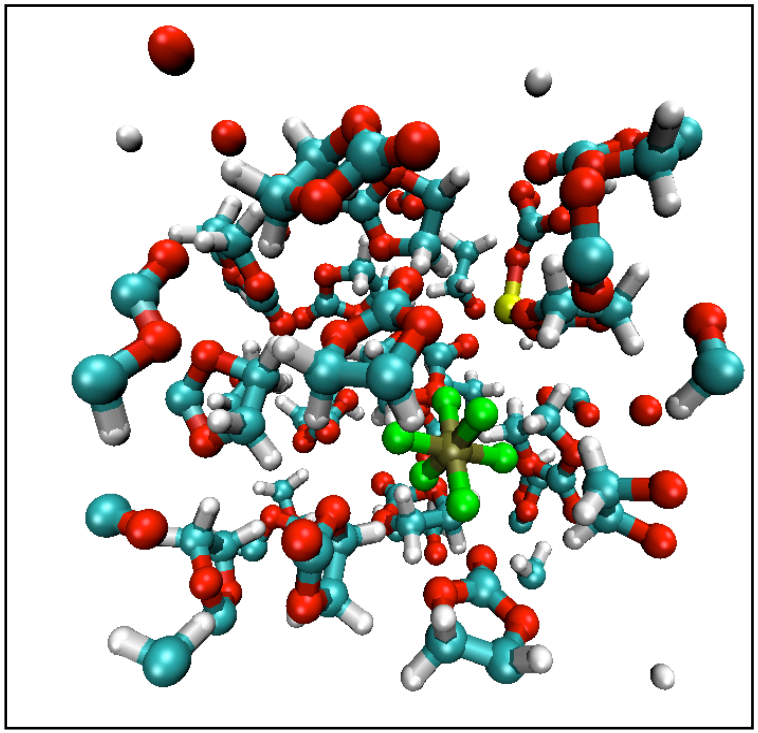
Properties of Liquid Electrolytes for Li-ion Battery Applications from First Principles Molecular Dynamics



Spontaneous solvation of $LiPF_6$ in Ethylene-Carbonate

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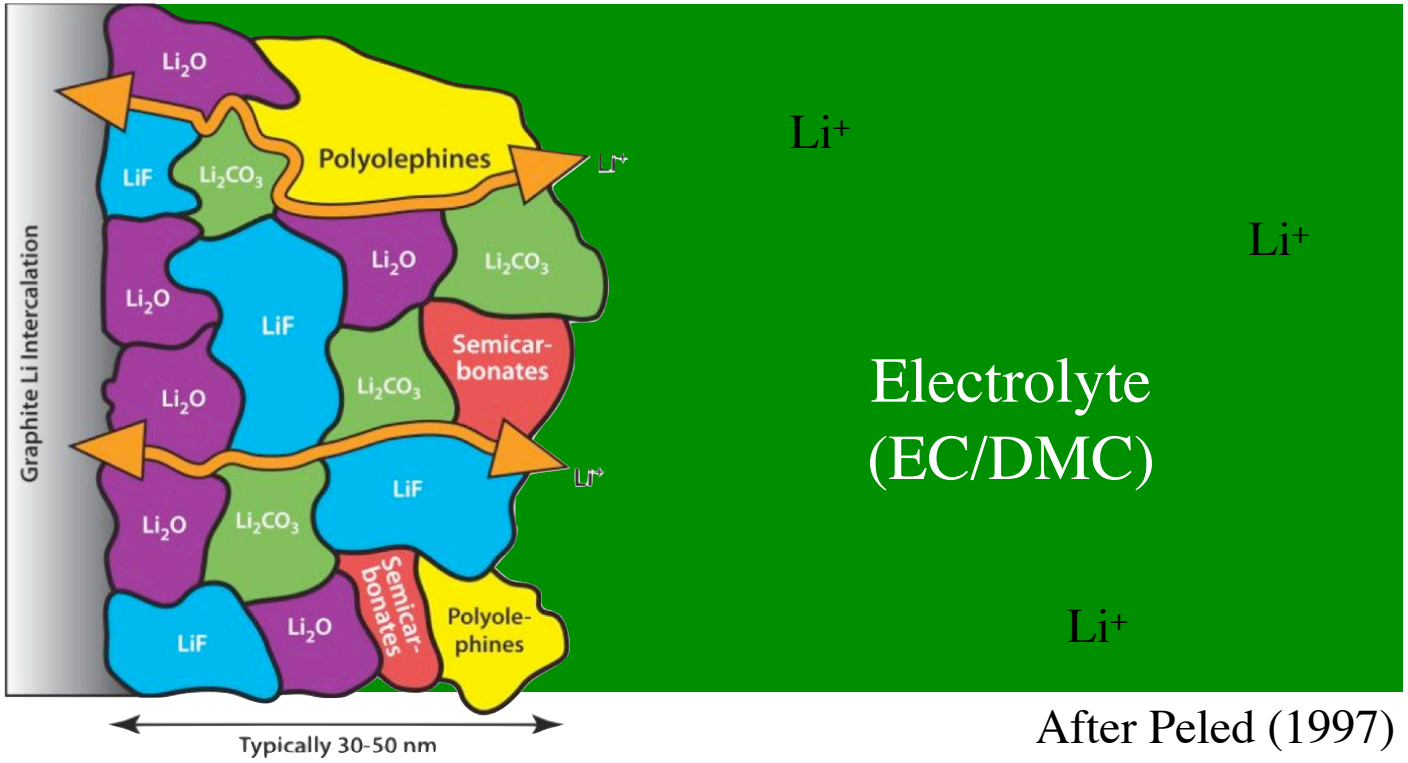
Support: FIRST EFRC, US DOE, Office of Science, BES award ERKCC61. Computers: NERSC

OAK RIDGE National Laboratory

One of our long term goals

Understand and optimize the structure and properties of solid-electrolyte interfaces (SEI)



After Peled (1997)

SEI formed through reaction + breakdown of electrolyte at electrode and in presence of Li salt

Short term goal

Study properties of Li salt in Ethylene and Propylene carbonates

Method

First principles molecular dynamics

- Most accurate method for reactions in solution and at interfaces; Will eventually be required for SEI components
- Can be used to validate faster/cheaper/less accurate approaches (LCAO; tight binding; reactive classical; classical)

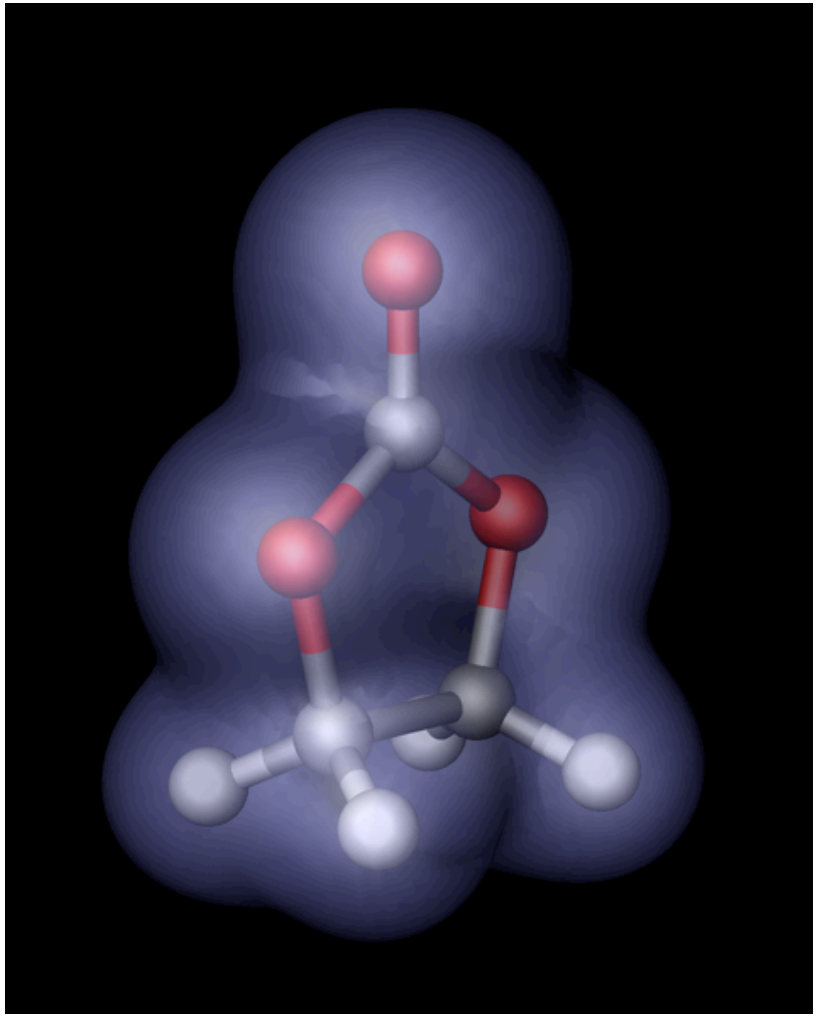
Supercells with 27 EC/PC molecules, 1 $LiPF_6$ (~0.5 M)

Born-Oppenheimer MD, 0.5fs timestep, up to 25ps trajectory

Plane wave PAW pseudopotential method

PBE functional. Tested Grimme dispersion “PBE-D2”

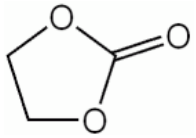
We contrast Ethylene & Proplyene carbonates



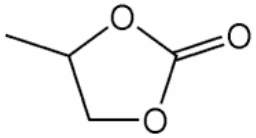
Ethylene carbonate
$C_3H_4O_3$

Structures are similar, differing only by an additional methyl group on PC

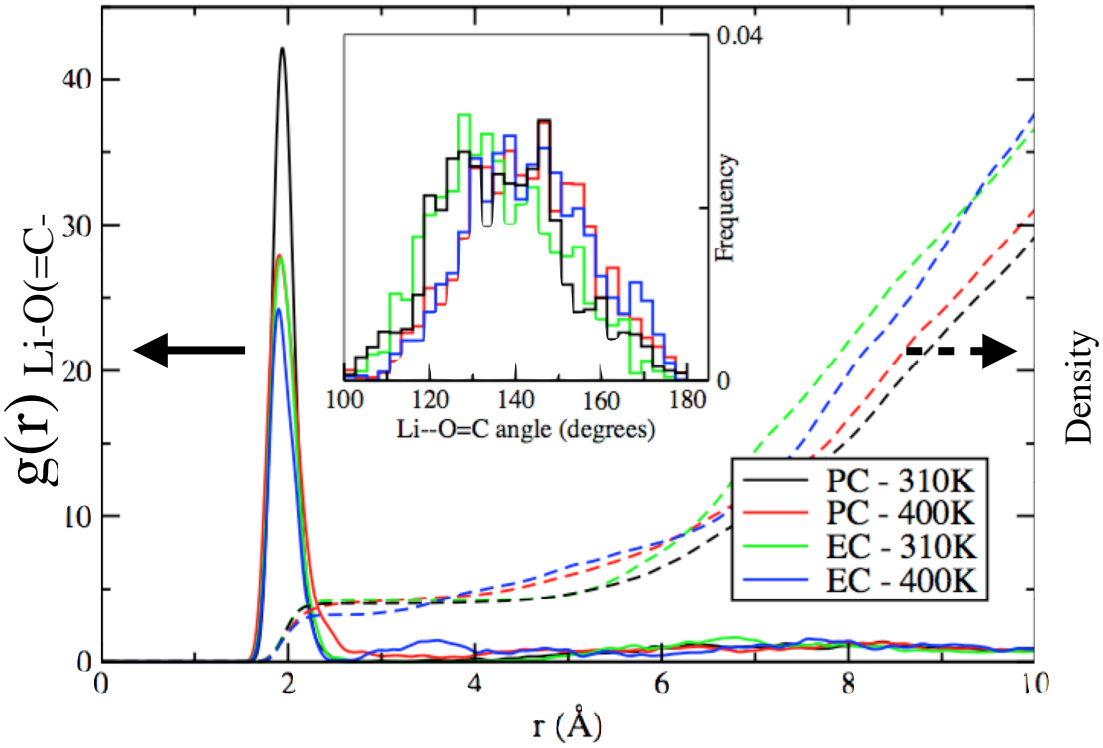
EC: $C_3H_4O_3$



PC: $C_4H_6O_3$



Li Partial radial distribution function and coordination number

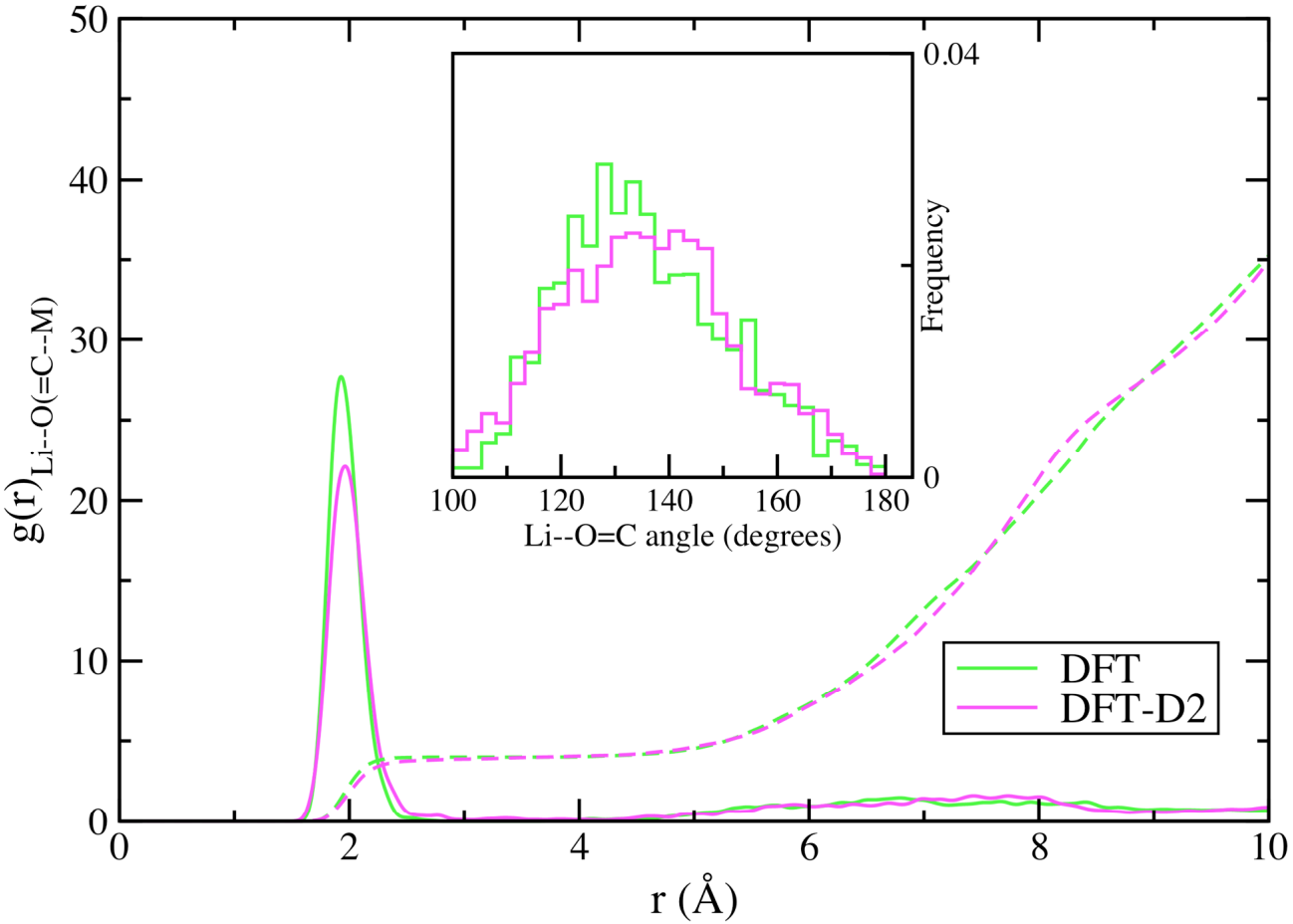


1st Li solvation shell 4 EC or PC molecules (neutrons: 4.5 at 1.5M, classical: 3.6 EC 298K)

Li-O (carbonyl) distance 1.92/1.94 A in EC/PC @ 310K (neutrons: 2.04 A in PC)

No F^- in 1st coordination shell consistent with neutron scattering (Kameda JPCB 2007 111 6104) & in contrast to classical MD (Borodin JPCB 2006 110 4971)

Van der Waals tests find similar results



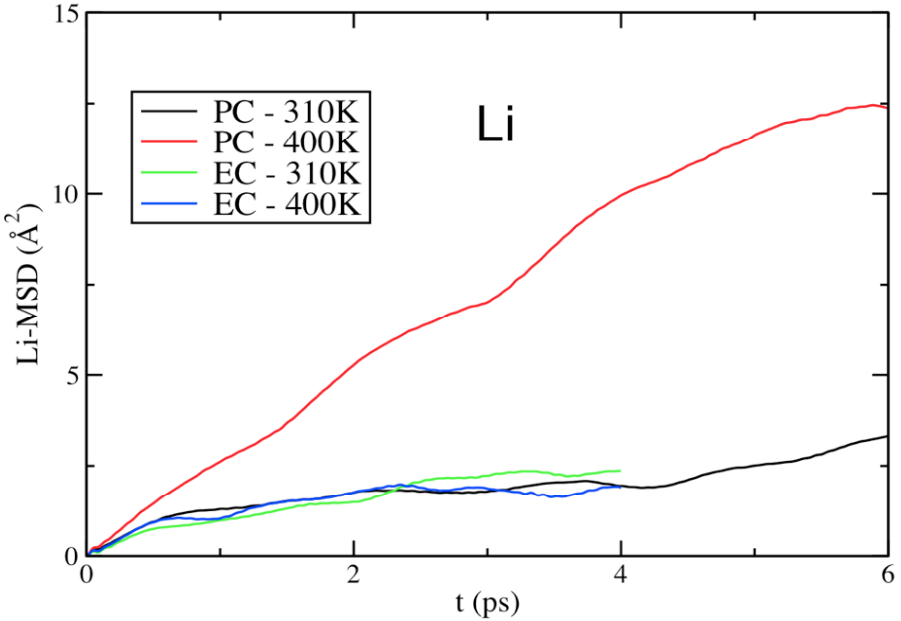
Grimme's empirical vdw potential (PBE-D2)

Small changes support dominant role of electrostatic interactions

Li diffusivity

Computed from mean-square displacements

Very reasonable agreement with experiment despite short simulation times



Li in EC

Calc. ~1.0x10^{-9} m^2/s (310,400K)

Expt. ~0.62x10^{-9} m^2/s (298K) for 0.5M $LiPF_6$ via NMR measurements

Yang J. Mol. Liq. (2010) 154 131

Li in PC

Calc. ~0.7 x10^{-9} m^2/s (310K)

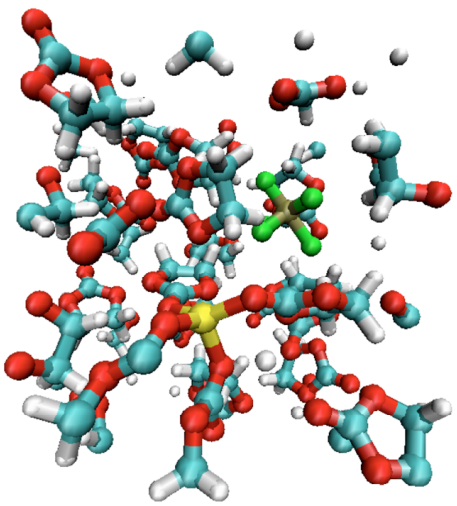
Calc. ~3.7x10^{-9} m^2/s (400K)

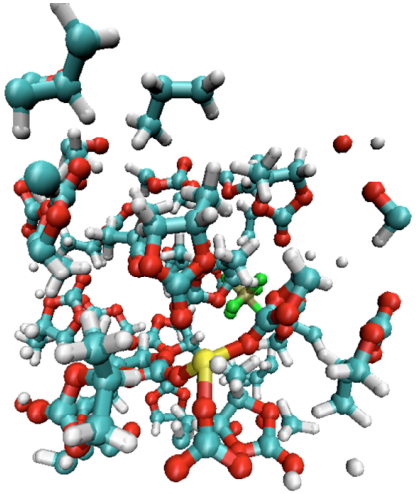
Expt. ~0.4x10^{-9} m^2/s (298K)

Nishida ECS Trans. (2008) 6 1

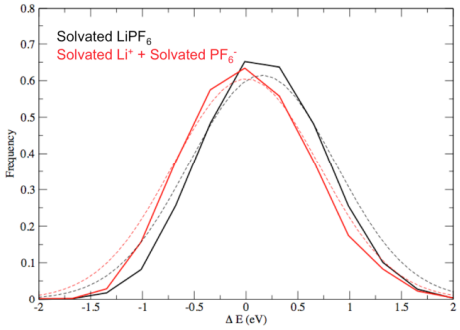
Rapid solvation of $LiPF_6$ in EC

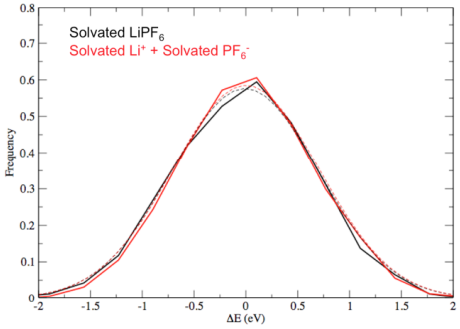
$LiPF_6$/EC





$LiPF_6$/PC

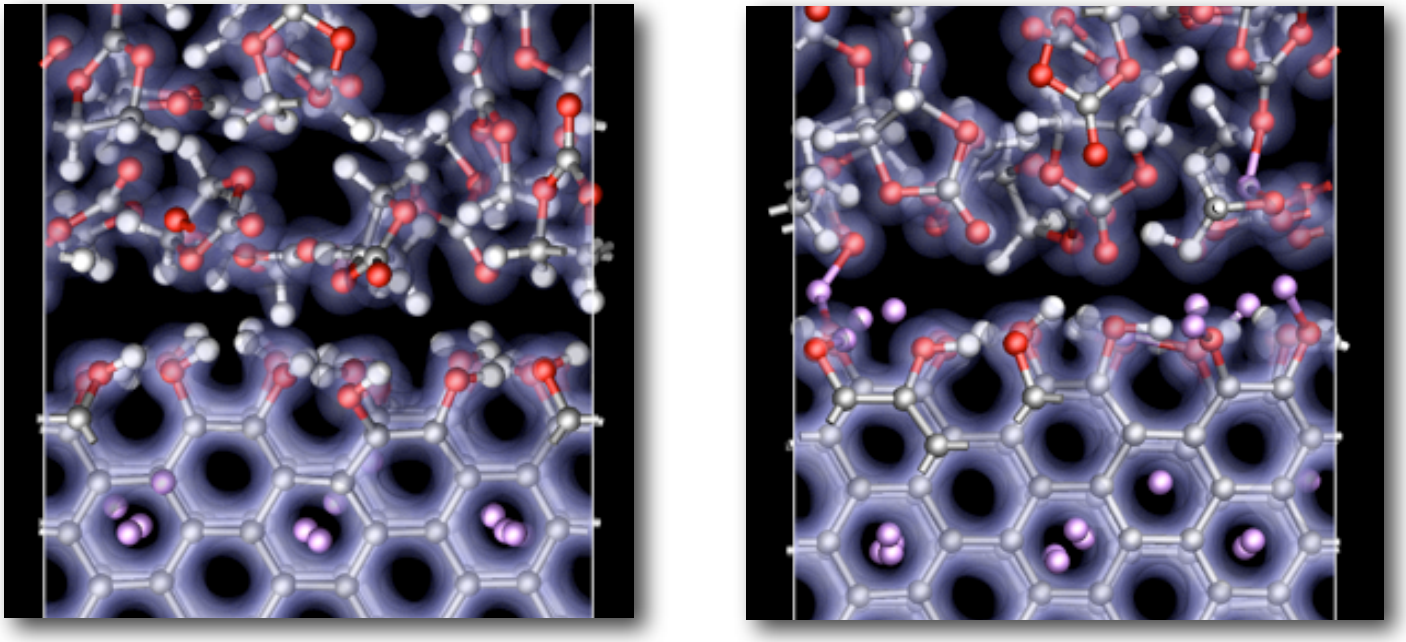




Li solvation significantly more energetically favourable in EC than PC at 310K

Simulations with lithiated carbon anode

Li poor



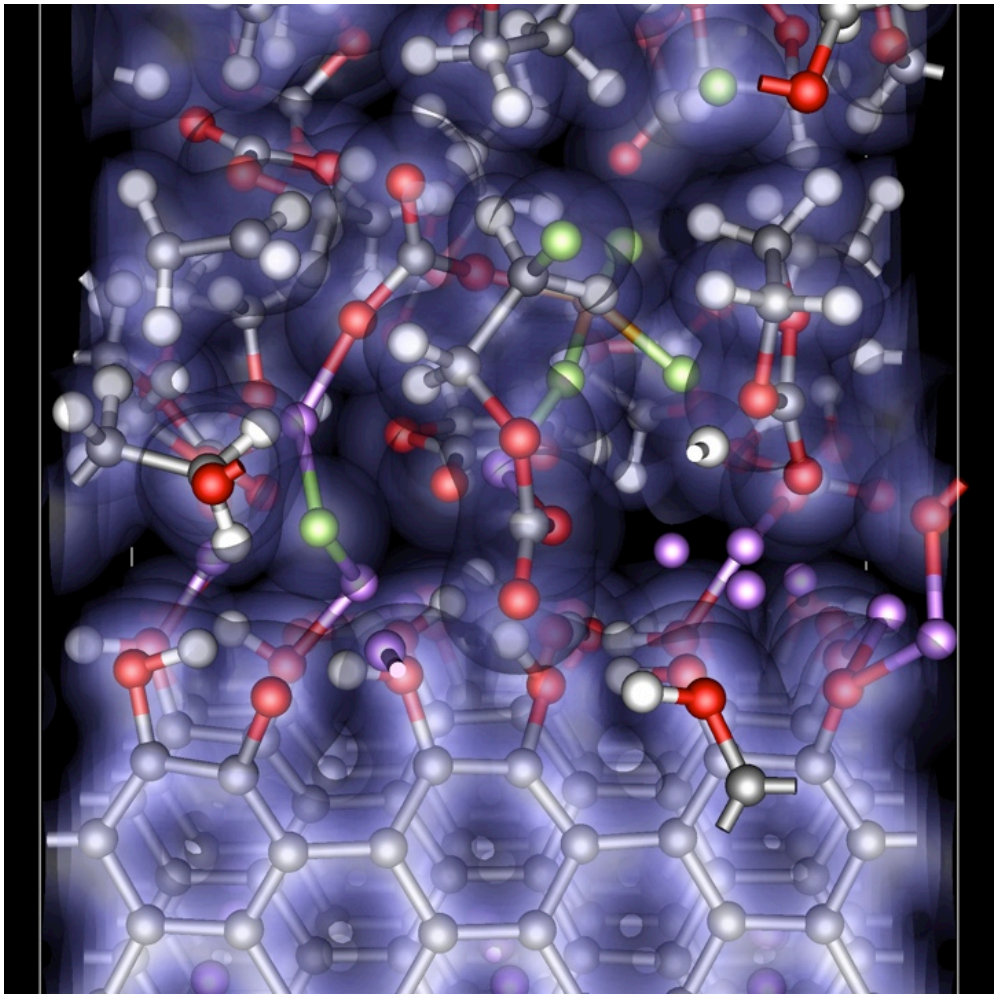
Li rich

- **Many configuration necessary for statistics, but...**
- **Reductive components already seen after few ps**
  - **c.f. K. Leung & J. L. Budzien PCCP (2010) 12 6583**
- **Li poor OH terminated edges display excluded volume**
- **Li rich OH terminated edge appear to show ordering of EC**

Simulations with lithiated carbon anode, EC and $LiPF_6$ salt

- LiF formation
- Polymerization
- Further breakup of PF5?

- Checks are ongoing to determine how representative these observations are, to assess rates, & to identify and understand reaction mechanisms

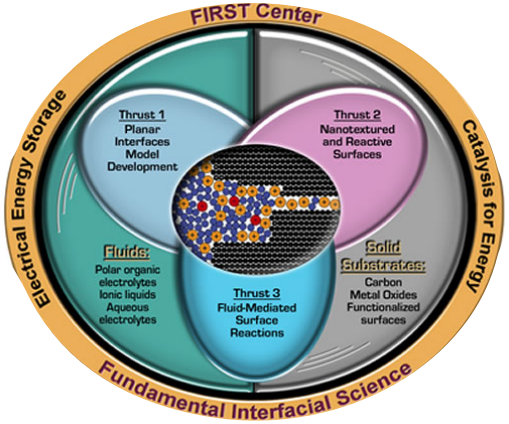


Isosurface of DFT charge density. Bonds are guide to the eye

Summary

P. Ganesh et al. JPCB **115** 3085 (2011) 10.1021/jp2003529

- **Additional structure, dynamics analysis, comparison with experimental spectroscopies in paper**
- **Overall good agreement with available experiment**
- **PBE DFT gives accurate results:**
  - **More accurate than existing empirically fit classical models**
  - **1st neighbour shell possibly too tight**
- **Promising for application to electrode interface models**



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