SAND2017 - 8118C

Modeling the Impact of Sulfonate Concentration on Proton Diffusion in Hydrated SDAPP

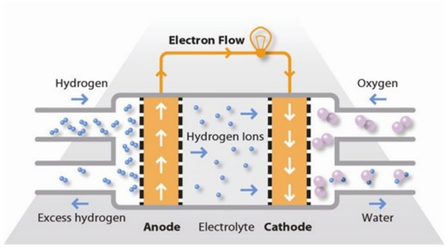
Jennifer Antonia Clark & Amalie L. Frischknecht, Center for Integrated Nanotechnologies, Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY
Office of Science
cint.lanl.gov

Polymer Electrolyte Membranes

What is an electrolyte membrane and how is it used?

Polymer electrolytes are used as membrane separators in fuel cells and various types of batteries.



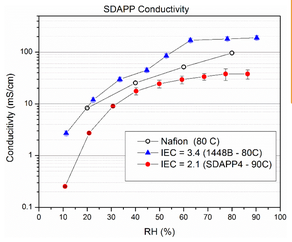
The membrane must have:

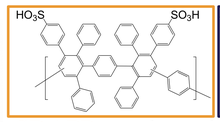
- Mechanical properties and dimensional stability capable of separating electrodes
- Thermal stability
- Efficient proton conductivity

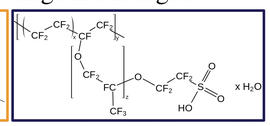
What are we using now and how do we make it better?

The current polymer electrolyte used as a proton exchange membrane, Nafion, does not meet DOE targets for these membranes.

Sandia owns an alternative polymer, Sulfonated Diels-Alder Polyphenylene (SDAPP) which is closer to meetings DOE targets.







SDAPP conducts better than Nafion with the right sulfonate concentration

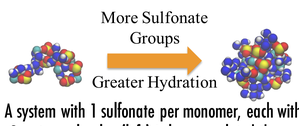
How can we alter polymer chemistry and topology to increase proton transport?

Previous Atomistic Simulations

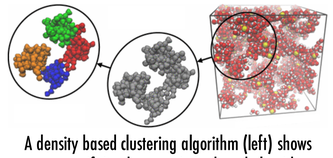
Previous works showed that polymer morphology affects ion transport[1].

A density based clustering algorithm applied to atomistic (AA) simulations of three monomer chains, brought new insight into understanding SDAPP[2] as an ion transporter.

Larger degrees of hydration and sulfonation were found to yield a percolated morphology, which is conducive to ion and proton transport.



A system with 1 sulfonate per monomer, each with 3 water molecules (left) is less percolated than a system with 4 sulfonate groups per monomer, each with 10 water molecules (right) [2]

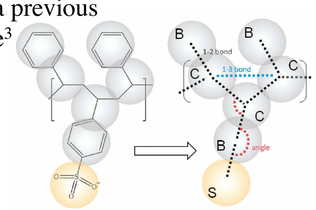


A density based clustering algorithm (left) shows more specificity than proximity based algorithm (center)

Adapting a Dissipative Particle Dynamics Force Field for SDAPP

To better understand this system we need to access larger length and time scales, and model proton diffusion.

Our coarse-grain (CG) model is based on a previous model produced for sulfonated polystyrene[3]



DPD Nonbonded Potential Model:

$$\boldsymbol{F_{ij}(r_{ij})} = \boldsymbol{F_{ij}^{(C)} + F_{ij}^{(D)} + F_{ij}^{(R)}}$$

Conservative Force:

$$\boldsymbol{F_{ij}^{(C)}(r_{ij})} = a_{ij} w(r_{ij})\, \boldsymbol{r_{ij}}/r_{ij}$$

Drag Force:

$$\boldsymbol{F_{ij}^{(D)}(r_{ij}, v_{ij})} = -\gamma w(r_{ij})^2 (\boldsymbol{r_{ij}} \cdot \boldsymbol{v_{ij}})$$

Random Force:

$$\boldsymbol{F_{ij}^{(R)}(r_{ij})} = \sqrt{2\gamma kt}\, w(r_{ij})\, r_{ij} \theta_{ij} \boldsymbol{r_{ij}}/r_{ij}$$

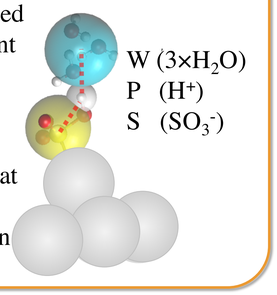
Where θ_{ij} fluctuates with time and

$$w(r_{ij}) = 1 - \frac{r_{ij}}{R_C}$$

- All beads have the same size and mass
- Repulsion parameters are derived from infinite dilution activity coefficients
- All self interaction parameters are equal and based on the compressibility of water

DPD Innovations

1. **Charge smearing:** A coulombic potential used with DPD must also be soft and lack divergent behavior to allow for a longer time step. A Slater-type decay function has solved this problem in DPD systems[4,5].
2. **Proton Coordination:** A Morse potential, that represents proton coordination, correctly models the ratio of proton and water diffusion coefficients as well as sulfonate K_a.

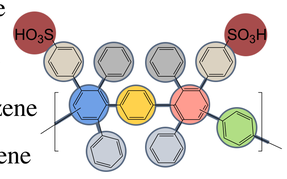


Extending DPD Force Field for Sandia's SDAPP

To apply the above force field to our system we need to define harmonic bond and angle potentials.

7 benzene definitions with 3 bond and 7 angle potentials are needed to describe the correct conformation of this benzene based system

- BM Meta-Benzene
- BP Para-Benzene
- BE External Benzene
- BI Internal Benzene
- B1 Benzene between BI and BE
- B2 Benzene between BE and B3
- B3 Benzene between B2 and BI



- All Benzene beads have the same nonbonded interactions
- Bond and angle definitions were fit using Boltzmann Inversion to define conformation

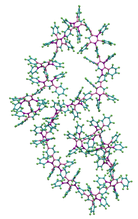
Comparison of Atomistic and DPD Models

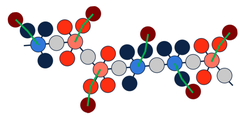
Our bead definitions acceptably match the atomistic results for a 10 monomer polymer in water.

We compared the radius of gyration of the AA and DPD polymers.

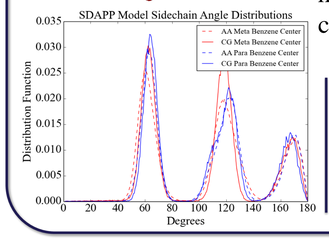
AA Radius of Gyration: 30.2 Å

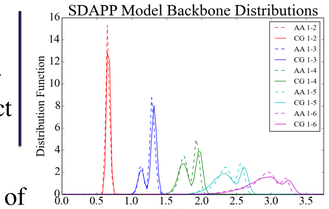
DPD Radius of Gyration: 38.9 Å



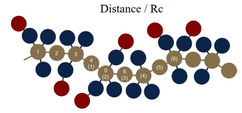


The groups connected to a benzene center have the correct conformation





The stiffness of the polymer chain is consistent with atomistic simulations



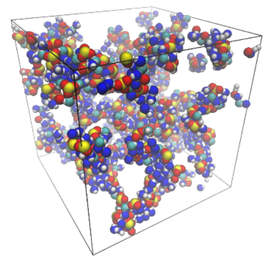
Comparing Membrane Properties

How do we confirm the effectiveness of our model?

We will reproduce clustering distributions with respect to sulfonation and hydration

What can we obtain with our new model?

1. Insight into how morphology affects proton diffusion in larger systems
2. How sulfonate mechanistically aids in proton transport
3. Mechanical properties of SDAPP with various morphologies



Atomistic percolated system [2]

References

1. Hall, et al., *Physical Review Letters* **106,** 127801 (2011); *Journal of American Chemical Society* **134**, 574 (2012); *Macromolecules* **45**, 8097 (2012)
2. Abbott, L. J., A. L. Fischknecht, *Macromolecules* **50**, 1184 (2017)
3. Lee, M., A. Vishnyakov, A. V. Neimark, *The Journal of Chemical Physics* **144**, 014902 (2016)
4. Gonzalez-Melchor, M., et al., *The Journal of Chemical Physics* **125**, 224107 (2006)
5. Lee, M., A. Vishnyakov, A. V. Neimark, *Journal of Chemical Theory and Computation* **11**, 4395 (2015)

Los Alamos NATIONAL LABORATORY EST.1943

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525

Sandia National Laboratories