Understanding The Effects of Different Counterions in Proton-Exchange Membranes using Molecular Dynamics

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Abstract
PFSA ionomers, especially Nafion, are the most common material used for proton-exchange membranes in polymer-electrolyte fuel cells due to their good ionic conductivity and chemical stability. Nafion ionomer has sulfonate groups at the end of each of their side chains, allowing for many interactions between counterions; these counterion interactions affect the morphology of the system. In order to explore the effects of different counterions, we will perform molecular dynamics simulations on Nafion and investigate the changes in the nanoscale morphology of the system. Energy minimization, equilibration, and production steps were performed on a system of fifty ten-monomer chains of Nafion, packed into a 10x10x10 nm cube and solvated with water and enough Na⁺, Co²⁺, or Fe²⁺ ions to maintain electroneutrality. The radial distribution functions for each of the counterions around the oxygen of the sulfonate groups were then calculated, along with the diffusion coefficients which were extracted from mean squared displacement calculations. The higher valency ions (Co²⁺ and Fe²⁺) interacted significantly more with the sulfonate groups, as they formed denser solvation shells that lay closer to the sulfonate groups, as well as showing lower diffusion coefficients when compared to the sodium ions.

Nafion: The Premier Ionomer for Proton-Exchange Membranes

• Per-fluorinated sulfonic acid (PFSA) ionomers are known for their ionic conductivity and chemical stability
• Used as proton-exchange membranes in polymer-electrolyte fuel cells
• Nafion was the first commercially produced PFSA ionomer and remains the leading PFSA ionomer used today
• Nafion chain constructed using Avogadro

Figure 1. Chemical structure of Nafion and morphology when hydrated, https://doi.org/10.1007/s10008-020-04520-6

• Phase separation arises due to hydrophobic backbone and hydrophilic side chains

How do different counterions affect the nanoscale morphology of Nafion?

Modeling Nafion Using Molecular Dynamics Simulations

• Molecular Dynamics (MD) obtains evaluates the time evolution of many-particle systems by computing Newton’s equations of motion
• Use GROMACS software, OPLS-AA forcefield, TIP4P-Ew water model

Figure 2. Nafion polymer chain (10 monomers) constructed using Avogadro (left), where 50 chains were then packed into a 10x10x10 nm cube and solvated with water and a counterion.

• Created a system of Nafion chains solvated with water and counterions:
  • Na⁺, Co²⁺, Fe²⁺
• Energy Minimization:
  • Relaxation of system to optimize starting position
• Equilibration:
  • NVT: Stabilize temperature
  • NPT: Stabilize Pressure
  • 8 iterations of 2 NVT, 1 NPT
• Production:
  • Ran simulation for 100 ns

Figure 3. Visualizaion of the water channels after simulation (Nafion chains are hidden).

Table 1. The diffusion coefficients for the water molecules and the counterions obtained through the calculation of their mean squared displacements.

<table>
<thead>
<tr>
<th>Counterion</th>
<th>D of Counterion (cm²/s)</th>
<th>D of Water (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.1313 x 10⁻⁵</td>
<td>0.3399 x 10⁻⁵</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>0.0195 x 10⁻⁵</td>
<td>0.3552 x 10⁻⁵</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.0277 x 10⁻⁵</td>
<td>0.3716 x 10⁻⁵</td>
</tr>
</tbody>
</table>

Conclusions

• Co²⁺ and Fe²⁺ ions have denser solvation shells around and lie closer to the sulfonate groups, therefore there are a greater number of stronger interactions compared to Na⁺.
• Co²⁺ and Fe²⁺ ions have a lower diffusivity also indicating there are more interactions
• Future work:
  • Compare to experimental results
  • Use a more accurate forcefield
  • Find coordination numbers

References