SAND2016-11426D

Nanoscale Structure and Morphology of Sulfonated Polyphenylene Polyelectrolytes via Atomistic Simulations

Lauren J. Abbott and Amalie L. Frischknecht
Org. 1814, Sandia National Laboratories

Sandia National Laboratories

Introduction

Polymer electrolyte membranes (PEMs) are being explored as an ion-conductive layer to use between the anode and cathode in fuel cells (Fig. 1). State-of-the-art PEMs include perfluorosulfonic acid polymers, like Nafion, which have flexible backbones and side chains that readily form distinct ionic domains. However, they often suffer from high cost, reduced performance at high temperatures and low water contents, and long-term degradation.

Sulfonated Diels-Alder polyphenylene (SDAPP) is a promising alternative to Nafion.[1,2] It has an aromatic backbone with six pendant phenyl groups per repeat unit, which provide up to six sites for post-sulfonation (Fig. 2). SDAPP forms thermally and mechanically robust membranes with high ionic conductivities and low methanol crossover.

In this work, we performed atomistic molecular dynamics (MD) simulations to study the nanoscale structure and morphology of the aggregated ionic domains formed in SDAPP. We systematically varied the sulfonation level as the number of sulfonate groups per monomer (S = 1, 2, 4) and the hydration level as the number of water molecules per sulfonate group (λ = 3, 5, 10, 20).

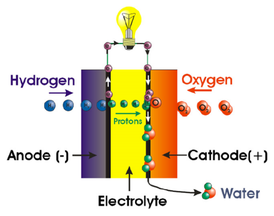


Figure 1: PEM fuel cell[3]

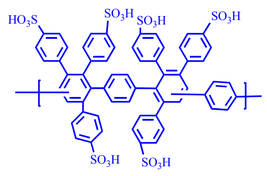


Figure 2: Structure of SDAPP

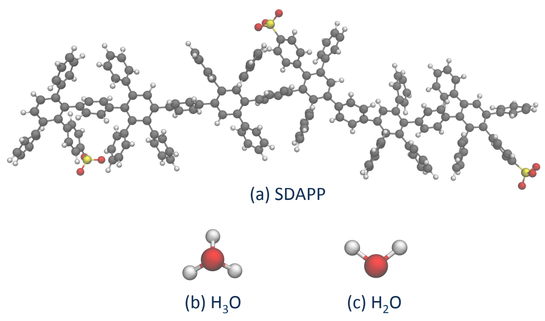
Computational Methods

Structure generation:

- Initial structures built via Enhanced Monte Carlo[4]
- 5 boxes with random initial configurations
- 70 SDAPP trimers, water and hydronium ions (Fig. 3)
- Equilibration at high temperatures and pressures
- Box lengths of 66-91 Å, densities of 1.1–1.3 g cm^{-3}

Simulation details:

- OPLS-AA force field for polymer interactions
- TIP4P/2005 water model, 4-site hydronium ion model
- MD simulations performed in LAMMPS[5]
- 12 Å short-range cutoff, long-range interactions via PPPM



(a) SDAPP

(b) H_3O (c) H_2O

Figure 3: Molecules in atomistic simulations

Local Structure of Ionic Domains

Local structure around the sulfonate groups (Fig. 4):

- Sulfonate groups were more hydrated by water molecules with increasing sulfonation and hydration levels
- Hydronium ions moved more often from the first to second solvation shell at higher hydration levels
- Sulfonate groups moved further apart at higher hydration levels, but not at higher sulfonation levels

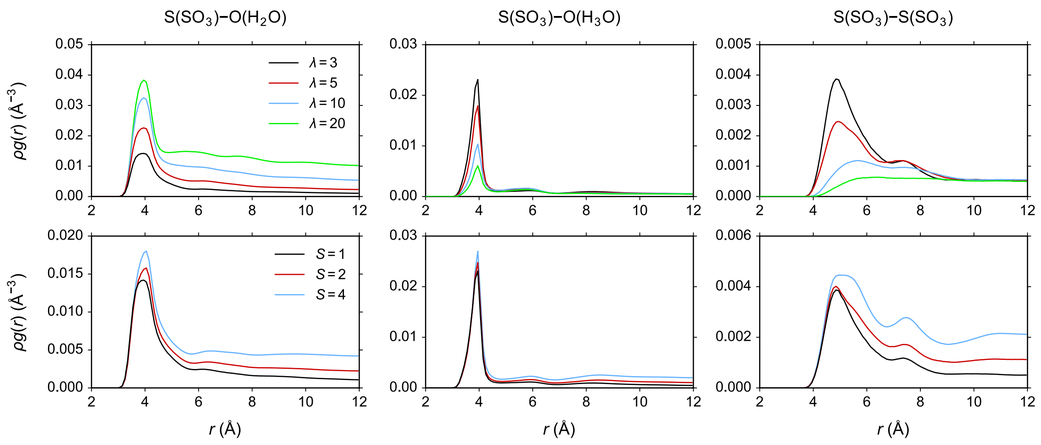
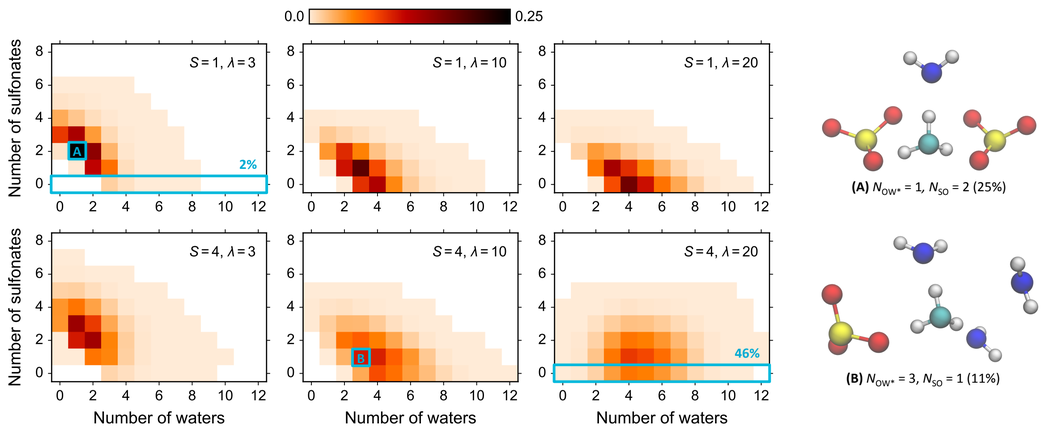


Figure 4: Partial radial distribution functions varying the hydration level (top) and sulfonation level (bottom)

Local structure around the hydronium ions (Fig. 5):

- Hydronium ions were often coupled to one or more sulfonate groups at low hydration levels
- Hydronium ions were surrounded by more water molecules and fewer sulfonate groups at higher hydration levels



(A) N_{OW*} = 1, N_{SO} = 2 (25%)

(B) N_{OW*} = 3, N_{SO} = 1 (11%)

Figure 5: 2D histograms of sulfonate and water coordination numbers around hydronium ions (left) and example snapshots (right)

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND No. 2011-XXXXP

Connectivity of Ionic Aggregates

Distance-based clustering algorithm[6]:

- Clusters were assigned using cutoff distances between hydrogen bonding O–O and O–H pairs (Fig. 6)
- Aggregated became more fully percolated with increasing hydration and sulfonation levels (Fig. 7, left)
- Almost all systems had a large percolated cluster containing nearly all of the sulfonic groups (Fig. 7, right)

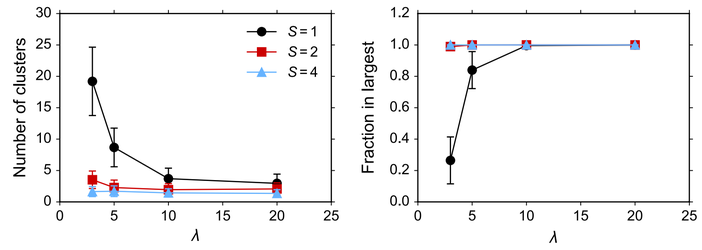


Figure 7: Number of clusters (left) and fraction of SO_3 groups in largest cluster (right)

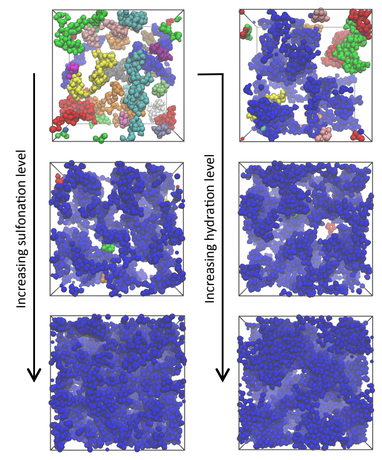


Figure 6: Snapshots of distance-based clusters, each shown in a different color

Size and Shape of Ionic Aggregates

Density-based clustering algorithm[7]:

- Clusters were identified by regions of high local density separated by relatively large distances (Fig. 8)
- Aggregates maintained a similar number of ionic groups, but gained water molecules at higher sulfonation and hydration levels (Fig. 9)
- Aggregates grew only slightly in size and became more spherical in shape at higher sulfonation and hydration levels (Fig. 10)

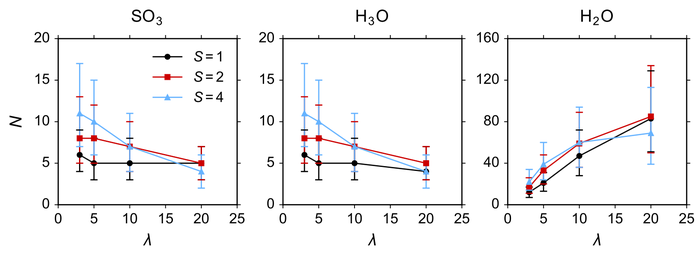


Figure 9: Number of SO_3 (left), H_3O (center), and H_2O (right) groups per cluster.

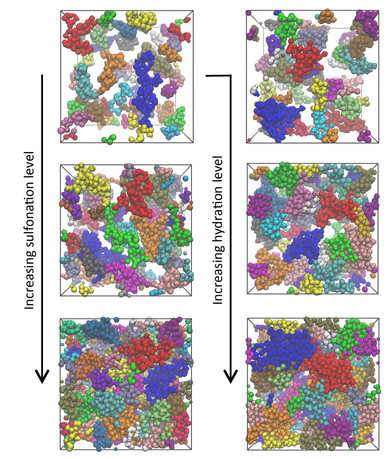
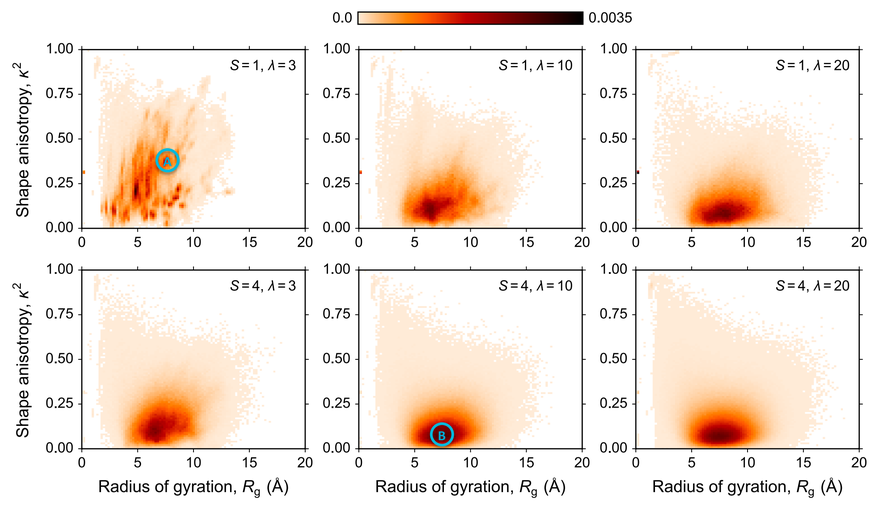
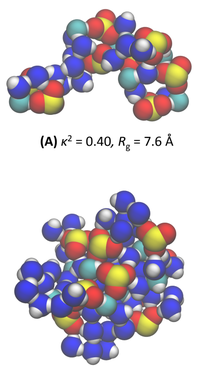


Figure 8: Snapshots of density-based clusters, each shown in a different color





(A) κ^2 = 0.40, R_g = 7.6 Å

(B) κ^2 = 0.05, R_g = 7.7 Å

Figure 10: 2D histograms of cluster shape κ^2 versus cluster size R_g (left) and example shapshots (right)

Conclusions

At higher hydration levels:

- Sulfonate groups were more well hydrated by water molecules
- Hydronium ions migrated out of the first hydration shell of sulfonate groups more often
- Ion transport would be improved due to the reduced strength between the ionic groups

At higher sulfonation and hydration levels:

- Ionic domains were better connected and mostly fully percolated throughout the system
- Ionic aggregates had a greater number of water molecules and were more spherical in shape
- Ion transport would be improved due to percolated ionic domains that are well hydrated

References

1. Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A.; *Macromolecules* **2005**, *38*, 5010-5016.
2. Tang, Z.; Lawton, J. S.; Sun, C.-N.; Chen, J.; Bright, M. I.; Jones, A. M.; Papandrew, A. B.; Fujimoto, C. H.; Zawodzinski, T. A.; *J. Electrochem. Soc.* **2014**, *161*, A1860-A1868.
3. Peighambardoust, S. J.; Rowshanzamir, S.; Amjadi, M.; *Int. J. Hydrogen Energy* **2010**, *35*, 9349-9384.
4. in 't Veld, P. J.; Rutledge, G. C.; *Macromolecules* **2003**, *36*, 7358-7365. http://montecarlo.sourceforge.net
5. Plimpton, S.; *J. Comput. Phys.* **1995**, *117*, 1-19. http://lammps.sandia.gov
6. Bolintineanu, D. S.; Stevens, M. J.; Frischknecht, A. L.; *Macromolecules* **2013**, *46*, 5381-5392.
7. Rodriguez, A.; Laio, A.; *Science* **2014**, *344*, 1492-1496.