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Title

HPC4Mfg with Sepion

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CRADA Final Report Form

Date: March 10, 2020

PI: David Prendergast

CRADA AWD No.: AWD00002193 CRADA FP No.: FP00005093

LBNL Report Number: _____

OSTI Number: _____ (SPO to add)

1. Parties: Sepion Technologies and Lawrence Berkeley National Laboratory
(Identify Parties to the CRADA)
2. Title of the Project: HPC4Mfg with Sepion
3. Summary of the specific research and project accomplishments:

The key major goal of this CRADA was the realization of a computational workflow for the generation of polymer models with determinable equilibrium porosity (maximal density at ambient conditions) based on inspiration for the chemical formulation from experiment, determination of semi-classical force-field parameters based on molecular fragment quantum chemistry calculations, and classical molecular dynamics simulations under thermostatic and barostatic conditions to realize a converged mass density and pore structure.

This goal was accomplished using QChem as the quantum chemistry package of choice for determining force-field parameters such as partial charges and polarization terms, with CP2K used for large ab initio MD simulations. Subsequent LAMMPS semi-classical molecular dynamics simulation were then performed using a simulated annealing protocol that involved thermal and pressure ramping to reach a maximal density for polymer models of fixed but finite length packed within a large supercell. Void analysis was then used to estimate the porosity of the simulated polymers for comparison with experiment. These results agreed with gas adsorption measurements of porosity and associated measured mass densities.

Calculations were performed through a generous HPC allocation at NERSC, administered by the HPC4Mfg program.

Five polymer chemistries were explored, supplied by Sepion.

4. Deliverables:

Deliverables met	Party (LBNL, Participant, Both)	Delivered to Other Party?
Workflow development for polymer porosity predictions for five polymer chemistries	LBNL	Yes

5. Identify (list below) and attach all publications or presentations at conferences directly related to the CRADA:

Poster presentation at HPC4Mfg events: "Improving the Manufacturability, Performance, and Durability of Microporous Polymer Membranes for Li-S Batteries using First-Principles Computer Simulations" by Tod Pascal and David Prendergast.

6. List of Subject Inventions and software developed under the CRADA: (Please provide identifying numbers or other information.)

None.

7. A final abstract suitable for public release:

(Very brief description of the project and accomplishments without inclusion of any proprietary information or protected CRADA information.)

A computational framework was developed for predictive determination of polymer membrane porosity based solely on proposed polymer chemistry employing a multi-scale theoretical approach. The resulting polymer structures matched measured density and porosity measurements and established a protocol for future predictions.

8. Benefits to DOE, LBNL, Participant and/or the U.S. economy.

Sepion can make use of this approach to initiate computational exploration of a wide range of polymer chemistries to determine which factors are most important in defining porosity of controlled dimensions in polymers for use in energy storage applications.

To meet industry targets, next-generation batteries with high specific energy (Wh/kg) are essential. Efforts to commercialize light-weight, energy-dense lithium-sulfur secondary batteries (2510 Wh/kg) have been stalled by ongoing problems with the battery's separator membrane, which should prevent cross-over of active material from cathode to anode that, if unchecked, limits cycle-life. However, Sepion Technologies' polymer membranes yield

long-lasting lithium-sulfur cells. Advancing to 10 Ah battery prototypes, Sepion faces challenges in membrane manufacturing related to polymer processing and the molecular basis for membrane performance and durability. High-performance computing offers critical new insight into these phenomena, which in turn will accelerate product entry into the market.

This application highlights the advantages of coupling synthesis, characterization and supercomputing capabilities via theoretical modeling at LBNL.

9. Financial Contributions to the CRADA:

DOE Funding to LBNL	\$129,476
Participant Funding to LBNL	\$0
Participant In-Kind Contribution Value	\$25,896
Total of all Contributions	\$155,372

** "Proprietary Information" means information, including data, which is developed at private expense outside of this CRADA, is marked as Proprietary Information, and embodies (i) trade secrets or (ii) commercial or financial information which is privileged or confidential under the Freedom of Information Act (5 U.S.C. 552 (b)(4)).*

HPC4Mfg Final Report

Project Title: Improving the Manufacturability, Performance, and Durability of Microporous Polymer Membranes for Li-S Batteries using First-Principles Computer Simulations

Company Name: Sepion Technologies

Principle Investigator (PI) Contact Information (include all co-PIs)

Name: Brett A. Helms (PI)

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Company/Division: Sepion Technologies

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Nationality: USA

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National Laboratory PI Contact Information (if known)

Name: David Prendergast

Email: dgprendergast@lbl.gov

Phone number: 510-486-4948

Computational Resources used for Project:

System	Time (MCH)	Commercial Software	Custom Software
monomers A – C (gas phase optimization)	50,000 CPU hrs	C2PK/Q-Chem 5.0	
Condensed phase simulations	150,000 CPU hrs	LAMMPS 06/2017	

Lab PI: David Prendergast (LBNL)
Company PI: Brett Helms (Sepion)
Months Completed: 12
Costed Funds: \$129,476

Short Project Description:

We employed ab-initio simulations and quantum chemical calculations to develop a computational framework for simulating the microscopic structure and mechanical properties of novel polymer membranes used in lithium sulfur batteries. To meet industry targets, next-generation batteries with high specific energy (Wh/kg) are essential. Efforts to commercialize light-weight, energy-dense lithium-sulfur secondary batteries (2510 Wh/kg) have been stalled by ongoing problems with the battery's separator membrane, which should prevent cross-over of active material from cathode to anode that, if unchecked, limits cycle-life. However, Sepion Technologies' polymer membranes yield long-lasting lithium-sulfur cells. Advancing to 10 Ah battery prototypes, Sepion faces challenges in membrane manufacturing related to polymer processing and the molecular basis for membrane performance and durability. High-performance computing offers critical new insight into these phenomena, which in turn will accelerate product entry into the market.

Technical Summary:

We focused on optimizing parameters for a semi-classical, polarizable force field to allow for 100ns simulations of systems containing 100,000s of atoms. These are the bare minimum dimensions (temporal and physical) for realistic modelling of Sepion's membranes. To this end, we have advanced an empirical force field for these systems, derived from quantum chemical inputs, which is semi-classical, in the sense that it allows for spontaneous charge transfer, in addition to accounting for atomic polarization. This physics is built on top of the standard classical elements: electrostatics and dispersion forces. We find that an accurate inclusion of all of these force-field components is critical, due to the reorganization of electronic charge on atoms seen in quantum chemistry calculations of the (isolated) dimers compared to the associated monomers:

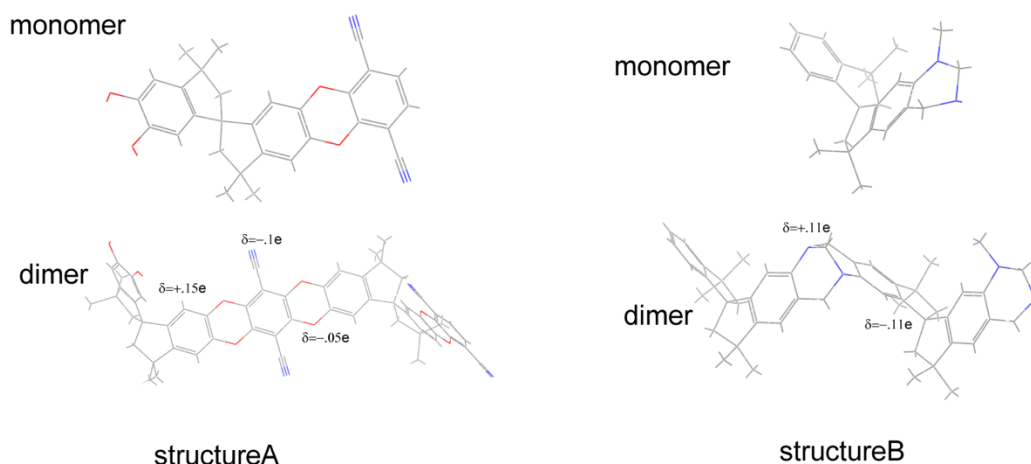


Fig 1.

We note that models employing fixed point charges will necessarily miss this charge transfer effect and lead to spurious electrostatic interactions in the condensed phase systems. This completes the milestone for task 1.

Using our semi-classical force field, we have simulated the condensed-phase, dry polymer systems (see list of monomers in supporting figure 1 at the end of document), and ascertained the average pore sizes:

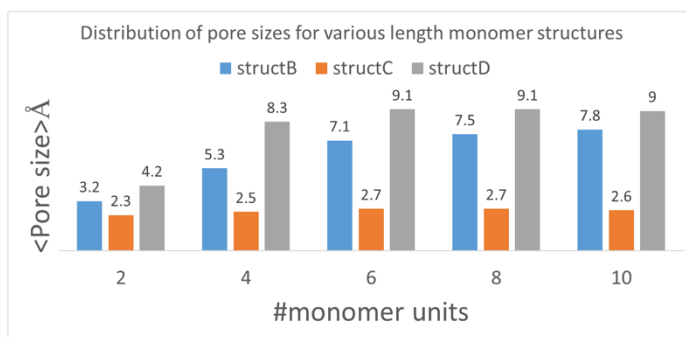
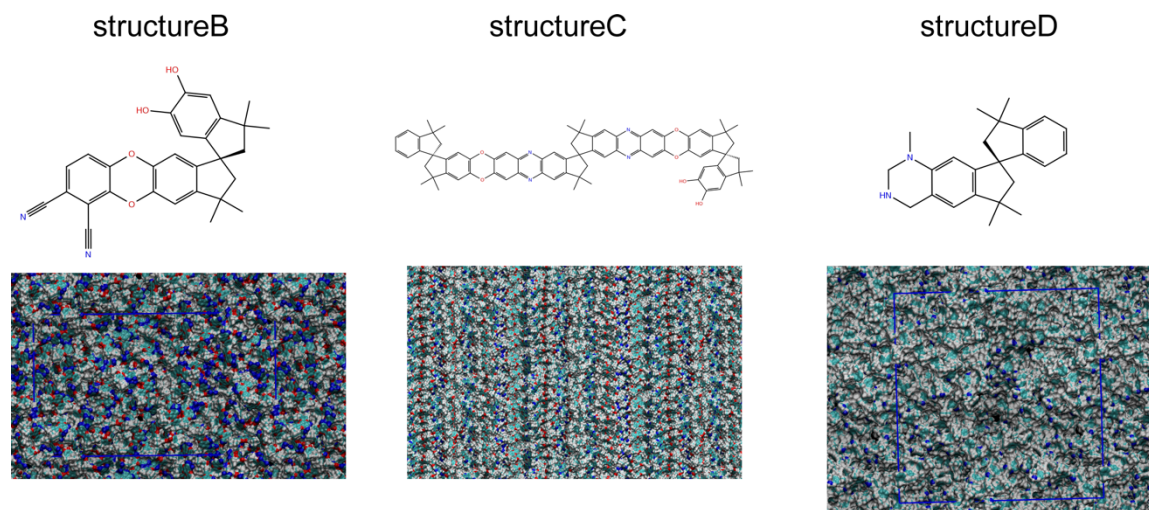


Fig 2.

Figure 3 is a top down view of the simulation cells and the pores obtained from annealing the system.

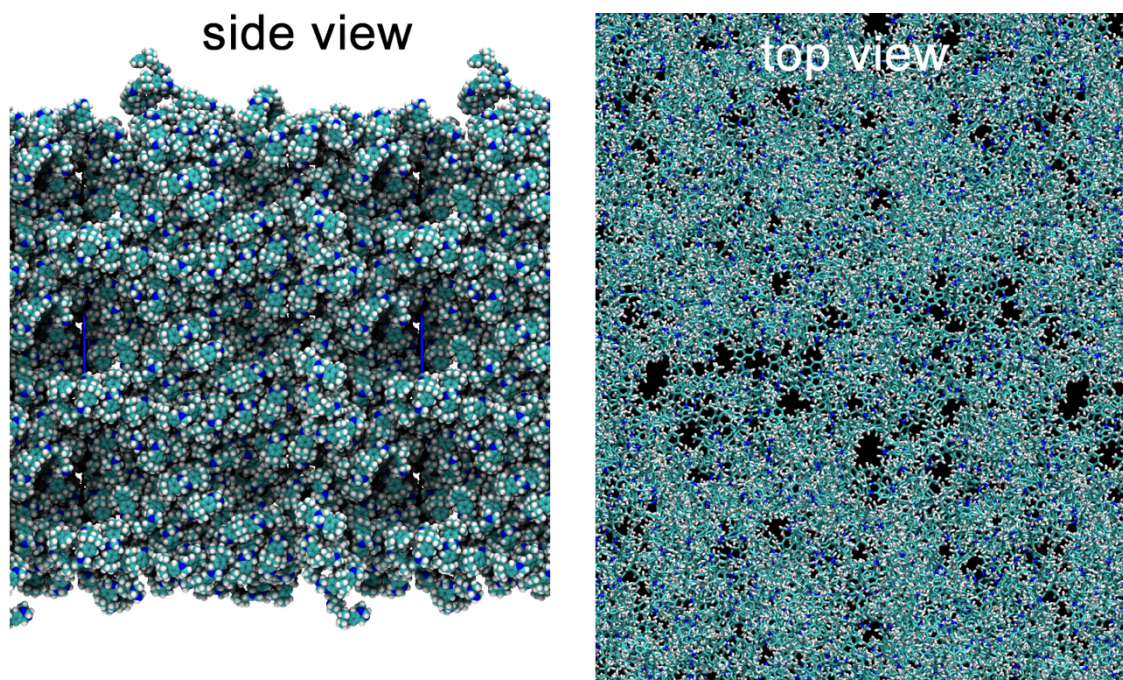


Fig 3

The pore sizes were calculated using an in-house procedure: solvent molecules are introduced at random into the equilibrated membrane structure; any overlap with membrane atoms or previously placed solvent molecules leads to that site being excluded in the final pore volume calculations. This is performed until each site in the membrane has been visited at least once. Subsequent analysis of the placed solvent molecules yield an estimate of the pore dimensions.

We note that our pore-sizes are in good agreement with the experimental results (see supporting figure 2), thus validating our model. This completes the milestone for task 2.

Note that the flat conformation of polymer C leads to quite small pores and self-assembled stacks of oligomers. We will explore this system further introducing random kinks in the monomers based on sampling rather than molecular dynamics, for which the barriers to interconversion are too high for equilibration at ambient temperature. This may increase the pore size estimates.

Details on Computational Resources Used:

Quantum Chemistry Calculations

We developed a first-principles force field by fitting the interaction energies of the monomer units to a semi-classical, core-shell model with charge equilibration. The monomer interaction energies were obtained from Q-Chem 5.0 calculations, employing the triple-zeta 6-311G**++ basis set and the B3LYP hybrid functional. Additional optimization of the parameters was obtained from 10ps condensed phase, 298K molecular dynamics simulations, using the CP2K simulation engine at the PBE/vdw-DF2 level of theory, for densities ranging from 2.0 g/cm³ – 0.5 g/cm³.

Semi-Classical molecular dynamics simulations

Using our force field, we performed long time-scale MD simulations of the various ladder polymers with lengths of 2,4,6,10, and 14 monomer units. The inclusion of dynamic charge transfer and polarization physics in our model increases the computational cost by an order of magnitude, yet is 6 orders of magnitude more efficient than first principles simulations. A supercell containing 128 polymers was annealed from 298K – 2000K in 3 cycles over 50ns, and the final structure equilibrated for an additional 50ns at 298K.

Solvent simulations

We developed a force field for the commonly used DOL:DME solvent mixture, as well as for the Li-TFSI salt. We studied the solvent-induced infiltration and swelling of the various polymer membranes.

Issues or concerns:

We have developed a robust platform for performing these simulations, which, being the first of its kind, consumed considerable time and computational resources. Further progress to understanding the technologically relevant questions concerning the chemistry of these membranes are now feasible, but may require a further extension.

Figures:

Figure 1. Gas-phase optimized geometry of ladder polymer A and B, used in Sepion's advanced polysulfide-blocking PIM membranes. The monomer and dimer units are shown. The regions on the dimer that differs significantly to the dimer in partial atomic charges are indicated.

Figure 2. Molecular structure, and condensed phase morphology of ladder polymers B,C and D. The condensed phase pictures are the last of a 100ns molecular dynamics simulation of 1000 polymer (8 monomer chains) units. The distribution in the polymer pore widths for various length chains is shown.

Figure 3: Snapshot of final 298K structure from a 60ns molecular dynamics simulation of 125 units of ladder polymer D (8 monomer unit polymer), showing the ~1nm pores.

Supporting figures (from previous reports/proposal):

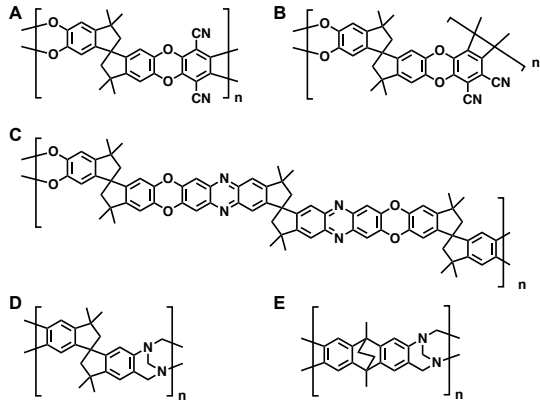


Fig. 1. Representative chemical structures for the ladder polymers used in Sepion's advanced polysulfide-blocking PIM membranes.

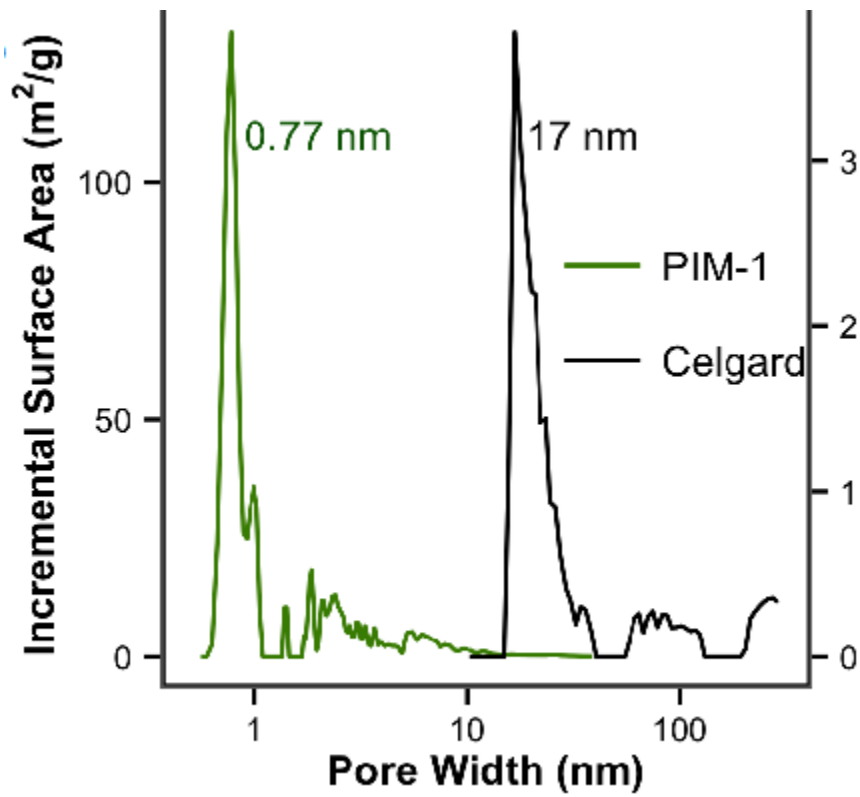


Fig. 2. Representative pore-size distribution for PIMs used in Sepion's membranes.