

Force Field Generation for Li⁺ - and Na⁺ - Nafion[®] by Quantum Chemistry Calculations

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Background

Nafion[®] (Fig. 1) with added Li⁺ or Na⁺ ions can be used in Ionic Polymer Metal Composites (IPMC) as a sensor or as an electrically controlled actuator.

In order to improve the performance of a Nafion-based actuator, especially its ion conductivity, a good understanding of its ion-exchange mechanisms are necessary, preferably at the atomic level. Such information can be obtained via Molecular Dynamics (MD) simulations.

The accuracy of the MD results depend heavily on the quality of the Force Field used for the simulations, especially for the interactions between the cations and the Nafion sulphonate groups. [1,2]

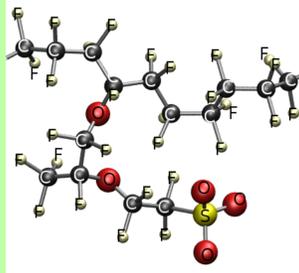


Fig 1. Nafion[®] structure

Quantum Calculations

The model

* A single Nafion side-chain with one coordinated Li⁺ or Na⁺ ion

* First analysis without water (Fig. 2)

* Second analysis with one water molecule (Fig. 3) in a fixed position relative to the ion as they both are moved together along the axis when scanning the potential curves.

Calculation details

The trajectory data from the earlier MD-simulation of 20 wt % hydrated Na⁺ nafion with 15 H₂O per sulfonic-group [1] were analyzed to extract the most common conformation of the Nafion side-chain.

The obtained geometry was used as starting point for the Quantum Chemical (QC) calculations of the complexes.

Density Functional Theory in the form of the B3LYP functional and two split valence basis sets were used: 6-31+G(d,p) and 6-311+G(d,p).

Basis Set Superposition Error was compensated by the conventional Counterpoise method.

The Gaussian 03 package was used for all QC calculations.

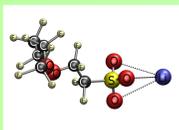


Fig 2. QC model: 3-coordinated Li⁺ without water.

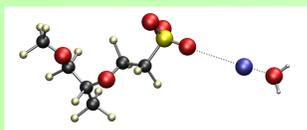


Fig 3. QC model: 1-coordinated Li⁺ with one water molecule.

Force field development

For three series of relative positions of the ions, comparative energy values were achieved by QC calculations.

Long distance energy values between the ion and atoms in the side-chain were calculated from a predefined MD Force Field, excluding the S and O atoms of the sulphonic group.

The Li...S and Li...O potentials were fitted with the following formula, where A, B, C, D were constants and r was distance:

$$E(r) = Ae^{-\frac{r}{B}} - C\frac{1}{r^6} - D\frac{1}{r^4}$$

Fitting objective was to minimize the sum of square errors of the energy values calculated from the entire MD FF at each data point to those calculated from the QC. The error values were weighted by the Boltzmann factors for each point.

Zero energy was set at the bottom of the potential well (Figs. 4, 5) or at the potential of the configuration with the largest S...Li distance used (Fig. 6).

MD simulations

Molecular Dynamics (MD) - calculations of every movement in a group of atoms and ions via the Newtonian equations of motion.

The model

MD box content:

- * 4 oligomers of Nafion with 10 sidechains on each strand
- * 40 cations, Li⁺ or Na⁺
- * 600 water molecules.

Initial dimensions of the simulation box: 40Å x 40Å x 40Å.

Simulation details

* Pressure 1.01325 bar (for NPT)

* Timestep 1 fs

* Multiple timestep technique with 0.2 fs timestep within the limits of a 6 Å sphere

* Sampling after every 1000th timestep (1 ps interval)

* A local version of the DL_POLY software.

Two Force Fields (FF) were used. The first FF was based on QC without water and the improved FF was based on QC with one water molecule.

First FF

with Li⁺ ions:

- * 1 ns, NVT ensemble, T=293K
- * 3 ns, NPT ensemble, T=293K.

With Na⁺ ions:

- * 1 ns, NVT, T=293K
- * 4 ns, NPT, T=293K.

The improved FF, with Li⁺ ions

* NVT, 1 ns, T=293K.

NVT, annealing sequence:

- * 3 ns, T=373K
- * 300 ps, T=2000K
- * 300 ps, T=373K.

NPT:

- * 2 ns, T=353K
- * 2 ns, T=373K.

NPT with external electric field:

- * 2 ns, T=353K, E=1, 2, 3, 4, 5 MV/m
- * 2 ns, T=373K, E=1, 2, 3, 4, 5 MV/m.

Results

Typically 3-4 cations and 3-4 sulphonic groups form clusters, surrounded by several water molecules (Fig. 7).

The first S...S coordination sphere radius is 4.4 Å (Fig. 8).

Electric fields above 4 MV/m cause a second S...S coordination sphere to form at around 5.8 Å (Fig. 8) and significantly increase the mobility of the Li⁺ ions (Fig. 9).

At E=5 MV/m the clusters of ions and sulphonic groups become larger and elongated both along and across the direction of the electric field (Fig. 10). The first S...S coordination sphere contains the initial small cluster of 3-4 sulphonic groups and the S...S distances of 5-6.5 Å can be measured between the sulphur atoms of previously separated small clusters that have now fused together. The effect is somewhat weaker at higher temperatures.

Self-diffusion coefficient for Li⁺ ion when fitted without water, at T=293K: D=1.3·10⁻⁸ cm²/s. With the improved forcefield, at T=353K: D=8.0·10⁻⁸ cm²/s (Fig. 8).

Volume contraction at the beginning of the NPT simulation stages significantly reduces Li⁺ diffusion.

Increasing the temperature from 353K to 373K increases diffusion coefficient and maximum travel distance (maximum displacement vector length from the ion's initial position) by 1.5 times.

The ions move within 9 Å radius of their initial positions during the 2 ns of simulation run at E<3 MV/m and T=353K (Fig. 11), but a small number of ions move considerably longer distances at E>=4 MV/m. (Fig. 12). The ions traveling a long distance do not appear under fields of E=3MV/m.

The Li...O (sulphonic group) RDF has a sharp peak at 1.9 Å representing the first coordination sphere. The second coordination sphere radius is 4 Å (Fig. 13). The coordination sphere radii were the same in all simulations.

Adding water lowers the potential well depth by ~10 kcal/mol.

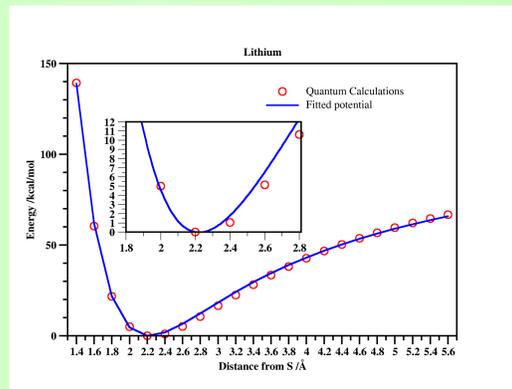


Fig 4. Potential well shape for Li⁺...SO₃⁻ without water.

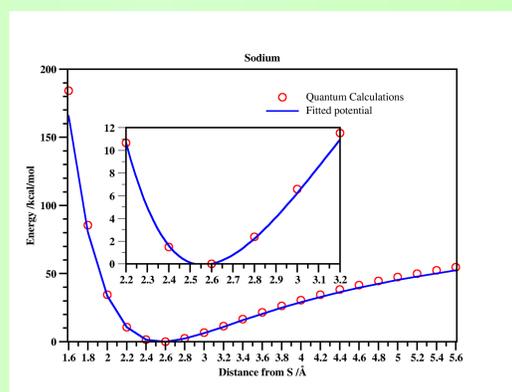


Fig 5. Potential well shape for Na⁺...SO₃⁻ without water.

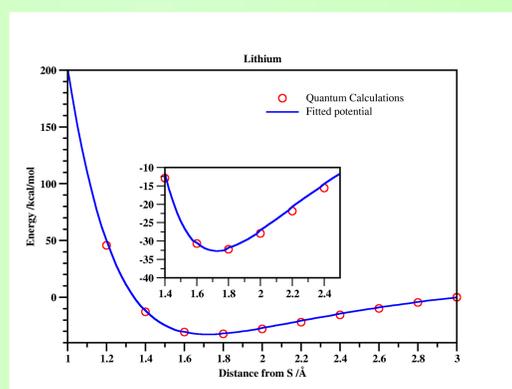


Fig 6. Potential well shape for Li⁺...SO₃⁻ with water.

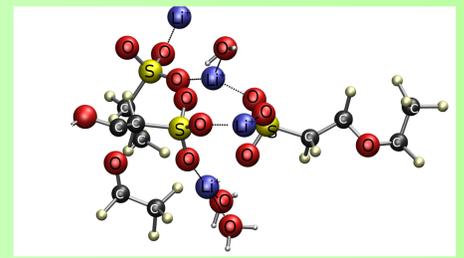


Fig 7. Typical cluster structure of ions, chain ends and water after MD simulations.

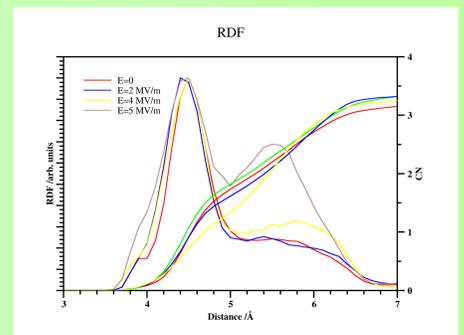


Fig 8. S...S Radial Distribution Functions and Coordination Numbers for different strengths of electric field, T=353K.

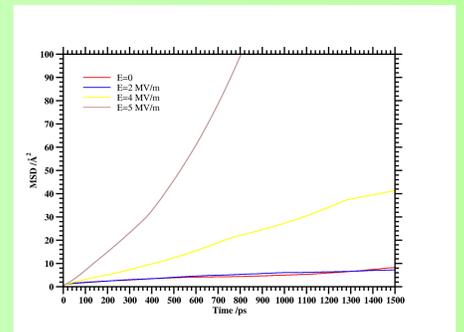


Fig 9. Li⁺ Mean Square Displacement for different strengths of electric fields, T=353K.

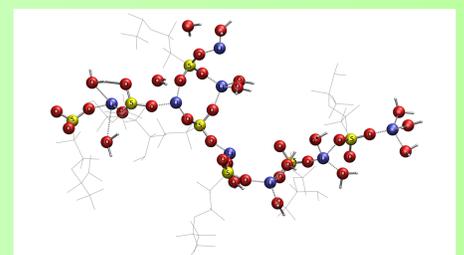


Fig 10. Long cluster formed along the direction of the electric field. Sulphonic groups and Li⁺ ions shown. Side-chains depicted with thin lines. E=5 MV/m, T=353K.

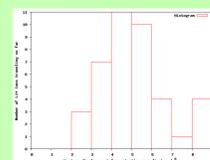


Fig 11. Histogram of Li⁺ ion displacements. E=2MV/m, T=353K.

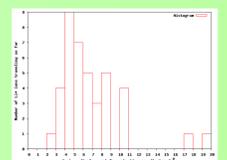


Fig 12. Histogram of Li⁺ ion displacements. E=4MV/m, T=353K.

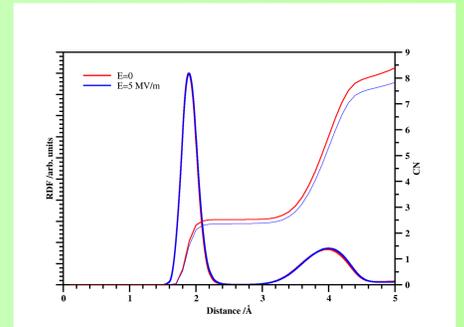


Fig 13. Radial Distribution Functions and Coordination Numbers for lithium ions and oxygens of the sulphonic groups. T=353K.

References

- [1] D. Brandell, A. Ainla, A. Liivat, A. Aabloo, *Proceedings of the SPIE*, **6168** (2006), 61680G.
- [2] E. Soolo, A. Liivat, H. Kasemägi, T. Tamm, D. Brandell, A. Aabloo, *Proceedings of the SPIE*, **6927** (2008), 69270E.