Lithium Ion Solvation and Diffusion in Bulk Organic Electrolytes from First Principles Molecular Dynamics

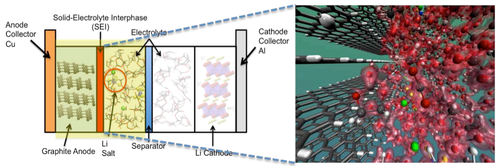
Mitchell T. Ong, Vincenzo Lordi, Erik W. Draeger, and John E. Pask

Lawrence Livermore National Laboratory

DGDFT Collaboration: Lawrence Livermore National Laboratory, Lawrence Berkeley National Laboratory, University of California, Berkeley

ISCR | SciDAC Scientific Discovery through Advanced Computing | BERKELEY LAB | Berkeley UNIVERSITY OF CALIFORNIA

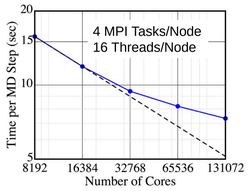
Project Goals



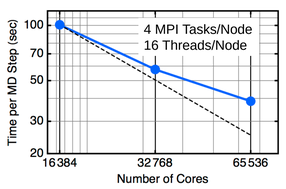
- Examine the transport properties and solvation structures of Li ions in the bulk electrolyte and at the interface
- Understand the reaction mechanisms and dynamics at the anode-electrolyte interface that lead to SEI formation and growth
- To achieve these goals, we perform massively parallel first principles molecular dynamics (FPMD) simulations at unprecedented time and length scales
- Enable design of new anode-electrolyte combinations for safe, reliable, high-capacity, high-charge rate batteries

Qbox on Blue Gene/Q

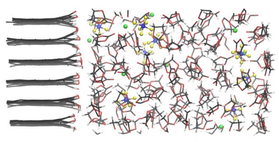
63 EC + 1 $LiPF_6$:
638 Atoms, 2190 Electrons



4L Graphite + 98 EC + 6 $LiPF_6$:
1700 Atoms, 6020 Electrons



6L Graphite + 120 EC + 8 $LiPF_6$:
2014 Atoms, 7164 Electrons



- 638 atoms in 8 sec/MD step
- 1700 atoms in 40 sec/MD step
- Excellent scaling up to 65536 cores
- 2014 atoms in 79 sec/MD step over 4096 BG/Q nodes, 65536 cores
- ESM method for applying electric field implemented in Qbox for FPMD

Simulation Details

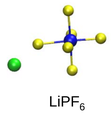
Cyclic
Ethylene Carbonate (EC)

$C_3H_4O_3$

Linear
Ethyl Methyl Carbonate (EMC)

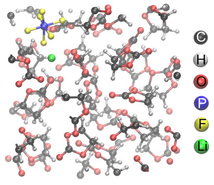
$C_4H_8O_3$

Lithium Salt
Lithium Hexafluorophosphate



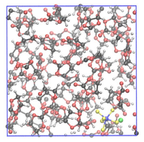
$LiPF_6$

Simulation Details

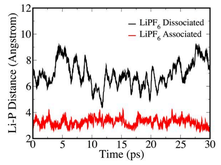


- DFT/PBE-GGA PAW potential (VASP)
- 450eV cutoff
- NVT (Nose-Hoover at 330K)
- Verlet algorithm
- 0.5 fs time step
- 5ps equilibration (7.5ps for EC)
- 30ps after equilibration for statistics

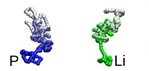
Li^+ Solvation: Ethylene Carbonate



System Details
- 63 EC + 1 $LiPF_6$
- 0.23M $LiPF_6$
- 638 Atoms
- 2190 Electrons
- Box Length: 19.283 Å
- Density: 1.32 g/cc



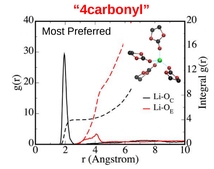
$LiPF_6$ Dissociated



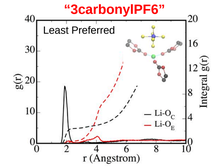
$LiPF_6$ Associated

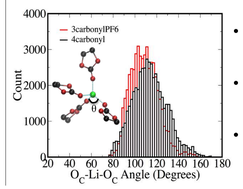
- Two total trajectories where Li^+ and PF_6^- initially associated or dissociated
- Both ions either remain associated or dissociated for duration of simulation
- Larger fluctuations in Li-P distance when ions are dissociated
- Correlated motion still exists between Li and P even when dissociated

"4carbonyl"



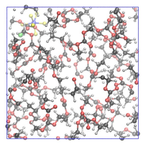
"3carbonylPF6"



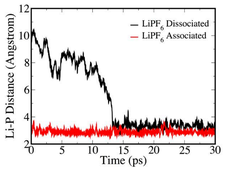


- "4carbonyl" more energetically favorable by ~0.21eV
- PF_6^- nearby allows only solvation by 3 carbonyl atoms
- Average O_c-Li-O_c angle ~110° indicating tetrahedral solvation shell

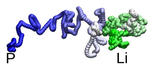
Li^+ Solvation: Ethyl Methyl Carbonate



System Details
- 42 EMC + 1 $LiPF_6$
- 0.22M $LiPF_6$
- 638 Atoms
- 1812 Electrons
- Box Length: 19.521 Å
- Density: 1.01 g/cc



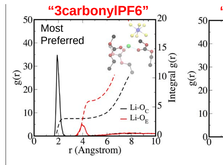
$LiPF_6$ Dissociated



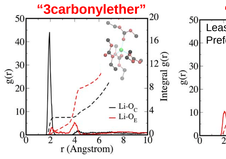
$LiPF_6$ Associated

- When initially dissociated, $LiPF_6$ re-associates during simulation
- PF_6^- moves greater distance to re-associate with Li^+
- Trajectories indicate Li^+ motion confined locally
- Motion of Li^+ and PF_6^- in EMC more uncorrelated than in EC

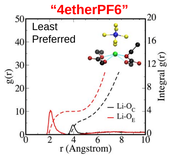
"3carbonylPF6"

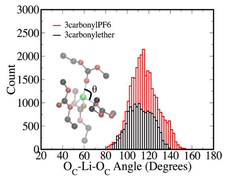


"3carbonylether"



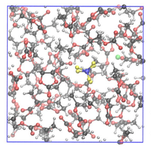
"4etherPF6"



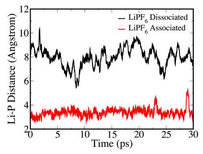


- "3carbonylPF6" preferred
  - More favorable by 0.17eV than "3carbonylether"
- "4etherPF6" not tetrahedral
  - Least energetically favorable
- "3carbonylether" and "3carbonylPF6" prefer tetrahedral orientation

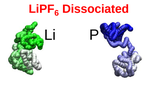
Li^+ Solvation: Mixed EC/EMC Electrolyte



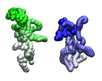
System Details
- 15 EC + 35 EMC + 1 $LiPF_6$
- 0.23M $LiPF_6$
- 683 Atoms
- 2028 Electrons
- Box Length: 19.392 Å
- Density: 1.165 g/cc



$LiPF_6$ Dissociated

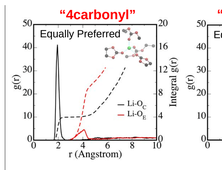


$LiPF_6$ Associated

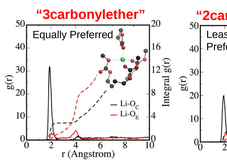


- Both ions either remain associated or dissociated
- Larger fluctuations when $LiPF_6$ separated
- Both Li^+ and PF_6^- motion confined locally
- Ionic motion more confined to local region similar to EC
- Motion of ions more correlated than EMC

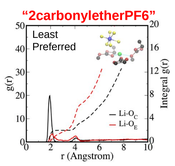
"4carbonyl"

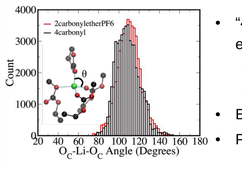


"3carbonylether"



"2carbonyletherPF6"

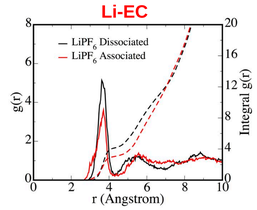




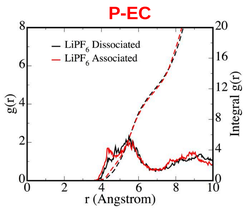
- "4carbonyl" and "3carbonylether" are equally favorable
  - "3carbonylether" contains 3 EMC and 1 EC
  - 1 EMC replaced by EC to get "4carbonyl"
- EC solvation slightly favored over EMC
- Preference for tetrahedral arrangement

PF_6^- Solvation

Li-EC



P-EC



- More structure for Li-EC pair correlation function indicates better solvation for Li^+
- Residence times for solvent molecules around PF_6^-:
  - **EC**: 43-90ps (better solvation)
  - **EMC**: 24-29ps
- Li^+ residence time effectively infinite, beyond length of simulation
- PF_6^- predicted to be more mobile than Li^+ due to weaker solvation

Li^+ and PF_6^- Diffusion

MSD

D_{Li} (10^{-6} cm^2/s)	Associated	Dissociated
EC	7.8 ± 0.5	5.2 ± 0.8
EMC	4.5 ± 1.6	9.6 ± 1.6
3:7 EC/EMC	3.4 ± 0.8	2.6 ± 1.3

VACF

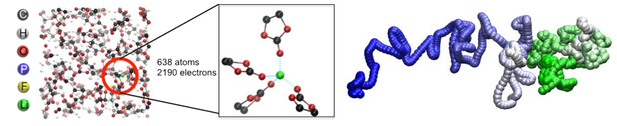
D_{Li} (10^{-6} cm^2/s)	Associated	Dissociated
EC	7.8 ± 1.9	7.9 ± 1.3
EMC	5.1 ± 1.5	10.1 ± 2.1
3:7 EC/EMC	5.1 ± 1.1	

D_P (10^{-6} cm^2/s)	Associated	Dissociated
EC	14.8 ± 2.9	7.1 ± 0.9
EMC	8.4 ± 3.3	30.8 ± 8.8
3:7 EC/EMC	4.6 ± 1.3	5.7 ± 2.4

D_P (10^{-6} cm^2/s)	Associated	Dissociated
EC	14.4 ± 2.0	9.2 ± 1.0
EMC	10.7 ± 0.7	28.6 ± 5.7
3:7 EC/EMC	6.2 ± 0.9	9.5 ± 1.4

- Faster diffusion for Li^+ seen in EMC than EC; agrees with experiments
- Li^+ diffusion in mixed electrolyte case similar if not less than EC
- Differences in Li^+ diffusion likely due to Li^+ solvation structure
- PF_6^- diffuses faster than Li^+ due to weaker solvation

Conclusions



- Solvation structure strongly dependent on electrolyte. Li^+ prefers tetrahedrally-coordinated first solvation shell.
- The amount of correlated motion between ions dependent on solvation structure and can be quantified by diffusivity.
- Faster diffusion for Li^+ seen in EMC than EC. Size of coefficient tied to solvation structures.
- PF_6^- counter-ion diffuses faster than Li^+, but is more weakly solvated by solvent molecules.
- Understanding how to make Li move faster will improve cycling rate in batteries.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Support for this work was provided through Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences.

LLNL-POST-651414