Supplementary Material

Mechanical stretching-induced orientation of anion exchange membrane to improve ion conductivity

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# Molecular dynamics simulation

In the following sections, the equilibrium molecular dynamics methods utilized in this work are presented. The molecular force field can be divided into all-atom field, joint atom field, coarse-grained field and reactive molecular field. The all-atom force field considers the interaction of each atom in the molecule. It is generally believed that the mass of the atom is concentrated around the center of the atom, and the force of the atom is also located in the center of the atom. Although the all-atom force field is more accurate, due to the consideration of the interaction between each atom, it requires a huge amount of calculation. In order to reduce this, we use a joint atom force field approach, such as the *ab initio* COMPASS (condensed-phase optimized molecular potential for atomistic simulation studies) force field [Sun, 1998]. In the COMPASS force field, the mass of a hydrogen atom connected with a carbon atom is superimposed to the center of the carbon atom, and the effects of other atoms on the hydrogen atom are also superimposed on the center of the carbon atom to form a joint carbon‒hydrogen atom, which greatly reduces the complexity and parameters of the force field. Thus, the COMPASS force field is a collection of many particles in the unit of an atom or atom group. It takes complicated functional forms, including off-diagonal cross-coupling terms and high-order force constants into consideration. Functional groups and non-bond parameters are completely parameterized. The potential energy is expressed by the following equations:

|  |  |
| --- | --- |
|  | (S1) |
|  | (S2) |
|  | (S3) |
|  | (S4) |
|  | (S5) |
|  | (S6) |

The energy expression is shown as Equations (S1) ‒ (S6) [Yang et al., 2000]. The potential energy of the system can be expressed as the sum of valence terms and non-bond interaction terms. is the sum of the potential energies of all atoms *i* in the computational domain, which is related to . The valence terms include internal coordinates of bond, angle, torsion angle, out-of-plane angle, and cross-coupling terms, where , , , included in valence terms signify bond lengths, angles, torsion angles, and out-of-plane angle, respectively, as shown in Equation (S2). The subscript “0” in Equation (S2) represents the reference value, parameters without subscript represent the actual value at the instant, and *K* is a constant, all of which are related to . The non-bond interactions (including a Lennard‒Jones potential [McQuaid et al., 2004] for the van der Waals term and a Coulombic function for an electrostatic interaction) between atoms separated by two or more intervening atoms or between atoms from different molecules are studied, all of which are a function of the distance . In Equations (S4) ‒ (S5), is the distance between the atoms, *ε* and *σ* are the potential energy parameters, and *q* is the charge of the atom.

# Boundary and Initial Conditions

Three-dimensional periodic boundary conditions are adopted in this study. During the simulation, particles move out of and into the computational domain; the application of periodic boundary conditions means that the computational domain with *N* particles is surrounded by identical neighboring lattices, thus approximating a microscopic infinite material system.

The initial conditions include the initial position and initial velocity of each atom in the computational domain. The initial positions of the atoms were either specified randomly or from a previous calculation such as energy minimization. According to the target temperature, the initial velocities were created at random at the start of a dynamics run. At a given temperature, the initial velocity can be distributed according to the Maxwell rate distribution:

|  |  |
| --- | --- |
|  | (S7) |

where *mi* refers to the atom mass, *T* is the system temperature, and *kB* is the Boltzmann constant.

# Numerical method

The simulation process is used to solve the governing Newton's equations of motion by using the “Verlet velocity algorithm” [Yang et al., 2000] shown below:

|  |  |
| --- | --- |
|  | (S8) |
|  | (S9) |
|  | (S10) |

where is determined through Equation (2). Considering the accuracy and time of the simulation, the time step is selected according to reference [Allen and Tildesley, 1987].

In MD simulations, we need to determine the ensemble of simulations. This is a basic concept introduced when statistical methods are used to describe the statistical laws of thermodynamic systems. Thermodynamic properties of the computational domain include kinetic energy, temperature and pressure, etc. The kinetic energy of the system is related to the velocity of each atom:

|  |  |
| --- | --- |
|  | (S11) |
|  | (S12) |

where *NC* represents the number of constraints in the computational domain. Therefore, is the degree of freedom in the computational domain. In addition to energy and temperature, pressure is also an important quantity of the system. Pressure is calculated through using the virial theorem [Allen and Tildesley, 1987]. Thermodynamic pressure, volume, thermodynamic temperature, and internal virial are related in the following equations:

|  |  |
| --- | --- |
|  | (S13) |

where the virial *W* is defined as:

|  |  |
| --- | --- |
|  | (S14) |

with *ri* the position vector, and *Fi* the force on atom *i* experienced by all other atoms.

The annealing procedure proposed by Mabuchi and Tokumasu [Mabuchi and Tokumasu, 2014] was repeated for five cycles to generate the final structures for the dynamic simulation. During the dynamic simulation, the final polymer chain structures obtained were heated from 300 K to 500 K (a sufficient range of temperature differences to render the conformation reasonable) over a period of 500 ps in the constant-temperature, constant-pressure (NPT) ensemble [Ozmaian and Naghdabadi, 2015], followed by another 1000 ps in the constant-temperature, constant-volume (NVT) ensemble [Ozmaian and Naghdabadi, 2015].The temperature was controlled by the Nose‒Hoover method [Branka and Wojciechowski, 2000] in the simulation procedure, and the pressure was controlled by the Berendsen method.

In this study, the convergence tolerances of energy and force of geometry optimization are shown in Equation (S15)(S16); the convergence threshold was determined by the specified maximum energy and force change:

|  |  |
| --- | --- |
|  | (S15) |
|  | (S16) |

Once convergence is achieved, the system of atoms in the computational domain is considered to have reached equilibrium.

# Validation of the equilibration

Considering the balance between the calculation accuracy and calculation time, the time step was set as 1 fs according to reference [Mabuchi and Tokumasu, 2014]. The time step independent verification is carried out as shown in Figure S1 (a). The total energy and force of the system reaching equilibrium is 4.057×103 kcal mol1 and 8.871 kcal mol1 Å1, respectively. The convergence threshold for the specified maximum energy or force change is given as , and . Comparing the simulation results with the literature value, the density of PPO-TMA at strain = 0, *λ* = 10 is 1.095 g cm3 and an agreement between the experimental and theoretical model [Zhang and Duin, 2015] is observed, confirming the veracity of the parameter values used in the MD simulation. The densities of the simulated systems with different water content are shown in Figure S1 (b). To verify whether the total dynamics simulation time was sufficient, the simulation time was extended for an additional 4 ns. The density of simulation system reached the same value when the simulation time exceeds 500 ps, suggesting the simulation model had been adequately relaxed. Moreover, the influence of the unit lattice size on the equilibrium state was excluded by investigating the density evolution at different lattice sizes. In the models with lattice length of 40 Å and 60 Å, the system densities will eventually stabilize to the same value, respectively, which can further confirm the condition of the equilibrium state.



**Supplementary Figure 1.** (a) Time step independent verification; (b) The densities of the simulated systems.



**Supplementary Figure 2.** Density field (g cm-3) of polymer chains at (a) initial state and (b) stretched in *z*-direction; *z*-direction is the same as shown in Figure 1.



**Supplementary Figure 3.** The density field (g cm-3) of water cluster corresponding to different strains.



**Supplementary Figure 4.** Free volume of PPO-TMA membrane under mechanical deformation at different water contents.







**Supplementary Figure 5.** The radial distribution functions of (a) N‒N, (b) N‒Ow (oxygen atom in water molecule) and (c) N‒Oh (oxygen atom in hydroxide ion) at initial state and at 60% strain condition.

**Supplementary Table 1.** Coordination numbers (CNs) at un-stretched and 60% strain condition.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | N‒N | | N‒Ow | | N‒Oh | |
| *λ* | Un-stretched | Stretched | Un-stretched | Stretched | Un-stretched | Stretched |
| 5 | 6.214 | 6.053 | 4.976 | 4.792 | 8.252 | 7.733 |
| 10 | 4.727 | 4.885 | 4.476 | 4.253 | 6.596 | 6.043 |
| 15 | 3.975 | 4.154 | 3.514 | 3. 428 | 5.517 | 5. 671 |
| 20 | 3.011 | 3.446 | 2.369 | 2.132 | 4.332 | 4.471 |

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**Supplementary Figure 6.** Mean square displacements of hydroxide ion under different strains and various water content.

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