Advanced Molecular Modeling for Next-Generation Fuel Cell Membranes

Hypotheses: Molecular dynamics simulations can be used to quantify proton transport capabilities of amphiprotic materials for use in hydrogen fuel cells.

Introduction: Vehicular internal combustion engines are responsible for 28% of greenhouse gas emissions in the United States and are the second biggest source of these emissions (1). Proton exchange membrane (PEM) hydrogen fuel cells are a cleaner alternative to the internal combustion engine, emitting only water (2). The high cost of hydrogen fuel cells, however, impedes their success. Current fuel cells operate at low temperatures ($85^{O}C$) to maintain loading of the membrane with water. Water serves as the proton exchange fluid. Operating at these temperatures requires an expensive platinum catalyst (3). To overcome this problem I will implement cutting-edge modeling in the Scott Auerbach laboratory at UMass Amherst to develop anhydrous proton exchange materials and improve the viability of PEM fuel cells.

Among the most promising proton conducting materials are azoles – five-membered carbon and nitrogen rings that both accept and donate protons (4). To increase molecule stability, we tether them to oligomer chains. Oligomers offer a compromise between material stability and liquid-like flexibility, allowing for faster and more efficient proton motion (5). Molecular dynamics (MD) simulations enable the study of hydrogen bonding interactions of these systems. I propose investigating the hydrogen bond lifetime and reorientation rate of amphiprotes tethered to oligomers using MD simulations. I will accomplish the following goals: 1) Run atomistic MD simulations on tethered imidazole; 2) Run coarse-grain MD simulations on tethered imidazole; 3) Benchmark across length scales; 4) Use both models to investigate other azoles.

The project focus is on hydrogen bonding networks that govern proton diffusivity. Through modeling we relate microscopic properties to macroscopic performance to design new PEMs.

Background: To study hydrogen bonding networks formed by tethered amphiprotes, we run molecular dynamics (MD) simulations, which allow the observation of atomic-level changes. Efficient proton transport takes place via the Grotthuss mechanism, which involves the transport of a proton by the collective motion of many hydrogen bonds (Figure 1). This is reminiscent of bucket brigades to put out fires. The Grotthuss mechanism requires hydrogen bond networks followed by functional group rotation before transport of the next proton (6). Herein lies the challenge of designing efficient proton conductors: extended hydrogen bonding arises in solid-like systems, while rapid functional group rotation occurs in liquid-like systems. MD allows us to compare the atomic level trade-offs between extended hydrogen bond clusters and functional group dynamics. Balancing these parameters is vital for designing next-generation PEMs.

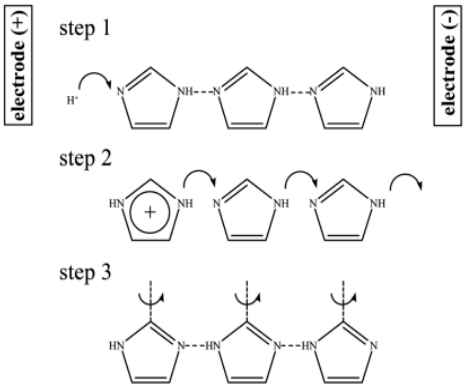

Figure 1: Grotthus mechanism of proton transfer in imidazole (6)

1) MD of tethered imidazole: Imidazole is promising because it offers long H-bond lifetime and fast reorientation compared to other azoles (5). I will use MD software DL-POLY to run atomistic simulations on imidazole oligomers. With NPT constant temperature and pressure simulations we extract volume parameters that we input into NVE constant volume and energy models. These simulations enable calculations of hydrogen bond cluster size, lifetime, and reorientation rate. These simulations cover extremely short times – on the order of 10^{-9} seconds. To study proton transfer over more realistic scales, the next step is coarse-grain modeling.

2) Coarse-grain modeling of tethered imidazole: In MD, the formation and reorientation of hydrogen bonds occur on the order of picoseconds (10^{-12} s) to nanoseconds (10^{-9} s), while the MD time step is femtoseconds (10^{-15} s), thus requiring prohibitively long simulations. Coarse-grained MD allow us to increase the time step by restricting atomistic degrees of freedom (such as vibrational modes between atoms.) Coarse-graining also allows us to consider systems approaching macroscopic dimensions of real membranes. I will build a coarse-grained model in Gromacs software using the Martini force field (7). Martini maps four functional groups (such as CH_2) to one coarse-grain bead. These beads imitate the behavior of the functional groups they represent by replicating their dipole moments. Atomistic simulations consist of 300 oligomers, but through coarse-graining we can model up to 4500 oligomers, an order of magnitude increase. This will enhance our understanding of the behavior of proton transfer fluids in an actual PEM.

3) Model benchmarking: We will benchmark coarse-grain models against atomic-level simulations to ensure that hydrogen bond properties agree across length scales. To do so I will work with Qinfang Sun, a graduate student in the Auerbach lab. She has built atomic-level simulations of azole liquids and oligomers, and her expertise will enable me to be successful. I will use her results to build a coarse-grained system to study long range interactions between molecules. By combining the results from our studies, we will have a much more complete picture of proton transfer and potential for use of tethered amphiprotic materials in fuel cells.

4) Expansion of model to other amphiprotes: Once the coarse-grain model is benchmarked, it becomes an effective tool for studying PEM materials. I will investigate how other azoles, including triazole, tetrazole, and pyrazole, change the nature of hydrogen bonding cluster size and lifetime. I will also study how oligomer backbone length affects these parameters, searching for balance between percolating hydrogen bonds and rapid reorientation dynamics.

Intellectual merit: My background as a chemical engineer is crucial for this project, combining my knowledge of chemistry with my engineering, problem-solving perspective. I will use my knowledge to build models that accurately represent material behavior. I will implement the models to study hydrogen bond capabilities of proton exchange materials. However, this project will not be as simple as determining which material offers the highest performance. I must find the optimal trade-off between hydrogen bond lifetime and reorientation rate. It is my responsibility to decide which materials are most promising for next generation PEMs.

Broader Impacts: Hydrogen fuel cells offer environmentally sustainable transportation. My research will further PEM development by identifying the most promising materials to focus on in lab testing. These materials have the potential to revolutionize PEM fuel cells, reducing cost and increasing cell lifetime. The goal of this research is to make fuel cells competitive with the internal combustion engine, offering an environmentally friendly and cost effective alternative. If successful, my research will give everyone access to affordable, green transportation.

References

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