \( \varepsilon_0 \) is the vacuum conductivity and \( \bar{r} \) is the distance between the LJ flat wall and adjacent beads of the molecular chains.

![Model A](image1.png) ![Model B](image2.png)

Figure 2: Configurations of molecular chains of Nafion membrane under the different loading conditions.

2.4 Loading condition

Figure 2 shows the configurations of molecular chains of the computational models for Nafion membrane under the two different loading conditions. In Model A, the periodic loading condition is
employed to six planes of the cubic unit cell. In Model B, the periodic loading condition is employed to the planes of the cubic unit cell vertical to the tensile direction. To the planes parallel to the tensile direction, external potential $U_{\text{external}}(\mathbf{F})$ is employed.

3 RESULTS

Figure 3 shows the macroscopic stress-strain relations of Nafion membrane under the different loading conditions. In the case of employing the periodic loading condition to all the planes of unit cell (Model A), the stress-strain relation is approximately linear and distinct yield points cannot be observed. Moreover, the effect of RH on the stress-strain relation is not obvious. In the case of employing the external potential to the planes parallel to the tensile direction (Model B), yield points appear distinctly and the dependence of RH is remarkable. Figure 4 shows the comparison between the smoothing curves of the computational results of Model B and the experimental data [9]. The tendency of the curves shown by computational results is quite similar to that of experimental data. Therefore, to reproduce the experimental data by MD method, the constitution of a computational model with LJ flat wall is indispensable.

![Figure 3: Macroscopic stress-strain relations of Nafion membrane under the different loading conditions.](image1)

![Figure 4: Comparison between computational and experimental results of Nafion membrane.](image2)
To clarify the mechanism of the effect of loading conditions on the macroscopic response of Nafion membrane, the development and the distribution of microscopic density of beads in the computational model is investigated. After the discretization of the unit cell by cubic elements as $22 \times 22 \times 22$, the number of beads inside each element is counted and then is divided by the volume of each element to derive the microscopic density of beads. Figure 5 shows the development of the number of elements with low density of beads which is smaller than 10.0nm$^{-3}$. Compared to that of Model A, the initial value of Model B is higher, especially for the case of RH60%. On the other hand, the value of Model A is almost constant throughout all deformation stages whereas that of Model B increases together with the macroscopic deformation. Therefore, it can be understood that the microscopic localization of the beads is remarkable and tends to evolve together with the macroscopic deformation when the computational model is under LJ flat wall loading condition. Figure 6 shows the distribution of density of beads at the center cross section of the unit cell. The distributions of density of beads at the initial and the last deformation stages of Model A is quite similar to each other, whereas the area with high value density of beads in Model B becomes widespread, especially for the case of RH60%.

![Figure 5: Development of the number of elements with low density of beads (<10.0nm$^{-3}$).](image)

4 CONCLUSIONS

In this paper, the effect of loading conditions on mechanical behavior of Nafion membrane has been investigated. It is found that the constitution of a computational model with LJ flat wall is indispensable to reproduce the experimental data by MD method. Furthermore, the microscopic localization of the beads is remarkable and tends to evolve together with the macroscopic deformation when the computational model is under LJ flat wall loading condition.

REFERENCES


Figure 6: Distribution of density of beads.