Study on mechanical model of Nafion membrane

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Abstract

To clarify the effect of density of entanglement points of molecular chains on mechanical behavior of Nafion membrane, we at first employ molecular dynamic (MD) method to constitute the computational models for Nafion membranes with different density of entanglement points of molecular chains. And then, MD simulation for Nafion membrane under simple tension is performed. The results show that relatively high deformation resistance together with a distinct yield point appears in the Nafion membrane, which has a high density of entanglement points of molecular chains.

Keywords: Nafion membrane, Mechanical behavior, Entanglement point, Molecular chain, MD

Introduction

Because of the high power density, high efficiency, fast start-up, and zero emission at the point of use, proton exchange membrane fuel cells (PEMFCs) 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 PEMFCs is currently limited by the mechanical endurance of polymer electrolyte membranes (PEMs) [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 investigating 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 pendent chains with sulfonated (SO_3^-) 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 just phenomenological ones and the change in the entanglement situation for the physical linkages of the molecular chain has not been accounted for explicitly.

Therefore, in this paper, to clarify the effect of density of entanglement points of molecular chains on mechanical behavior of Nafion membrane, we at first employ molecular dynamic (MD) method to constitute the computational models for Nafion membranes with different density of

entanglement points of molecular chains. And then, MD simulation for Nafion membrane under simple tension is performed and the relationship between the macroscopic yield behaviour and the movement of molecular chains is discussed.

MD Simulation Model

Figure 1 shows the structure formula of Nafion®. In this paper, polymer 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, CF_3. The total potential function of the molecular chain of Nafion membrane are given by

$$U_{total} = U_{bond}(r) + U_{angle}(\theta) + U_{torsion}(\phi) + U_{nonbond}(\bar{r}) + U_{coulomb}(\bar{r})$$

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

$$U_{bond}(r) = \frac{1}{2} k_b (r - r_0)^2$$

$$U_{angle}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

$$U_{torsion}(\phi) = \sum_{n=0}^{4} \frac{1}{2} V_n \left[1 - (-1)^n \cos(n\phi)\right]$$

$$U_{nonbond}(\bar{r}) = D_0 \left[\left(\frac{\sigma_0}{\bar{r}} \right)^{12} - \left(\frac{\sigma_0}{\bar{r}} \right)^{6} \right]$$

$$U_{coulomb}(\bar{r}) = \frac{q_i q_j}{4\pi\varepsilon_0 \bar{r}^2}$$

where k_b, k_θ, V_n, D_0 are constants, r_0 is equilibrium bond length, σ_0 is Lennard-Jones diameter, θ_0 is equilibrium angle, q_i, q_j are the electric charge held by i th and j th bead, and ε_0 is the vacuum conductivity.

The number of the group of monomers shown in Figure 1 is prescribed as $m = 4$, $x = 10$. The number of the beads of Nafion membrane is 21,000 and the number of molecular chains is 100. To clarify the effect of the density of entanglement points of molecular chains, two different models of membrane are constituted. One is a point-poor model, in which the number of entanglement point is poor, and the other is a point-rich model, in which 50 entanglement points have been added to the point-poor model equally. Figure 2 shows the configuration of molecular chains of the point-rich model. The equation of motion is solved using the velocity Verlet algorithm with time step 2fs. The simulation is performed using a periodic boundary condition for the x and y axial directed walls of the simulation model. All the simulations are done using the coarse-grained molecular dynamics program OCTA/COGNAC [7]. Relaxation of the simulation model is carried out for 50,000 time steps under constant-temperature of 300K and density conditions (NVT-Nose Hoover ensemble).

Simulation Result

Figure 3 shows the macroscopic stress-strain relation of Nafion membrane. The point-poor model shows an elastic-like response whereas the point-rich model shows an elastoplastic-like response.

To clarify the effect of the density of entanglement points on such macroscopic response, the microscopic movement of certain molecular chains has been investigated. Figure 4 shows the difference between the position of several beads of one molecular chain of point-rich model and its corresponding position when the molecular chain moves as a rigid solid. It can be understood that there are two different patterns of the movement of the molecular chain. One pattern is shown in Figure 4(a) that the difference of the position of all the investigated beads increases gradually. The other pattern is shown in Figure 4(b) that the difference of the position of several beads once increases dramatically at the deformation stage, marked as "A", and decreases quickly at the subsequent deformation stage whereas the difference of the position of the other beads is negligible. As a result, the molecular chains that behave in the pattern shown in Figure 4(a) attribute to the elongation of Nafion membrane whereas the molecular chains behave in the pattern shown in Figure 4(b) have no attribution to the deformation of Nafion membrane but have considerable relation with the macroscopic yield behavior of Nafion membrane. Table 1 shows the number of the corresponding molecular chains of each pattern for the point-poor and the point-rich model. The fraction of the molecular chains that behaves in the pattern shown in Figure 4(b) increases from 27% to 47% when the number of entanglement points of the molecular chain increases. Based on the results shown above, we imply that the increase of the number of entanglement points of molecular chain leads to the tendency of the network of molecular chains to deform more locally at the microscopic region and consequently much more deformation of molecular chains behaving in pattern shown in Figure 4(a) and much more possibility of movement of molecular chains behaving in pattern shown in Figure 4(b), i.e. macroscopic yield behavior of Nafion membrane.

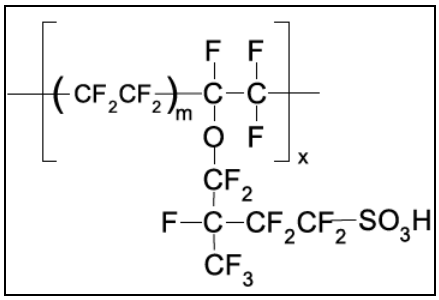


Figure 1. Structure formula of Nafion®

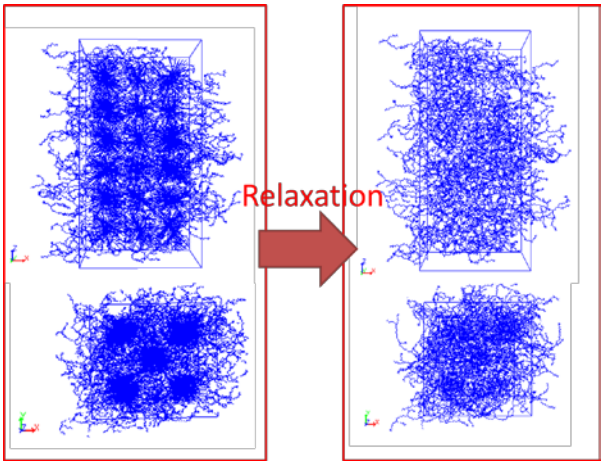


Figure 2. Configuration of molecular chains of the point-rich model of Nafion membrane

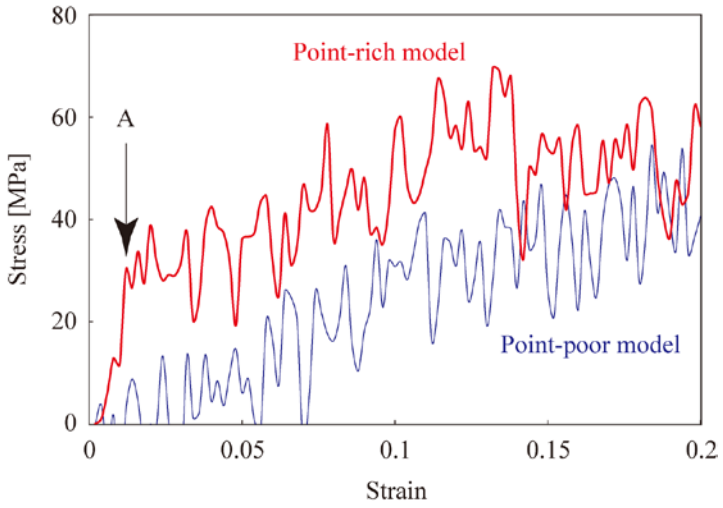
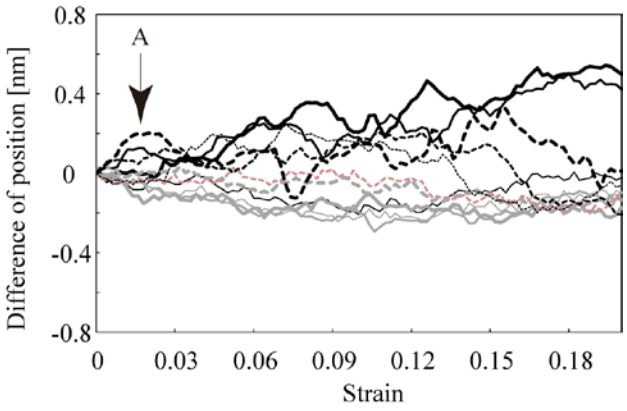
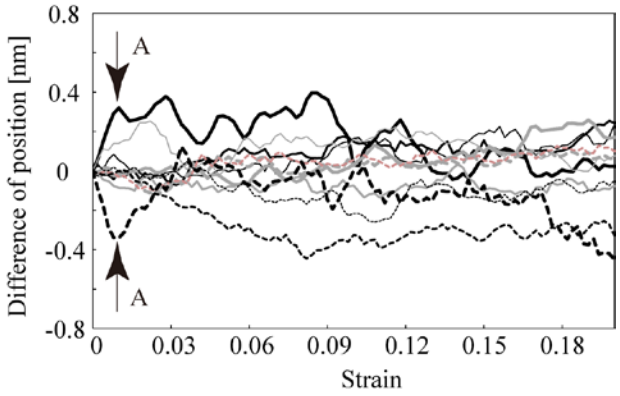


Figure 3. Macroscopic stress-strain relation of Nafion membrane



(a)



(b)

Figure 4. Movement of the beads inside the molecular chain of point-rich model of Nafion membrane

Table 1. Number of molecular chains

	Pattern shown in Figure 4(a)	Pattern shown in Figure 4(b)
Point-poor model	73	27
Point-rich model	53	47

Conclusions

In this paper, we constituted the MD computational models for Nafion membranes with different density of entanglement points of molecular chains and employed such models to clarify the relationship between the macroscopic yield behaviour and the movement of molecular chains. We found that the increase of the density of entanglement points of molecular chain leads to the tendency of the network of molecular chains to deform more locally at the microscopic region and consequently high deformation resistance together with a distinct macroscopic yield point of Nafion membrane.

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